

Supporting Information

for

Effects of solvent additive on “s-shaped” curves in solution-processed small molecule solar cells

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Detailed experimental procedures with physical and chemical analysis of compounds and additional device characterization data

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Materials and methods

Materials. All chemicals and reagents were commercially available and used as received. Anhydrous tetrahydrofuran and toluene for chemical reactions were obtained by passing through solvent dispensing systems. 4,7-Dibromo-5-fluorobenzo[*c*][1,2,5]-thiadiazole was purchased from 1-Material Inc. and used without further purification as received. Benzo-[1,2-*b*:4,5-*b'*]-bis-(2-bromo-4,4'-dihexyl-4*H*-silolo[3,2-*b*]-thiophene ¹ and (*E*)-octyl-3-(5-bromothiophen-2-yl)-2-cyanoacrylate ² were synthesized according to the literatures.

Nuclear magnetic resonance (NMR) spectroscopy. ¹H NMR were recorded on a Varian Unity Inova 500 MHz or 600 MHz spectrometer and ¹³C NMR were performed on a Varian Unity Inova 500 MHz or Bruker Avance 800 MHz spectrometer at room temperature using deuteriochloroform (or other given solvents) as internal reference. Chemical shifts are reported as δ values (ppm) relative to an internal tetramethylsilane (TMS) standard. 2D ¹H-¹H NOESY correlation experiments were acquired on a Varian Unity Inova 600MHz spectrometer at 25 °C for elucidating the fluorine regiochemistry of compound **2**.

Mass spectrometry (MS). Low-resolution field-desorption time-of-flight (FD-TOF) MS was performed on a Waters GCT Premier and high-resolution electrospray (ESI) MS was measured on a Waters Micromass QTOF2. All MS spectra were collected by the UCSB Department of Chemistry and Biochemistry Mass Spectrometry Facility.

Differential scanning calorimetry (DSC). The melting and crystallization temperatures were measured using a TA Instrument DSC (Model Q-2000) with a scan rate of 10 °C/min.

Cyclic voltammetry (CV). Solution electrochemical properties were performed using a CHI instrument model 730B in a three-electrode electrochemical cell with a glassy carbon working electrode, a Pt wire counter electrode, and a Ag wire pseudo reference electrode. CH₂Cl₂ was purified by distillation for cyclic voltammetry measurement. Redox potentials were measured in anhydrous CH₂Cl₂ with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte, and product concentration was kept at 1 mg·mL⁻¹. All potentials

reported here were calibrated with the ferrocene/ferrocenium redox couple (Fc/Fc^+) as internal standard. The corresponding HOMO and LUMO energy levels were acquired by correlating the onsets of oxidation and reduction to the Normal Hydrogen Electrode (NHE), assuming HOMO of Fc/Fc^+ to be 4.88 eV.

UV-visible absorption measurement. UV-vis spectra were recorded with a Beckman Coulter DU 800 series or a Perkin Elmer Lambda 750 spectrophotometer. All solution UV-Vis experiments were measured in CHCl_3 . Neat films were prepared by spin-coating at a spin speed of 1500 rpm from 10 mg/mL CHCl_3 solutions atop pre-cleaned glass substrates. Films were annealed on a hot plate for 2 minutes at given temperatures and cooled to room temperature for absorption measurements.

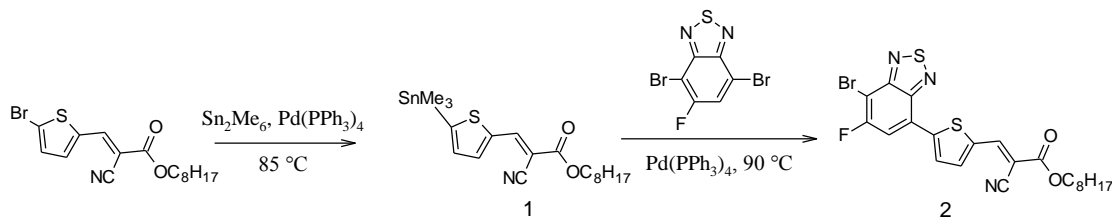
Solubility measurements. Prepared the calibration curve by measuring the absorbance of different solutions in CHCl_3 with a known concentration, and plotting λ_{max} vs. concentration, a linear relationship was observed. An over-saturated CHCl_3 solution was stirred vigorously for 48 hours at room temperature. The slurry was then filtered through a 0.45 μm PTFE filter. The filtrate was assumed to be a saturated solution. A 100 μL aliquot was then diluted to 50 mL with CHCl_3 . The UV-vis absorption spectrum was obtained and the concentration was determined using its standard calibration curve.

DFT theoretical calculations. The molecular geometry and photophysical properties of $\text{p-SiDT}(\text{FBTThCA8})_2$ at the molecular level were performed by Gaussian 09 program, in which the conformation of ground state and HOMO/LUMO orbitals were optimized by the density functional theory (DFT) using Beck's three-parameterized Lee-Yang-Parr exchange functional (B3LYP) with 6-311G(d,p) basis sets.

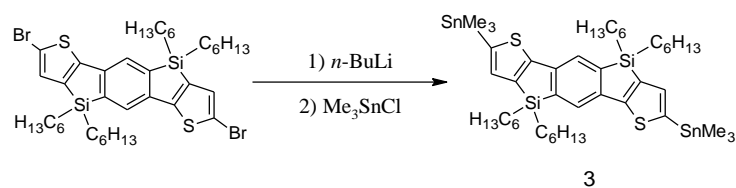
GIWAXS measurement. Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) patterns were collected at the Stanford Synchrotron Radiation Lightsource (SSRL) beamline 11-3 with an X-ray wavelength of 0.9752 \AA , at a 40 cm sample to detector distance at an incident angle of 0.12°. Samples were probed under a helium environment to minimize beam damage and reduce diffuse scattering. The measurements were calibrated using a LaB6

standard. Thin films were prepared by spin-coating from chloroform solution (10 mg/mL) atop silicon substrates at 1000 rpm.

