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Supporting Information

Influence of the π-Bridging Unit of Fused-Ring Acceptor on the Performance of Organic Solar Cells

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1.1 Materials and Instruments

Unless otherwise noted, all chemicals were purchased from commercial suppliers and used without further purification. The catalyst precursor $Pd(PPh_3)_4$ was prepared according to the literature and stored in a Schlenk tube under nitrogen atmosphere. Unless otherwise noted, all reactions were performed under an atmosphere of nitrogen and monitored by thin layer chromatography (TLC) on silica gel. Column chromatography was carried out on silica gel (200-300 mesh). ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 400 spectrometer. UV-visible absorption spectra were obtained on a PerkinElmer UV-vis spectrometer model Lambda 750. MS (MALDI-TOF) results were performed with an AutoflexIII instrument. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on TA2100 and Perkin-Elmer Diamond DSC instrument, respectively, under an nitrogen atmosphere at a heating rate of 10 ^{o}C/min to record TGA and DSC curves. Atomic force microscopy (AFM) measurements were performed under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating in the tapping mode. Transmission electron microscopy (TEM) was performed on Talos-f 200s operated at 200 kV. The thickness of the blend films was determined by a Dektak 6 M surface profile meter. The powder X-ray diffraction (XRD) patterns were collected using a PAN alytical X'Pert PRO MPD diffractometer with Cu KR radiation. The electrochemical behavior of the polymers was investigated using cyclic voltammetry (CHI 630A Electrochemical Analyzer) with a standard three-electrode electrochemical cell in a 0.1 M Bu_4NPF_6 solution in

CH_3CN at room temperature under an atmosphere of nitrogen with a scanning rate of 0.1 V/S. A Pt plate working electrode, a Pt wire counter electrode, and an $Ag/AgNO_3$ (0.01M in CH_3CN) reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium (F_c) redox system and assumption that the energy level of F_c is 4.8 eV below vacuum.

1.2 Solar Cells Fabrication and Characterization

PSCs were fabricated with the device configuration of ITO/ZnO/active layer (100 nm)/MoO_3 (85 Å)/Ag (100 nm). The conductivity of ITO is 20 Ω. A mixture of **PBDB-T** and small-molecule acceptor in 1,2-dichlorobenzene (DCB) was stirred at 90 ^oC at least two hours to ensure sufficient dissolution and then the blend solution was spin-coated (1200 rpm unless otherwise noted) onto ZnO layer to form active layer. On one substrate six cells with an effective area of 0.04 cm^2 for each were fabricated. Current-voltage characteristics were recorded using an Enli Technology Ltd., Taiwan (SS-F53A) under an AM 1.5G AAA class solar simulator with an intensity of 100 mW cm^{-2} as the white light source and the intensity was calibrated with a standard single crystal Si photovoltaic cell. The temperature while measuring the *J-V* curves was approximately 25 ^oC. The EQE measurements of PSCs were performed by the solar cell spectral response measurement system QE-R3011 (Enli Technology Ltd., Taiwan), which was calibrated by monocrystalline silicon solar cell in advance.

TableS1.Photovoltaic performance of devices fabricated with PBDB-T and **IDT-EDOT**.

D:A	Additives(%)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF(%)	PCE (%)
1: 0.5	-	0.88	17.20	55	8.35
1: 1.0	-	0.86	19.79	59	10.03
1: 1.2	-	0.86	20.37	58	10.19
1: 1.5	-	0.86	19.87	59	10.12
1: 2	-	0.84	17.03	45	6.45
1:1.2	-	0.86	20.70	58	10.29[a]
1:1.2	-	0.86	19.92	59	10.14[b]
1:1.2	DIO(0.2)	0.86	21.34	62	11.32[a]
1:1.2	DIO(0.4)	0.85	19.53	58	9.79[a]
1:1.2	DIO(1)	0.79	17.86	57	8.00[a]

[a] Rotation speed is 1500 rpm, [b] Rotation speed is 1800 rpm

TableS2. Photovoltaic performance of devices fabricated with PBDB-T and **IDT-PDOT.**

