Supporting Information

Significant Enhancement of Responsivity of Organic Photodetectors upon Molecular Engineering

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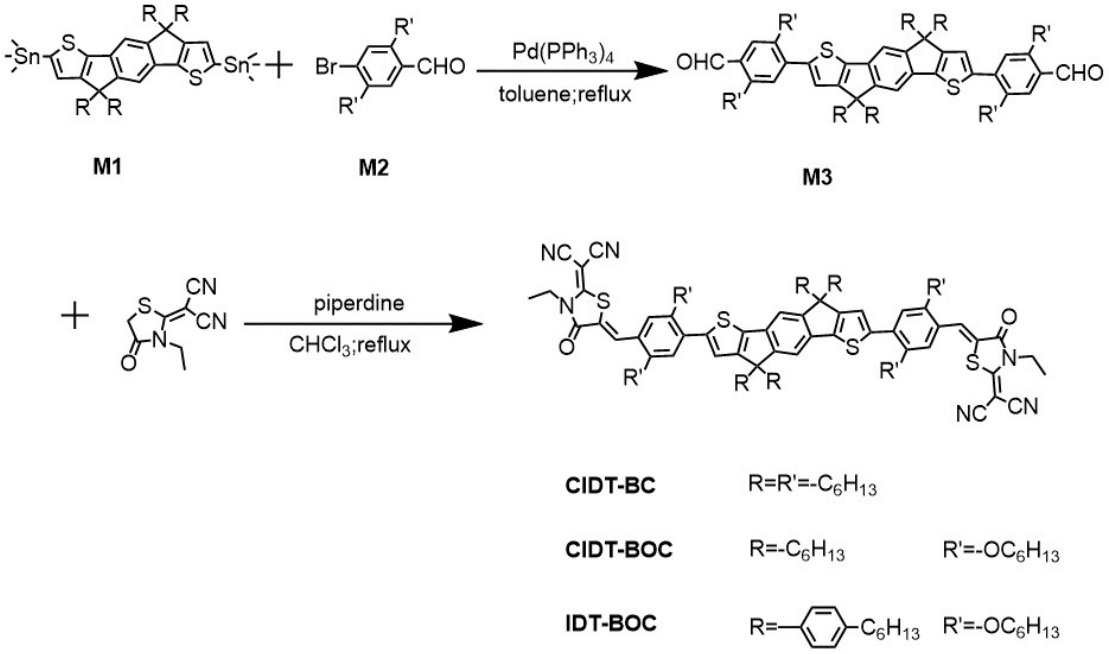
Experimental Section

Materials: All chemicals and reagents were used as purchased from commercial sources such as Energy Chemical and Sigma Aldrich without further purification unless otherwise noted. Solvents for chemical synthesis conducted under a nitrogen

atmosphere were purified by distillation. **M1**, **M2**, and **M3** were synthesized according to the literature reported.[1] Detailed synthesis and characterizations of the molecules are demonstrated below.



Scheme S1. Synthetic route of CIDT-BC, CIDT-BOC, and IDT-BOC

Synthesis of *CIDT-BC, CIDT-BOC, and IDT-BOC*

CIDT-BC: A mixture of **M3** (121.4 mg, 0.11 mmol) and rhodanine-$(CN)_2$ (127.5 mg, 0.66 mmol) in dry chloroform (20 mL) was carefully degassed before and after the addition of piperdine (0.2 mL) under N_2 atmosphere. After refluxed for 20 h, the reaction was cooled to room temperature. The solvent was evaporated and the solid was purified on silica column with DCM/petroleum ether (1:1, v/v) to give the product CIDT-BC as a red solid with a yield of 55 mg (34.8%). ^{1}H NMR (300 MHz. $CDCl_3$): δ 8.21 (s, 2H), 7.41 (s, 2H), 7.39 (s, 2H), 7.32 (s, 2H), 7.02 (s, 2H), 4.33-4.39 (q, J=4 Hz, 4H), 2.77-2.89 (t, J=3 Hz, 8H), 1.90-2.04 (t, J=2 Hz, 8H), 1.45 (t, J=2 Hz, 6H), 1.13-1.60 (m, 64H), 0.79-0.90 (m, 24H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 166.46, 166.09, 155.69, 153.16, 143.03, 142.66, 142.34, 139.48, 138.15, 135.90, 134.63, 132.63, 130.07, 129.62, 122.06, 117.78, 113.32, 113.05, 112.31, 56.06, 54.27, 40.65, 33.67, 33.21, 31.66, 31.14, 29.84, 29.21, 24.39, 22.68, 14.14. MS (MALDI-TOF) m/z: calculated for $C_{94}H_{124}N_6O_2S_4$, 1497.87; Found, 1498.50. Anal. Calcd. For

$C_{94}H_{124}N_6O_2S_4$: C, 75.35; H, 8.34; N, 5.61. Found: C, 74.72; H, 8.35; N, 5.30.