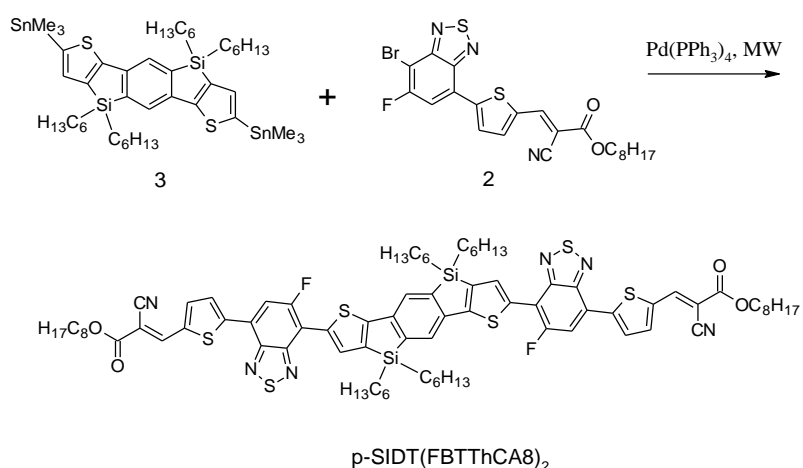
Synthetic procedure and characterization



Synthesis of (E)-octyl 3-(5-(7-bromo-6-fluorobenzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)-2-cyanoacrylate (2). In a N_2 filled glove box, hexamethylditin (982.8 mg, 3.0 mmol), (E)-octyl 3-(5-bromothiophen-2-yl)-2-cyanoacrylate (740.6 mg, 2.0 mmol), $\text{Pd}(\text{PPh}_3)_4$ (115.5 mg, 0.1 mmol), and dry toluene (20 mL) were combined in a 50 mL round bottle and then sealed. The reaction mixture was stirred and heated at $85\text{ }^\circ\text{C}$ for 18 hours. After cooling to room temperature, the solvent and excess amounts of hexamethylditin were removed by rotary evaporation. The crude material (E)-octyl 2-cyano-3-(5-(trimethylstannyl)thiophen-2-yl)acrylate (**1**) was used for the following procedure without further purification. A 50 mL round bottle was charged with crude **1**, 4,7-dibromo-5-fluorobenzo[c][1,2,5]thiadiazole (592.7 mg, 1.9 mmol), $\text{Pd}(\text{PPh}_3)_4$ (87.8 mg, 0.076 mmol) and dry toluene (30 mL) in a N_2 filled glove box. The reaction mixture was then sealed and stirred at $90\text{ }^\circ\text{C}$ for 3 days. Upon cooling, the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel with gradient eluent from CH_2Cl_2 /hexane (v/v, 1:3) to CH_2Cl_2 /hexane (v/v, 1:1). The product was washed with MeOH and then dried under vacuum overnight. The desired product **2** was obtained as yellow solid (425 mg, 42.8%). ^1H NMR (600 MHz, CDCl_3 , δ): 8.34 (s, 1H), 8.22 (d, $J = 6\text{ Hz}$, 1H), 7.89 (d, $J = 6\text{ Hz}$, 1H), 7.86 (d, $J = 12\text{ Hz}$, 1H), 4.32 (t, $J = 6\text{ Hz}$, 2H), 1.77 (q, $J = 7.5\text{ Hz}$, 2H), 1.45-1.41 (m, 2H), 1.34-1.28 (m, 8H), 0.89 (t, $J = 6\text{ Hz}$, 3H). ^{13}C NMR (125 MHz, CDCl_3 , δ): 162.7, 161.6, 159.5, 154.4, 154.3, 148.7, 145.9, 138.0, 137.8, 129.7, 125.8, 118.0, 117.7, 115.8, 100.5, 99.3, 99.1, 67.1, 31.9, 29.4, 29.3, 28.7, 26.0, 22.8, 14.3. HRMS (ESI-TOF) m/z , calcd for $\text{C}_{22}\text{H}_{21}\text{BrFN}_3\text{NaO}_2\text{S}_2$ $[\text{M}+\text{Na}]^+$: 544.0140; found: 544.0118.



*Synthesis of benzo[1,2-*b*:4,5-*b'*]bis(2-trimethylstannyl-4,4'-dihexyl-4*H*-silolo[3,2-*b*]thiophene) (3).* *n*-BuLi (1.6 M in hexane, 1.4 mL, 2.3 mmol) was injected dropwise via a syringe into a solution of benzo[1,2-*b*:4,5-*b'*]bis-(2-bromo-4,4'-dihexyl-4*H*-silolo[3,2-*b*]thiophene (793 mg, 1.0 mmol) in anhydrous THF (100 mL) at $-78\text{ }^{\circ}\text{C}$ under N_2 . The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 10 min and then a solution of trimethyltin chloride (498.2 mg in 3.5 mL dry THF, 2.5 mmol) was added quickly in one portion at $-78\text{ }^{\circ}\text{C}$. The reaction was stirred at room temperature for another 4 hours. Water was added to the reaction mixture and extracted with hexanes. The combined organic layer was dried over anhydrous MgSO_4 and the solvent was removed in vacuo. The solid was precipitated out in iced MeOH solution and filtered. Compound **3** was collected as pale yellow solid (950 mg, 98.9%). ^1H NMR (600 MHz, CDCl_3 , δ): 7.57 (s, 1H), 7.16 (s, 1H), 1.44-1.39 (m, 4H), 1.32-1.21 (m, 12H), 0.98-0.89 (m, 4H), 0.85-0.83 (m, 6H), 0.4 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3 , δ): 163.3, 142.4, 142.2, 140.7, 138.8, 138.0, 125.7, 33.2, 31.6, 24.3, 22.8, 14.3, 12.4, -7.9. LRMS (FD-TOF) m/z , calcd for $\text{C}_{44}\text{H}_{74}\text{S}_2\text{Si}_2\text{Sn}_2$ $[\text{M}]^+$: 962.28; found: 962.28.