D:A	V_{oc} (V)	J_{sc} (mA/cm^2)	FF(%)	PCE (%)
1: 0.5	0.85	5.26	49	2.18
1: 0.8	0.82	4.07	38	1.26

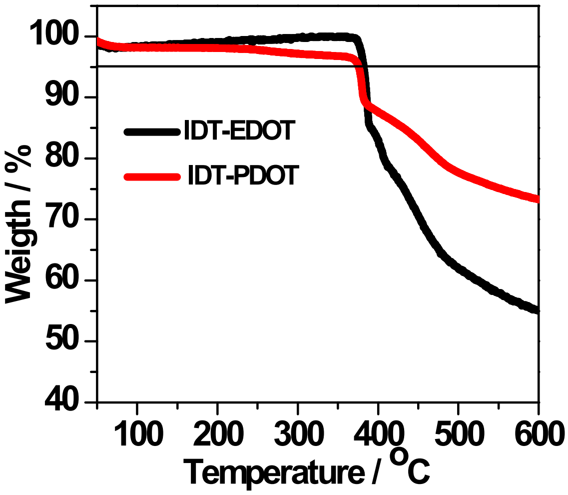


Figure S1. TGA curves of **IDT-EDOT** and **IDT-PDOT.**

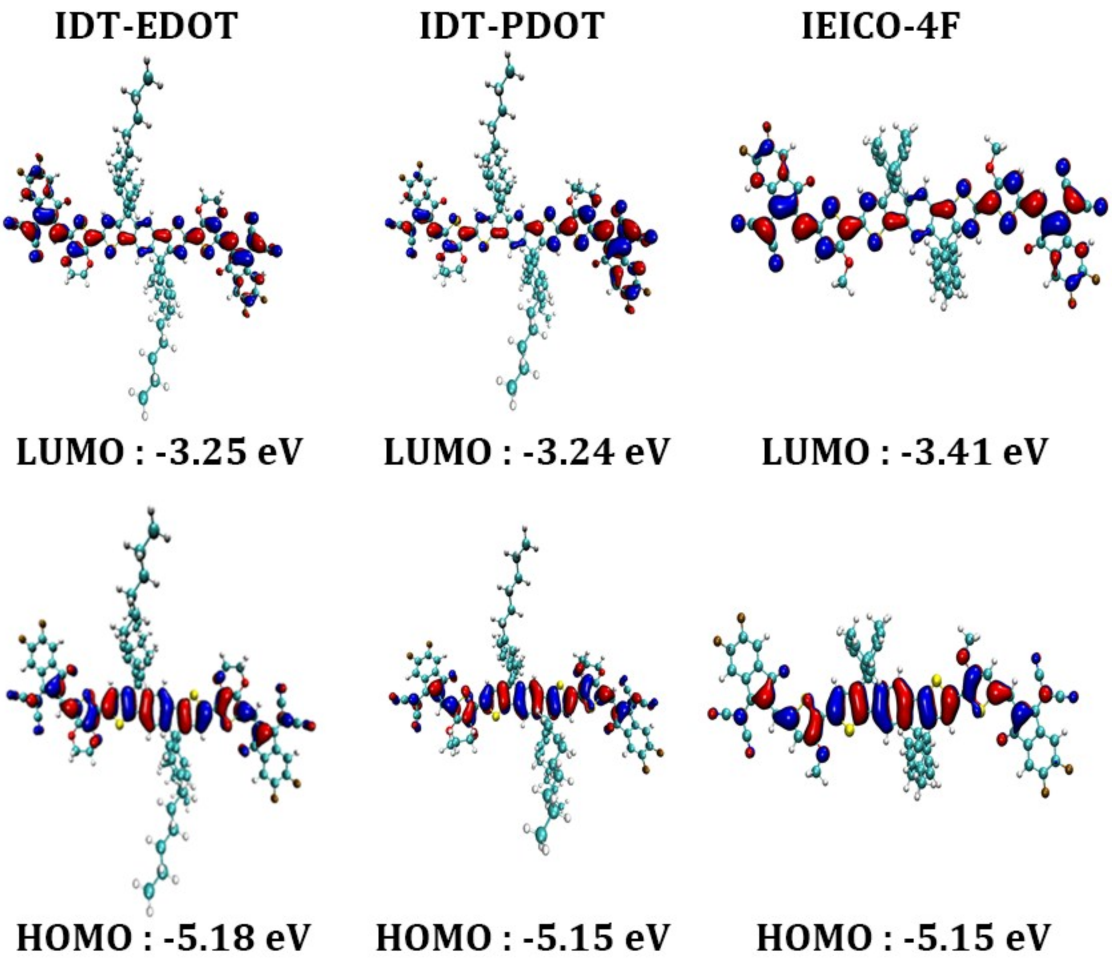


Figure S2. Frontier molecular orbitals calculated by density functional theory.

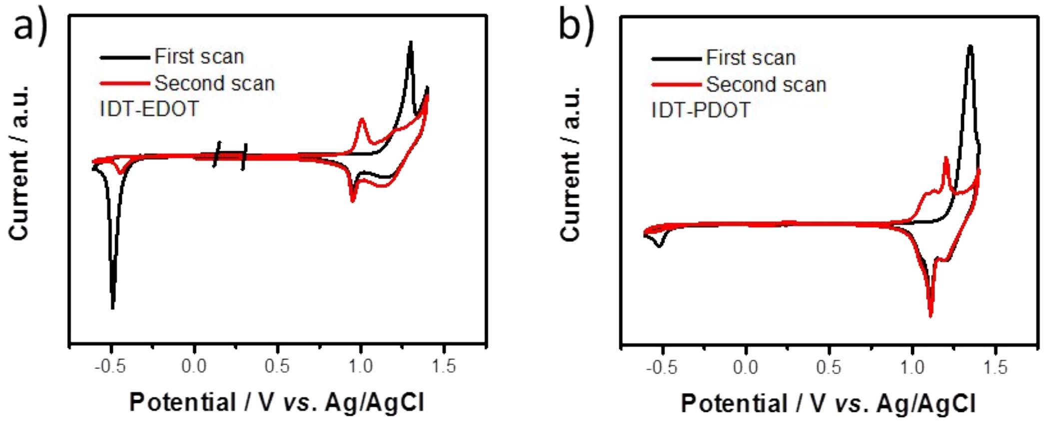