CIDT-BOC was synthesized as a purple solid in a yield of 60.4% using a similar method as above. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (s, 2H), 7.61 (s, 2H), 7.32 (s, 2H), 7.28 (s, 2H), 7.01 (s, 2H), 4.31-4.37 (m, 4H), 4.14-4.18 (m, 8H), 1.87-2.07 (m, 8H), 1.45 (m, 6H), 1.13-1.60 (m, 64H), 0.79-0.90 (m, 24H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 160.38, 166.11, 149.65, 147.61, 147.04, 143.13, 138.49, 137.03, 136.14, 134.08, 130.08, 126.52, 123.58, 115.96, 113.95, 108.89, 107.69, 106.45, 105.67, 104.69, 63.70, 63.53, 48.73, 48.00, 33.21, 34.37, 33.16, 25.58, 23.22, 22.93, 16.54. MS (MALDI-TOF) m/z: calculated for $C_{94}H_{124}N_6O_6S_4$, 1561.85; Found, 1562.3. Anal. Calcd. For $C_{94}H_{124}N_6O_6S_4$: C, 72.27; H, 8.00; N, 5.38. Found: C, 71.60; H, 7.80; N, 5.39.

IDT-BOC was synthesized as a purple solid in a yield of 53.2% using a similar method as above. ^{1}H NMR (300 MHz. $CDCl_3$): δ 8.23 (s, 2H), 7.61 (s, 2H), 7.46 (s, 2H), 7.19-7.21 (d, J=7 Hz, 8H), 7.17 (s, 2H), 7.07-7.09 (d, J=7 Hz, 8H), 6.96 (s, 2H) 4.30-4.35 (m, 6H), 4.06-4.10 (m, 8H), 2.54-2.58 (t, J=3 Hz, 4H) 1.85-1.93 (m, 8H), 1.25-1.62 (m, 64H), 0.85-0.93 (m, 24H). ^{13}C NMR (400 MHz,$CDCl_3$): δ 166.50, 166.23, 156.36, 153.89, 153.07, 149.26, 143.98, 141.85, 141.74, 135.71, 129.29, 128.46, 128.01, 120.39, 115.28, 100.00, 69.90, 63.07, 54.97, 35.69, 31.82, 31.68, 31.59, 31.51, 29.29, 29.06, 26.20, 25.80, 22.71, 22.64, 14.22. MS (MALDI-TOF) m/z: calculated for $C_{118}H_{140}N_6O_6S_4$, 1866.0; Found, 1866.9. Anal. Calcd. For $C_{118}H_{140}N_6O_6S_4$: C,75.93; H,7.56; N,4.50. Found: C,75.87; H,7.27; N,4.52.

Characterization: The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer with deuterated chloroform as the solvent and Tetramethylsilane (TMS) as an internal reference. Elemental analysis (EA) was performed on a FLASH EA 1112 Elemental Analyzer. Electrochemical cyclic voltammetry (CV) was performed on a CHI600E electrochemical workstation with a conventional three electrode configuration in dry

acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) as the supporting electrolyte with a scan rate of 50 mV s^{-1}. Pt wire, glassy carbon disks, and an Ag/AgCl electrode were used as the counter, working, and reference electrodes, respectively. A ferrocene/ferrocenium redox couple was used as an external standard. UV-vis absorption spectra were recorded using a Cary 60 UV-vis spectrophotometer at room temperature. Thermogravimetric analysis (TGA) measurements were carried out using a Shimadzu thermogravimetric analyzer (model DTG-60) under a continuous nitrogen flow at a heating rate of 10 ℃ min^{-1}. AFM images were obtained by NTEGRA Prima in the tapping mode. And TEM images were performed by HT7700Ex instrument at 110 kV accelerating voltage. The X-ray diffraction (XRD) measurements were performed on a Rigaku Smartlab diffractometer at a scan of 0.2°min-1 in the 2θ range from 2°to 20° with Cu ka radiation. Film-depth-dependent light absorption was recorded on a UV-Vis spectrophotometer (Lambda 950, Perkin-Elmer, USA).