Synthesis of p-SIDT(FBTThCA8)₂. To a 20 mL microwave vial was added compound **2** (493 mg, 0.94 mmol), compound **3** (432 mg, 0.45 mmol), $\text{Pd}(\text{PPh}_3)_4$ (26 mg, 0.023 mmol), and dry toluene (13 mL) in a N_2 filled glove box. The reaction vial was sealed and loaded in a

Biotage microwave reactor with conditions as follows: 100 °C for 5 minutes, 120 °C for 5 minutes, 140 °C for 10 minutes and 170 °C for 50 minutes. Upon cooling, the volatiles were removed in vacuo. The crude product was purified through silica gel column with gradient eluent from CHCl₃/hexane (v/v, 1:1) to pure CHCl₃. Purification by column chromatography was carried out several times to ensure purity for device fabrication. The solid was reprecipitated and filtered with DCM/MeOH, DCM/pentane and DCM/ethylacetate sequentially. **p-SIDT(FBTThCA8)₂** (550 mg, 80.6%) was then obtained as bronze-colored solid after dried under vacuum for 24 hours. ¹H NMR (500 MHz, CDCl₃, δ): 8.41 (s, 2H), 8.33 (s, 2H), 8.24 (d, *J* = 5 Hz, 2H), 7.95 (d, *J* = 15 Hz, 2H), 7.88 (d, *J* = 5 Hz, 2H), 7.77 (s, 2H), 4.31 (t, *J* = 5 Hz, 4H), 1.80-1.74 (m, 4H), 1.53-1.46 (m, 8H), 1.45-1.41 (m, 4H), 1.39-1.25 (m, 40H), 1.12-1.01 (m, 8H), 0.91-0.84 (m, 18H). ¹³C NMR (200 MHz, CDCl₃, δ): 163.0, 160.9, 160.8, 159.0, 157.7, 153.4, 153.3, 149.8, 147.4, 147.3, 146.1, 143.2, 142.9, 140.7, 138.2, 137.1, 134.7, 134.6, 134.1, 134.0, 129.0, 126.0, 123.0, 122.9, 118.9, 118.8, 116.1, 114.4, 114.3, 99.5, 67.0, 33.2, 32.0, 31.7, 29.4, 29.3, 28.8, 26.0, 24.3, 22.9, 22.8, 14.3, 14.2, 12.4. LRMS (FD-TOF) *m/z*, calcd for C₈₂H₉₈F₂N₆O₄S₆Si₂ [M]⁺: 1516.55; found: 1516.46.

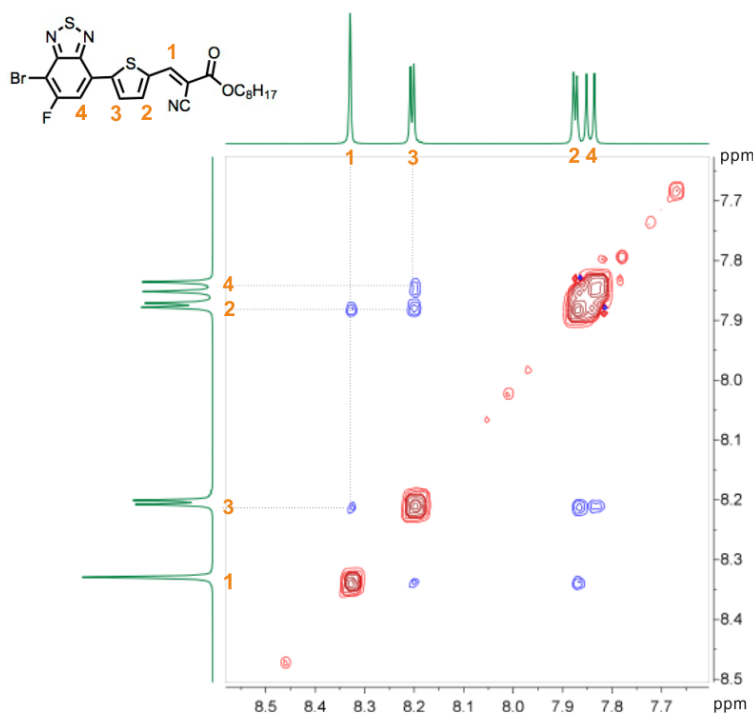


Figure S1: 2D ¹H-¹H NOESY spectrum of compound **2** in CDCl₃ expands to the selected aromatic region and the assignment of its regiochemistry.