Figure S3. Cyclic voltammograms of a）**IDT-EDOT** and b) **IDT-PDOT** as films on a Pt electrode measured in 0.1 M Bu_4NPF_6 acetonitrile solutions at a scan rate of 100 mV/s.

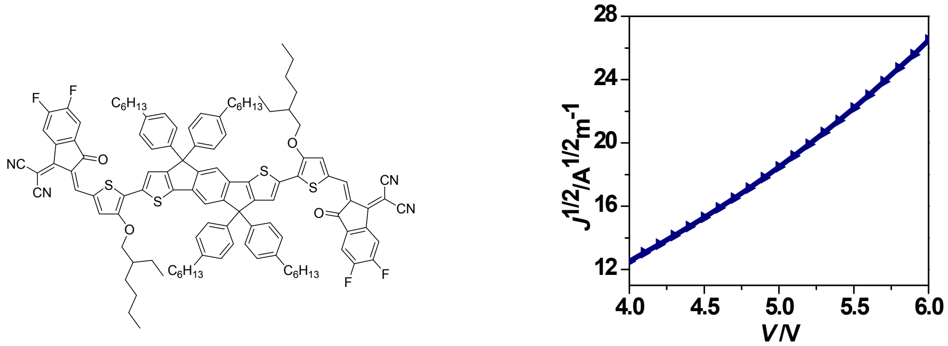


Figure S4. Chemical structure of **IEICO-4F** and electron mobility of blend film based on **PBDB-T: IEICO-4F**

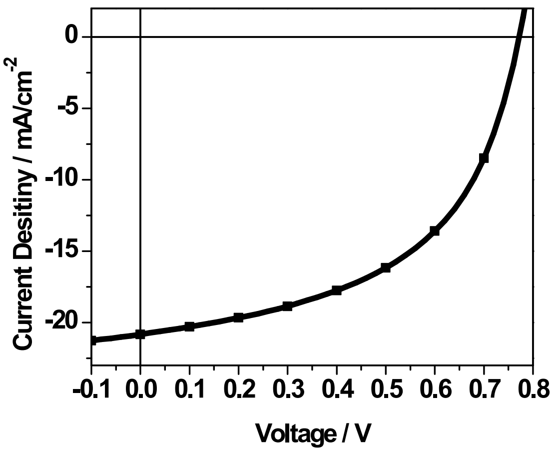


Figure S5 *J*–*V* curves of **PBDB-T: IEICO-4F** blend film.