Device fabrication and characterization: The organic photodetectors were fabricated with an inverted device structure ITO/ZnO/active layer/MoO_3/Ag. Patterned indium tin oxide (ITO) glass was cleaned by sequential sonication in detergent, deionized water, acetone and isopropanol for 30 min for each step. Then it was dried at 80 °C in an oven for 1 h and treated in an ultraviolet-ozone chamber for 30 min. The ZnO precursor solution (0.5 M zinc acetate dehydrate in 0.5 M monoethanolamine and 2-methoxyethanol) was spin-coated onto the ITO glass at 4500 rpm for 40 s, baked at 200 °C in air for 30 min. Subsequently, the substrate was transferred to a N_2 glove box. CIDT-BC, CIDT-BOC, or IDT-BOC was mixed with P3HT at a ratio of 1:1 in chloroform, respectively. Then the solution was spin coated on the substrate forming films of about 200 nm thickness. Then the films were transferred to the vacuum chamber of a thermal evaporator inside the same glovebox. MoO_3 (10 nm) and Ag (100 nm) were deposited sequentially by thermal evaporation under 10^{-5} Pa. The photoactive layer area of the device was 0.04 cm^2. The current density-voltage (J-V) characterizations were recorded under air mass (AM) 1.5G using a Newport solar

simulator. Besides, the incident photon to converted current efficiency (IPCE) spectrum under different biases was measured using Newport IPCE system.

Transient Absorption Characterization: Ultrafast transient absorption measurements of the pure or blend films on quartz were performed on a commercial fs-TAS system under the excitation of 400 nm laser with a pump fluence of ~10 μJ/cm^2.

Film-depth-dependent photo-harvesting characterization: Lambda 950 Spectrometer (PerkinElmer) and VARIAN Cary 5000 UV–vis–NIR Spectrophotometer were used for depth-resolved light absorption spectroscopy. The samples were prepared on ZnO/ITO substrates substrate. Film etching was performed in O_2 plasma with power 30 W and O_2 pressure about 10 Pa.

Space-Charge-Limited Current (SCLC) Measurement: The electron mobility was measured through the SCLC method by using a device architecture of ITO/ZnO /blend film/PDINO/Al by taking current–voltage curves and fitting the results to a space charge limited form, where the SCLC is described by:

$$J=9\varepsilon_0\varepsilon_r\mu(V_{appl}-V_{bi})^2/8L^3 \quad (1)$$

where ε_0 is the permittivity of free space (8.85×10^{-12} F/m), ε_r is the relative permittivity of the material (assumed to be 3), μ is the electron mobility, V_{appl} is the applied voltage, V_{bi} is the built-in voltage (for hole-only diodes, V_{bi} is 0.2 V; for electron-only diodes, V_{bi} is 0 V),[2] and L is the thickness of the film. By linearly fitting $J^{1/2}$ with V_{appl}-V_{bi}, the mobilities were extracted from the slope and L.

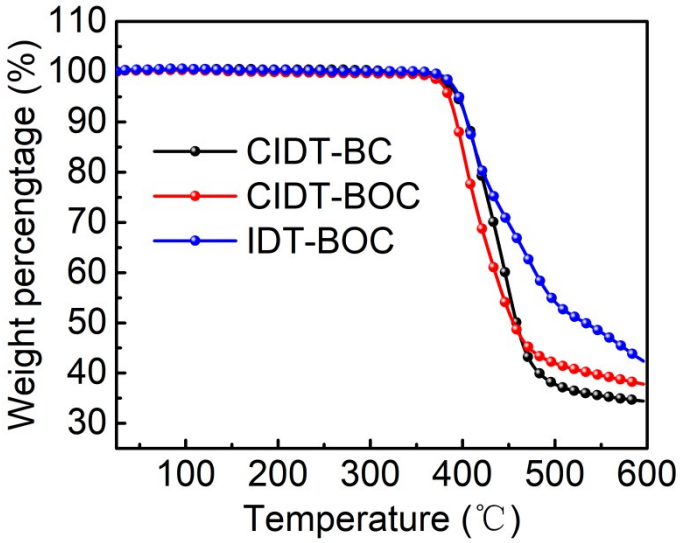


Figure S1. TGA curves of CIDT-BC, CIDT-BOC, and IDT-BOC.