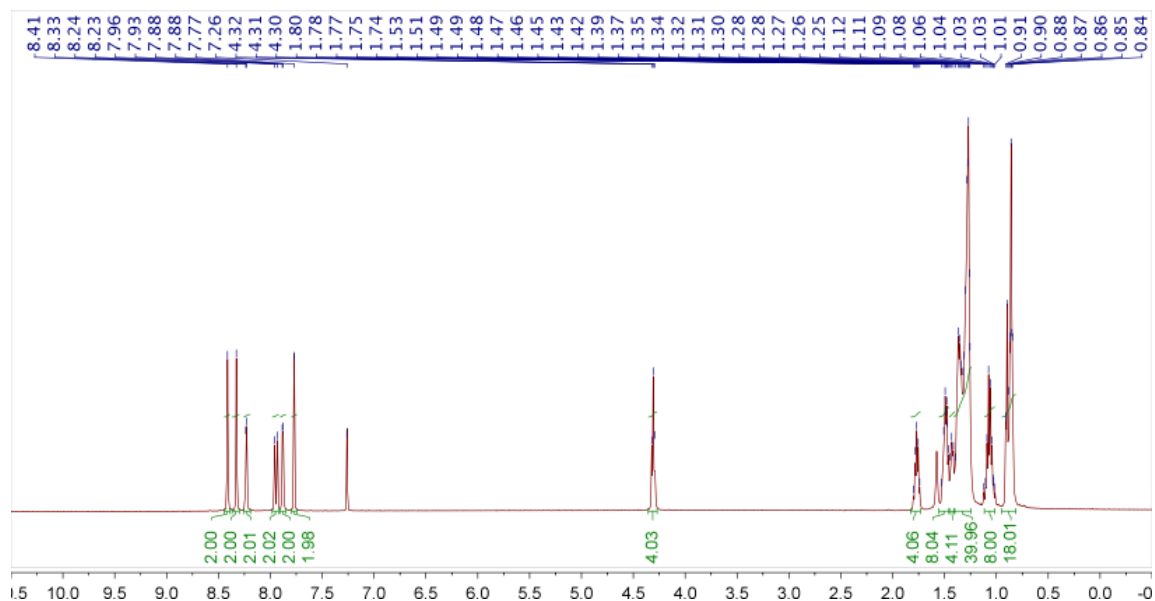


Figure S2. ^1H NMR spectrum of p-SIDT(FBTThCA8)₂ in CDCl_3 .

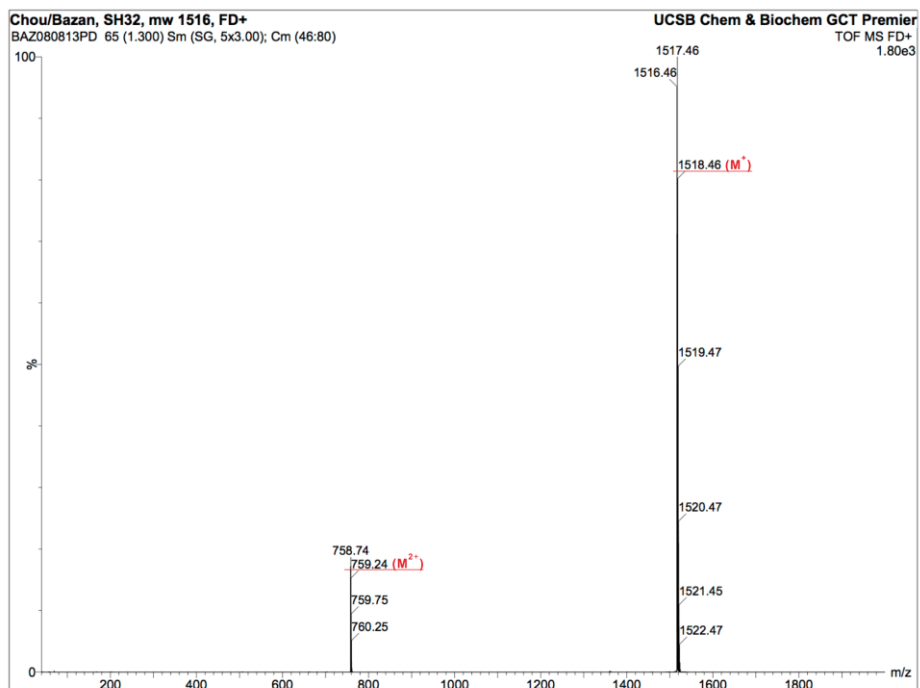


Figure S3: FD-TOF MS of p-SIDT(FBTThCA8)₂, showing double-charged species (M^{2+}).

Molecular characterization

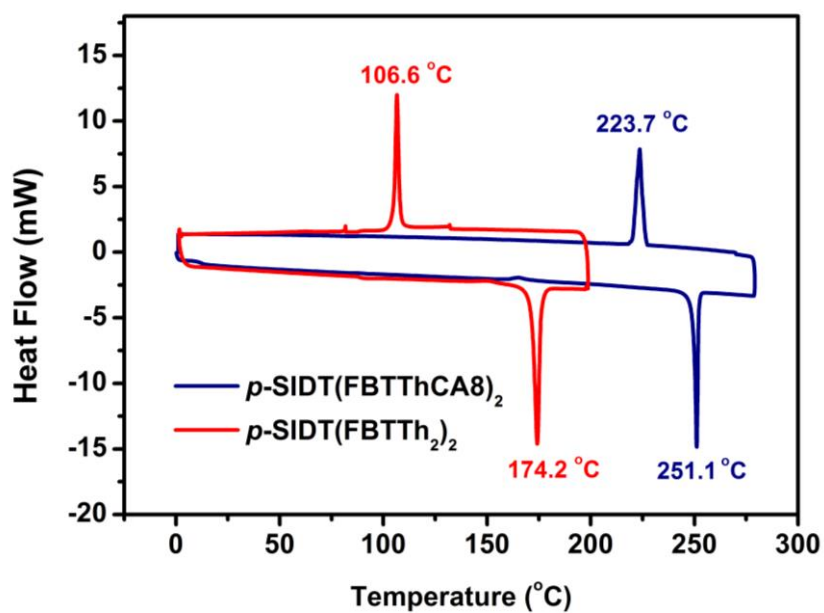


Figure S4: DSC thermograms showing melting (T_m) and crystallization (T_c) temperatures of p-SIDT(FBTThCA8)₂ and p-SIDT(FBTTh₂)₂.