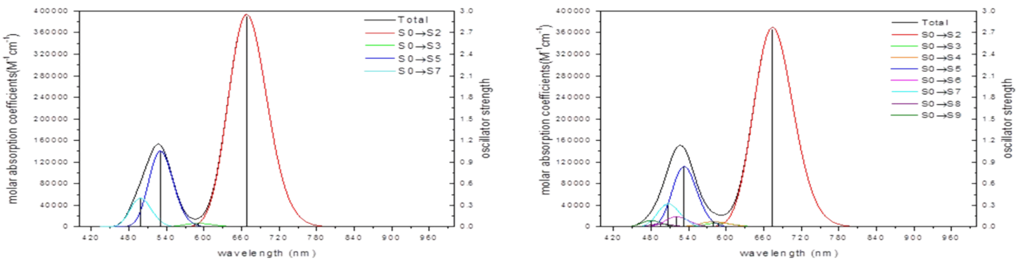


Figure S6. Simulated absorption spectrum based on DFT at PBE0/6-311G* level for **IDT-EDOT** and **IDT-PDOT.**

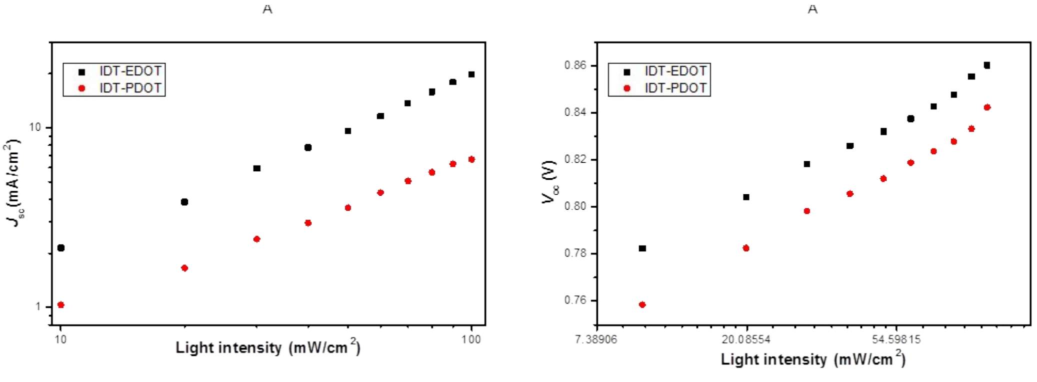


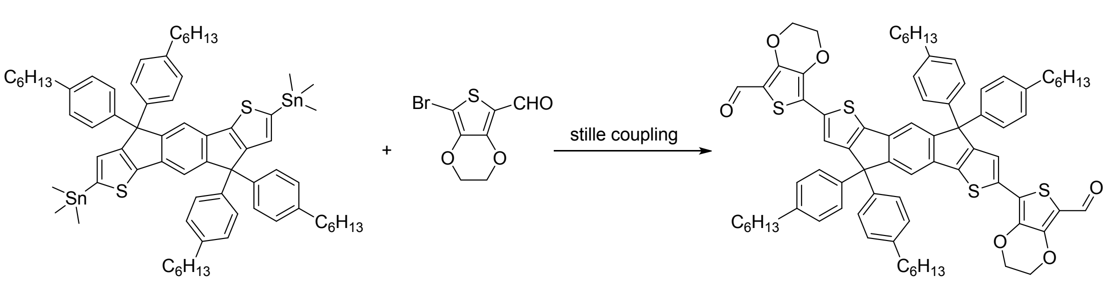
Figure S7. J_{sc} and V_{oc} on light intensity for **IDT-E(P)DOT** based devices.