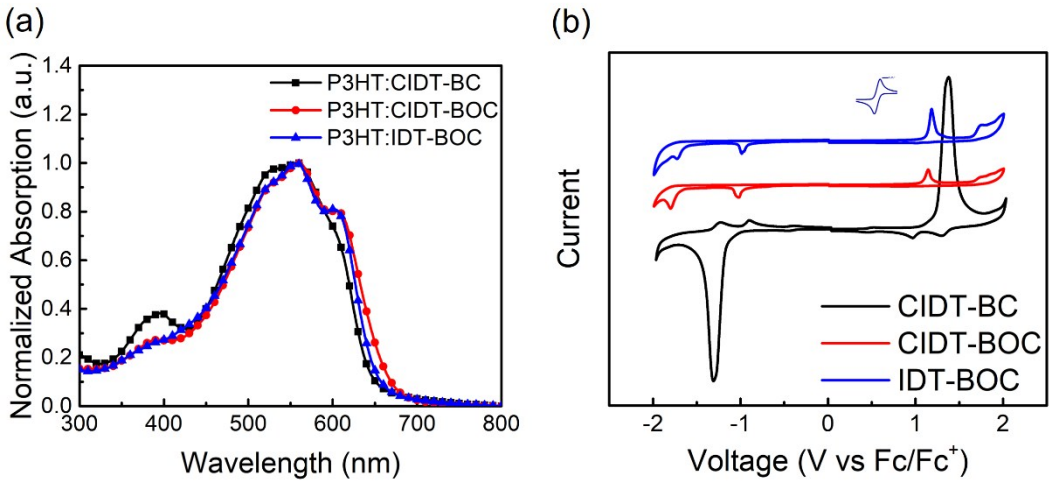


Figure S2. UV-vis absorption of the blend films (a); and Cyclic voltammograms of the small molecules as films on Glassy Carbon electrode in 0.1 M Bu_4NPF_6 solution in acetonitrile with a scan rate of 50 mV/s (b).

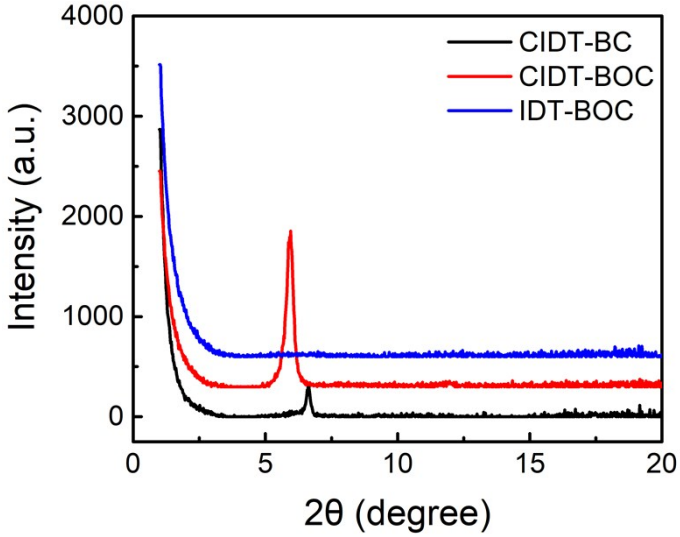


Figure S3. The out-of-plane X-ray diffraction diagrams of the small molecules as thin films spin-coated on quartz substrate.

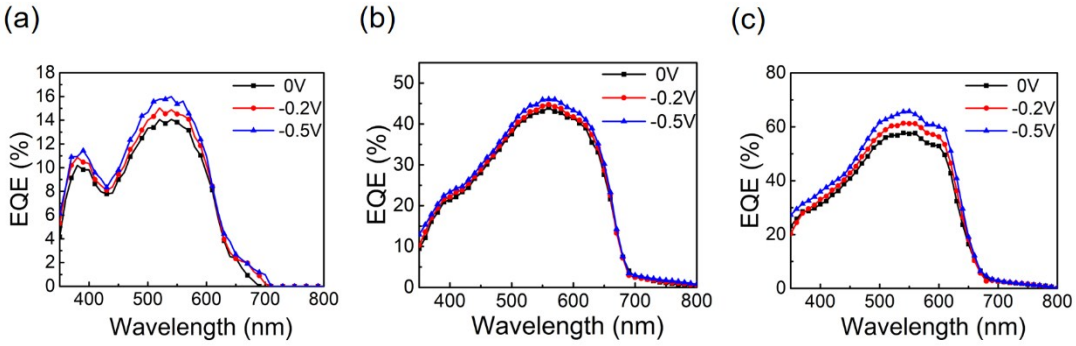


Figure S4. The external quantum efficiency (EQE) spectra of the photodetectors based on CIDT-BC (a); CIDT-BOC (b); and IDT-BOC at 0 V, -0.2 V, and -0.5 V, respectively.