Table S1: Photophysical and thermal characteristics of p-SIDT(FBTThCA8)₂ and p-SIDT(FBTTh₂)₂.

Molecule	solution absorption ^a		film absorption		thermal transitions
	λ_{\max} (nm)	ϵ (λ_{\max}) ($M^{-1}cm^{-1}$)	λ_{\max} (nm)	ΔE^{opt} (eV) ^b	T_m/T_c (°C)
p-SIDT(FBTThCA8) ₂	603	96630	650	1.65	223.7/ 251.1
p-SIDT(FBTTh ₂) ₂	571	65000	610	1.93	106.6/ 174.2

^a Measured in CHCl₃ at room temperature; ^b obtained from the absorption onsets in the films.

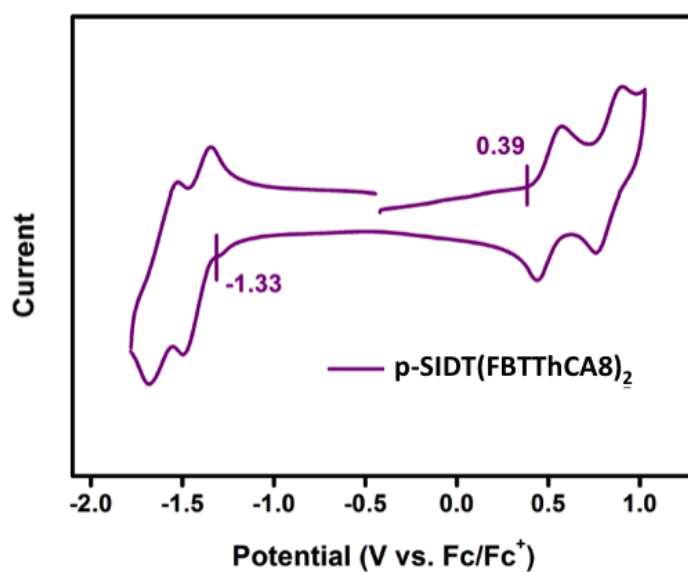


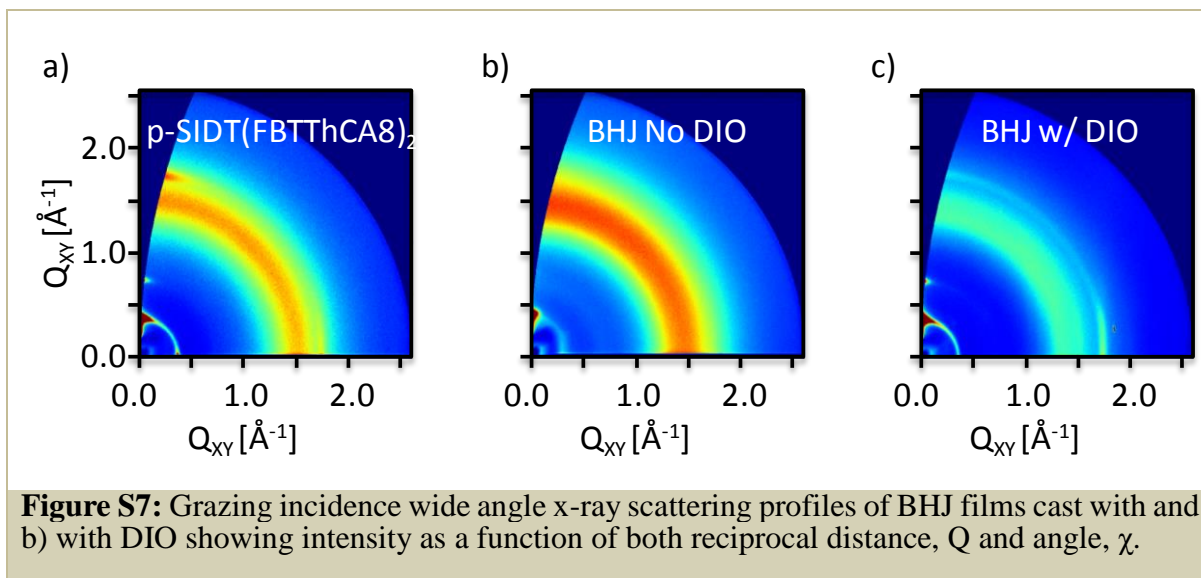
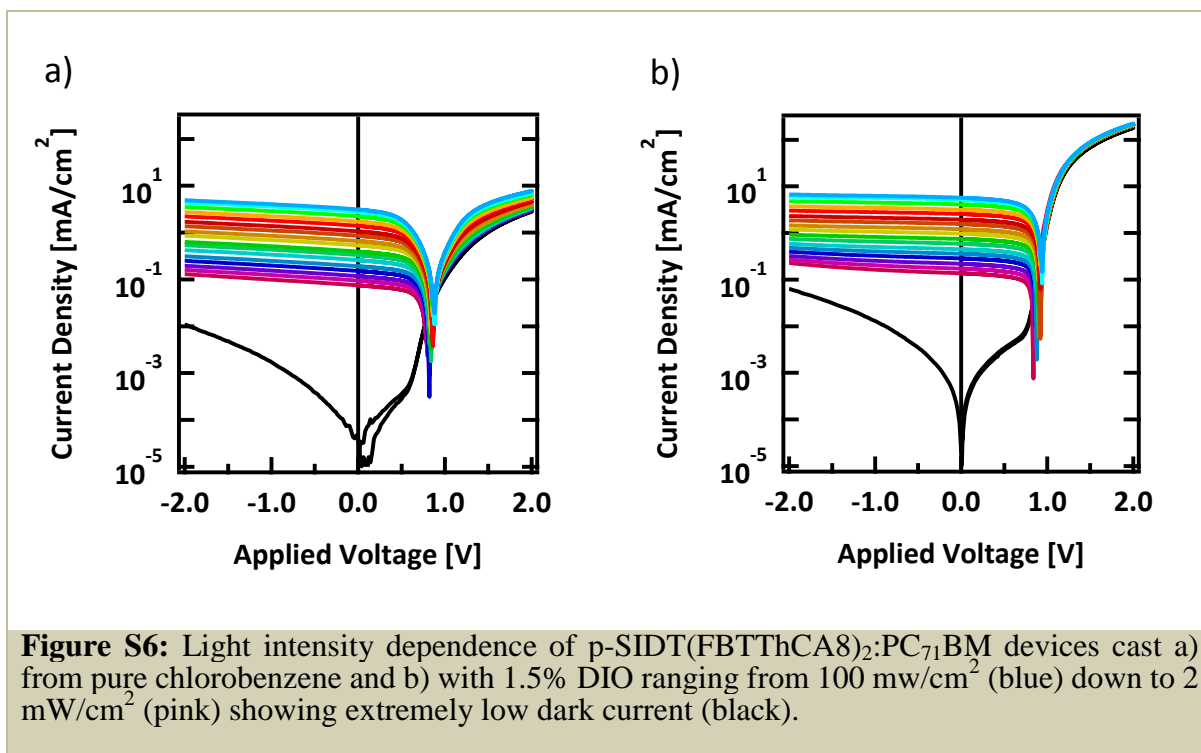
Figure S5: Cyclic voltammetry of p-SIDT(FBTThCA8)₂.