1.3 Space-Charge Limited Current Measurement

Hole/electron devices with a structure of ITO/PEDOT:PSS (30 nm)/active layer/Au and ITO/ZnO/active layer/Al were fabricated. A solution of **PBDB-T** and **IDTS** in 1,2-dichlorobenzene (DCB) was spin-coated onto PEDOT:PSS or ZnO to form active layer like OSC devices, and Au (Al) was thermally evaporated at a pressure of 10^{-4} Pa through a shadow mask. Dark *J–V* curves of the hole/electron devices were measured by the space-charge limited current (SCLC) method. Hole and electron mobilities of devices were measured by SCLC model and calculated according to equations reported in previous literature.[S1] Dark *J-V* curves were fitted by using the Mott-Gurney equation: $J = 9\varepsilon_o\varepsilon_r\mu V^2/8d^3$, where J is the space charge limited current, ε_o is the vacuum permittivity ($\varepsilon_o=8.85\times10^{-12}$ F/m), ε_r is the permittivity of the active layer ($\varepsilon_r = 3$), μ is mobility, and dis the thickness of the active layer

1.4 Synthesis

The starting material **1** was purchased from Derthon Optoelectronic Materials Science Technology Co LTD and the **Br-EDOT-CHO**, **Br-PDOT-CHO**, were synthesized according to the literature reported procedures.[S2]



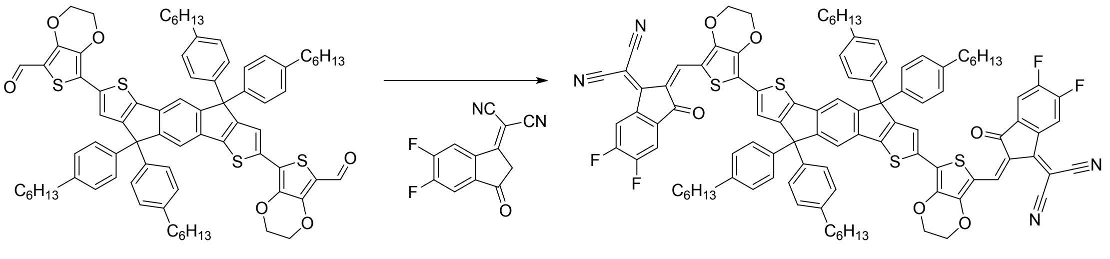
1 **Br-EDOT-CHO** **IDT(EDOT-CHO)$_2$**

IDT(EDOT-CHO)$_2$ was synthesized through Stille coupling with **1** and **Br-EDOT-CHO.**

A mixture of **1** (200 mg, 0.16 mmol) and **Br-EDOT-CHO** (120 mg, 0.48 mmol) in toluene was degassed before and after $Pd(PPh_3)_4$ (18 mg) was added. And the mixture was refluxed under N_2 overnight. After the reaction was finished, toluene was removed with rotary evaporator. The residue was chromatographically purified on silica gel column with DCM/petroleum ether (1:1, v/v) to give **IDT(EDOT-CHO)$_2$** as a yellow solid in a yield of 71% (141 mg).^{1}H NMR (600MHz, $CDCl_3$) δ: 9.87 (s, 2H), 7.40 (s, 2H), 7.34 (s, 2H), 7.14-7.16 (m, 8H), 7.07-7.08 (m, 8H), 4.40 (m, 8H), 2.56 (t, *J* = 7.8 Hz, 8H), 1.56-1.62 (m, 8H), 1.27-1.36 (m, 24H), 0.87 (m, 12H).

IDT(PDOT-CHO)$_2$ was synthesized through Stille coupling with **1** and **Br-PDOT-CHO.**

A mixture of **1** (254 mg, 0.21mmol) and **Br-PDOT-CHO** (120 mg, 0.46mmol) in toluene was degassed before and after $Pd(PPh_3)_4$ (20 mg) was added. And the mixture was refluxed under N_2 overnight. After the reaction was finished, toluene was moved out with rotary evaporator. The residue was chromatographically purified on silica gel column eluting with DCM/petroleum ether (3:1, v/v) to give **IDT(PDOT-CHO)$_2$** as an orange solid in a yield of 69% (184 mg).^{1}H NMR (600MHz, $CDCl_3$) δ: 9.90 (s, 2H), 7.42 (s, 2H), 7.29 (s, 2H), 7.14-7.16 (m, 8H), 7.07-7.08 (m, 8H), 4.36 (m, 4H),4.29 (m, 4H) 2.56 (t, *J* = 7.8 Hz, 8H), 2.35-2.38 (m, 4H), 1.55-1.61 (m, 8H), 1.27-1.35 (m, 24H), 0.87 (m, 12H).