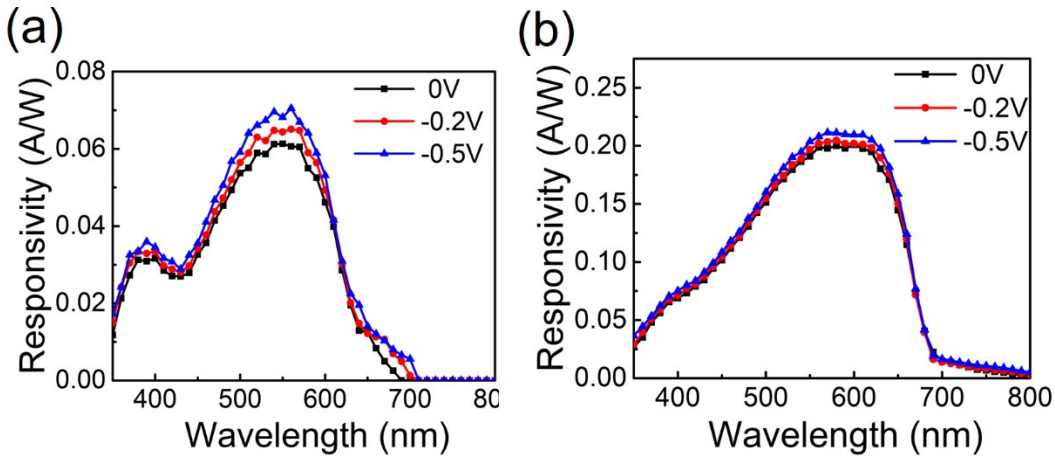


Figure S5. Spectral responsivity of the devices based on CIDT-BC (a) and CIDT-BOC (b) at different biases

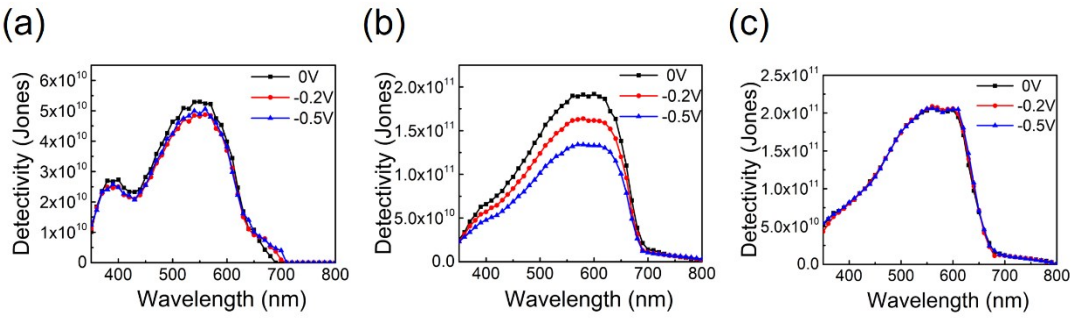


Figure S6. Spectral specific detectivities of the devices based on CIDT-BC (a), CIDT-BOC (b), and IDT-BOC (c) at different biases.