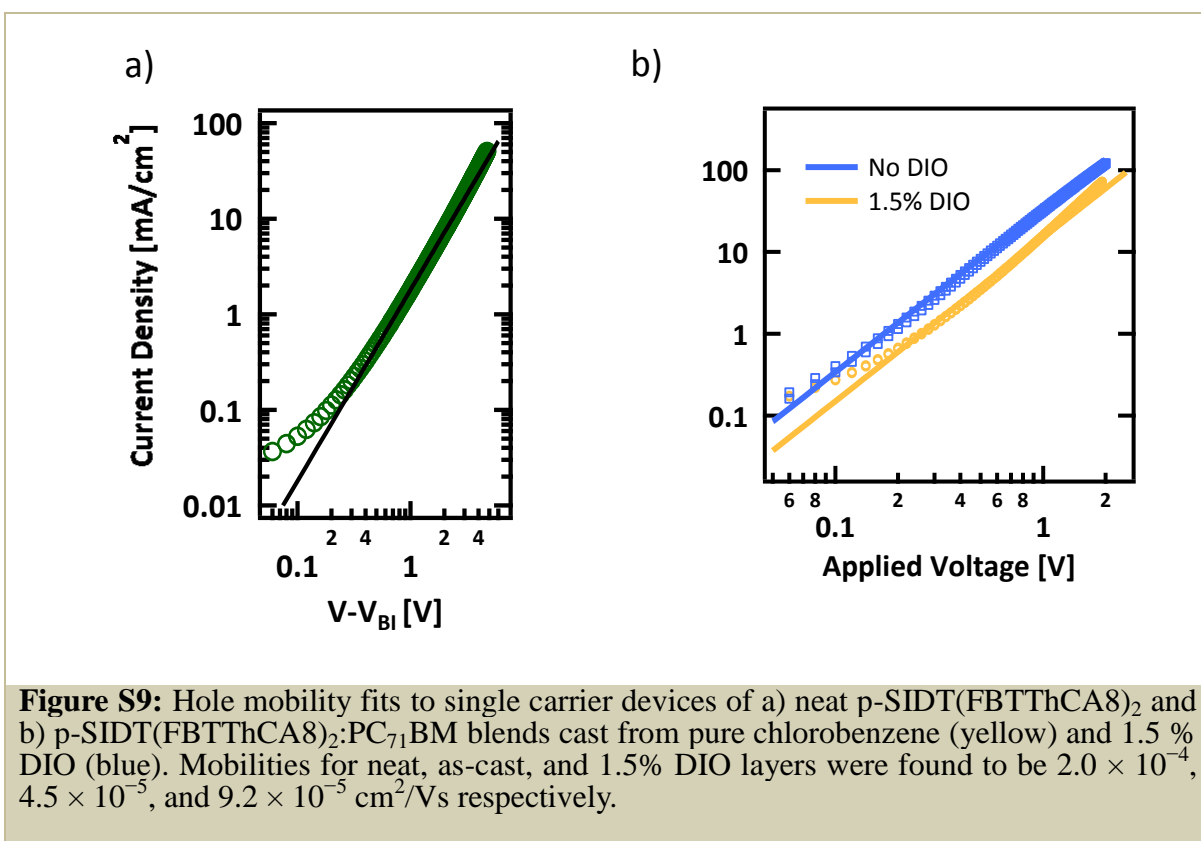
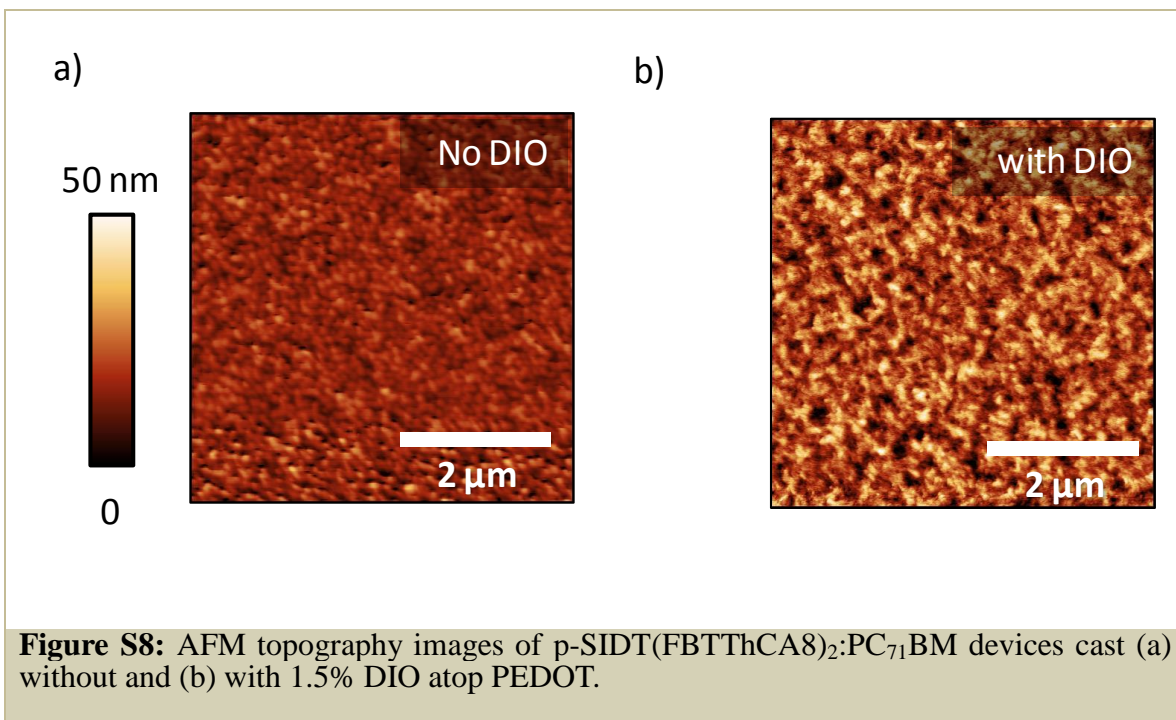
Table S2: Electrochemical and theoretical energy levels of p-SIDT(FBTThCA8)₂ and p-SIDT(FBTTh₂)₂.