Small molecule acceptor **IDT-EDOT.**

A mixture of **IDT(EDOT-CHO)$_2$** (150 mg, 0.12mmol) and **2** (140 mg, 0.61mmol) chloroform was carefully degassed before and after pyridine was added. The reaction was kept at room temperature under N_2 overnight. Then, the solvent was evaporated, and the residue was purified on silica gel column eluting with DCM/petroleum ether (1:1, v/v) to give **IDT-EDOT** as a dark blue solid in a yield of 70% (140 mg).^{1}H NMR (600MHz, $CDCl_3$) δ: 9.00 (s, 2H), 8.48-8.51 (m, 2H), 7.61-7.62 (m, 2H), 7.59 (s, 2H),7.49 (s, 2H), 7.15-7.16 (m, 8H), 7.09-7.11 (m, 8H),4.53-4.55 (m, 4H),4.43-4.45 (m, 4H),2.58 (t, J = 7.8 Hz, 8H), 1.57-1.63 (m, 8H), 1.28-1.35 (m, 24H), 0.87(m, 12H).^{13}C NMR (150 MHz,$CDCl_3$) δ: 186.45, 158.35,155.23, 153.08, 147.20, 142.01, 140.90, 136.69, 134.22, 128.58, 127.82, 123.84,118.17, 114.88, 114.70, 112.24, 112.10, 66.10, 64.72, 35.56,31.71, 31.34, 29.10, 22.58, 14.10. **Mass (MALDI-TOF):** *m*/*z*, calcd for $C_{102}H_{86}F_4N_4O_6S_4$: 1668.05; found: 1668.320.

Small molecule acceptor **IDT-PDOT.**

A mixture of **IDT(PDOT-CHO)$_2$** (180 mg, 0.14mmol) and **2** (180 mg, 0.78mmol) chloroform was carefully degassed before and after pyridine was added. The reaction was kept at room temperature under N_2 overnight. Then, the solvent was evaporated, and the residue was purified on silica gel column eluting with DCM/petroleum ether (3:1, v/v) to give **IDT-PDOT** as a dark blue solid in a yield of 29% (140 mg).^{1}H NMR (600MHz, $CDCl_3$) δ: 9.12 (s, 2H), 8.48-8.51 (m, 2H), 7.61-7.62 (m, 2H), 7.57 (s, 2H), 7.51 (s, 2H), 7.17-7.18 (m, 8H), 7.09-7.11 (m, 8H), 4.47 (m, 4H),4.35 (m, 4H), 2.58 (t, J = 5.2 Hz, 8H), 2.40-2.42 (m, 4H), 1.58-1.63 (m, 8H), 1.28-1.35 (m, 24H), 0.87 (m, 12H).^{13}C NMR (150 MHz,$CDCl_3$)δ: 186.45,158.69, 154.81, 147.69, 144.13, 143.23, 141.98, 140.96, 136.87, 136.74, 134.25, 132.81 128.57, 127.83, 123.24, 118.81, 114.89, 114.70, 112.28, 112.16, 72.21, 71.12, 35.56, 32.37, 31.72, 31.36, 29.69, 22.59, 14.10. **Mass (MALDI-TOF):** *m*/*z*, calcd for $C_{104}H_{90}F_4N_4O_6S_4$: 1696.568; found: 1696.319.

References

[S1] Goh, C.; Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Fréchet, J. M. J. *Appl. Phys.Lett.*, **2005**, *86*, 122110.

[S2] Jessing, M.; Brandt M.; Jensen K. J.; Christensen J. B.; Boas U. *J. Org. Chem.* **2006**, *71*, 6734