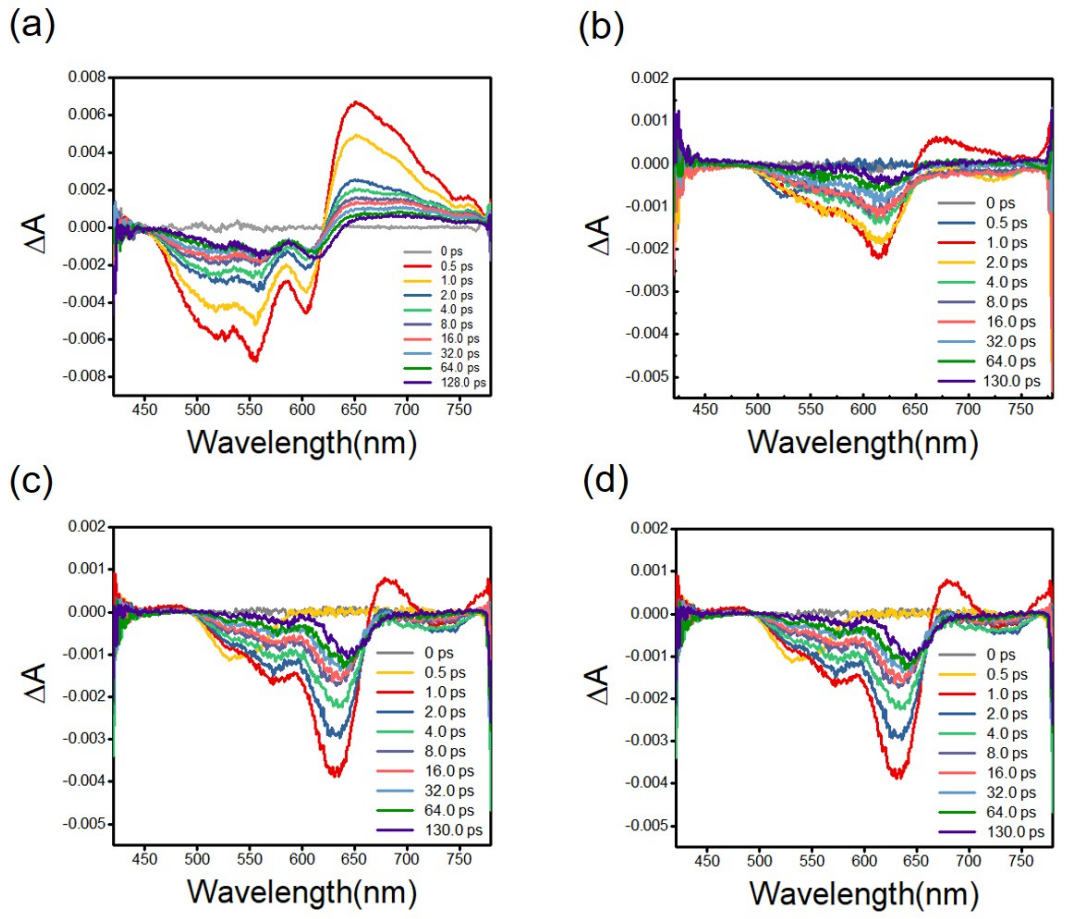


Figure S7. TA spectra of the neat films P3HT (a); CIDT-BC (b); CIDT-BOC (c); IDT-BOC (d).

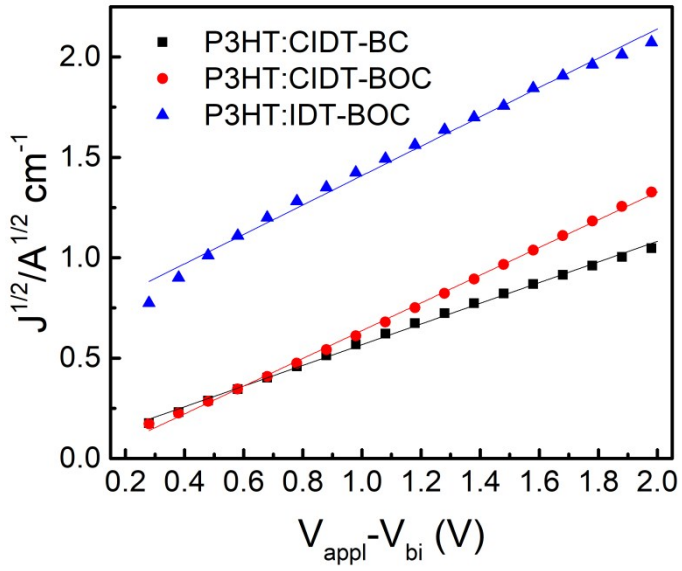


Figure S8. $J^{1/2}$-V plots for the electron-only devices of different blend films

(1) Liu, Y.; Zhang, Z.; Feng, S.; Li, M.; Wu, L.; Hou, R.; Xu, X.; Chen, X.; Bo, Z. Exploiting Noncovalently Conformational Locking as a Design Strategy for High Performance Fused-Ring Electron Acceptor Used in Polymer Solar Cells. *J. Am. Chem. Soc.* 2017**,** *139*, 3356.

(2) Lv, L.; Wang, X.; Dong, T.; Wang, X.; Wu, X.; Yang, L.; Huang, H. Significantly Improving the Efficiency of Polymer Solar Cells through Incorporating Noncovalent Conformational Locks. *Mater. Chem. Front.* 2017**,** *1*, 1317.