Molecule	Energy levels	
	$E_{\text{HOMO}}/E_{\text{LUMO}}/\Delta E^{\text{CV}}$ (eV) ^a	$E_{\text{HOMO}}/E_{\text{LUMO}}/\Delta E^{\text{DFT}}$ (eV) ^b
p-SIDT(FBTThCA8) ₂	-5.27/-3.55/1.72	-5.43/-3.53/1.90
p-SIDT(FBTTh ₂) ₂	-5.21/-3.36/1.85	-4.97/-2.96/2.01

^aDetermined by CV experiment; ^bcalculated by the DFT theoretical simulation of optimized geometry.

Device characterization





Hole only devices were fabricated for pristine p-SIDT(FBTThCA8)₂ and BHJ blends according to the structure ITO/PEDOT/active layer/MoO₃/Ag. The *J–V* characteristics of the

devices were measured in the dark. Injection current from the MoO₃ top contact was fit according to the Mott–Gurney Law for space charge limited current:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_p \frac{V^2}{L^3}$$

where ε_0 is the vacuum permittivity, ε_r is the relative dielectric of the active layer (assumed to be 3 in all cases), μ_p is the hole mobility V is the applied voltage minus a small built in voltage, and L is the active layer thickness, which for neat p-SIDT(FBTThCA8)₂ was varied between 250 and 350 nm and for BHJ blends were kept at 120 nm as in solar cells.

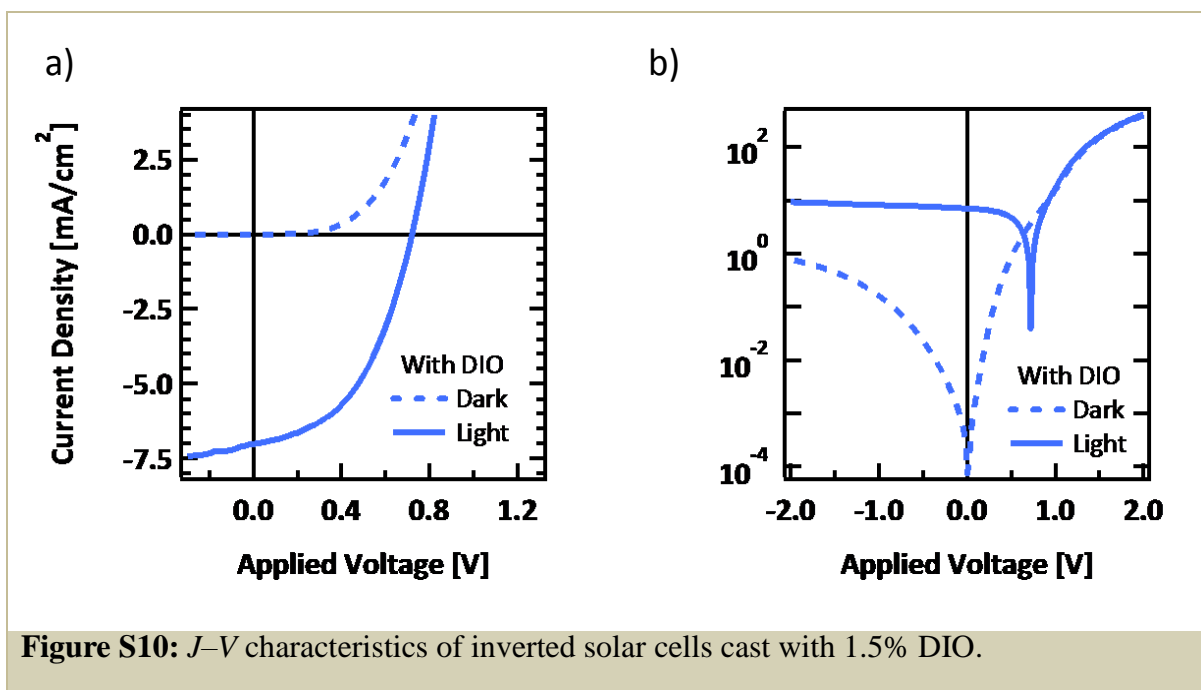
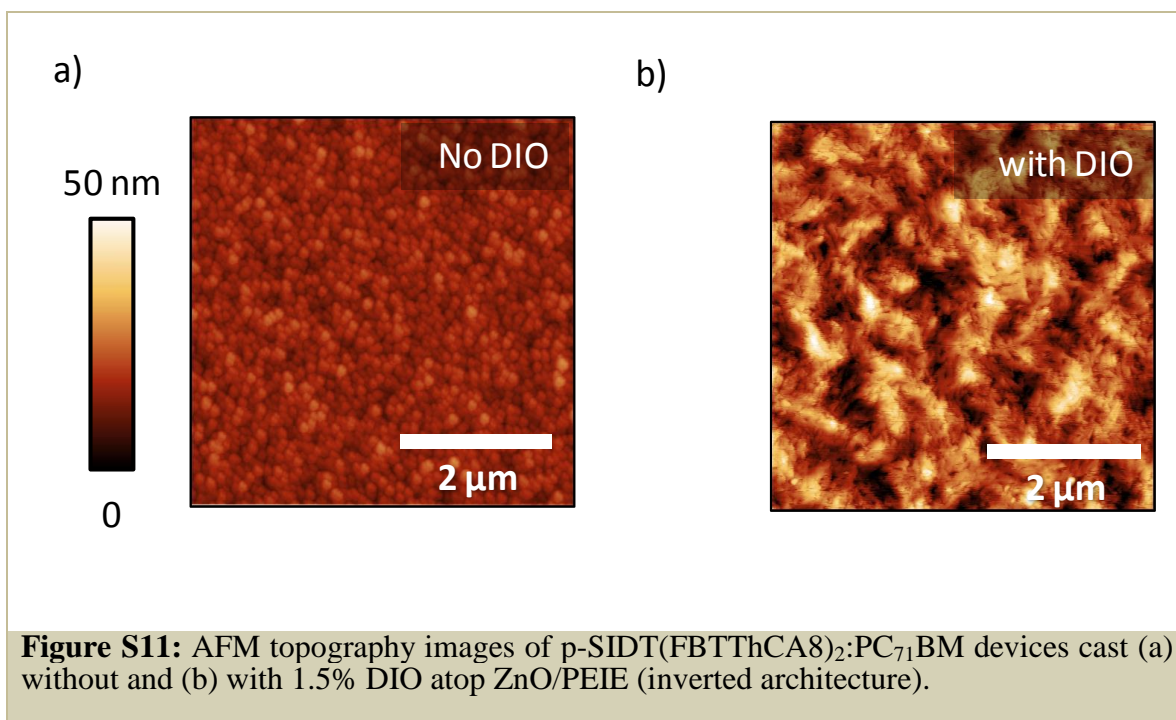


Figure S10: J – V characteristics of inverted solar cells cast with 1.5% DIO.

When the p-SIDT(FBTThCA8)₂:PC₇₁BM layer was cast with 1.5% DIO in the inverted architecture of ITO/ZnO/PEIE/BHJ/MoO₃/Al devices showed large dark current as shown above in Figure S10. Unfortunately this leads to extremely low V_{OC} and FF leading to low performance despite improved photocurrent compared to the standard architecture.



The high dark current observed for 1.5% DIO inverted devices likely is due to a change in morphology caused by casting atop the different substrates.. When the p-SIDT(FBTThCA8)₂:PC₇₁BM is cast with 1.5% DIO on ZnO/PEIE substrates (Figure S11 b), the roughness and size scale of the features increases dramatically. Films cast without additive, from pure chlorobenzene, show smoother, surfaces (RMS roughness < 3 nm) regardless of underlying substrate.

References

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- ² Y. Lin, Z.-G. Zhang, H. Bai, Y. Li, X. Zhan, *Chem. Commun.* **2012**, 48, 9655.