Perylenediimide dimer containing an asymmetric π-bridge and its fused derivative for fullerene-free organic solar cells

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Materials and Methods

All chemicals and solvents were purchased from commercial suppliers and used without further purification unless otherwise specified.

Methods ^{1}H NMR spectra was obtained using a Bruker Advance III 400 (400 MHz) nuclear magnetic resonance (NMR) spectroscope. Mass spectra (MALDI-TOF) were carried on a Micromass GCT-MS spectrometer. UV-vis absorption spectra were tested on Lambda950 (Perkin Elmer Instruments Co. Ltd, USA). Photoluminescence spectra was tested on Perkin Elmer Instruments (shanghai) Co. Ltd, USA. Thermogravimetric analysis (TGA) was recorded on Diamond TG/DTA under protection of nitrogen at a heating rate of 10 $°C{\cdot}min^{-1}$. Cyclic voltammetry (CV) was done on an electrochemical workstation with working electrode Pt plate, counter electrode Pt wire and standard calomel electrode (SCE) or Ag/AgCl electrode as reference electrode. The CV curves were recorded versus the potential of SCE, which was calibrated by the ferrocene-ferrocenium (Fc/Fc^+) redox couple, which absolute energy level is 4.8 eV below vacuum. The height and phase images of blend films were obtained on a Veeco Dimension 3100 atomic force microscopy (AFM) in the tapping-mode using an etched silicon cantilever. 2D-GIWAXS were conducted the SPring-8 on beamline BL46XU with X-ray wavelength of 1Å. The film samples were irradiated at a fixed angle of 0.12°. All tested samples were fabricated under the same condition of best-performance devices on the cleaned Si substrates.

Fabrication and characterization of photovoltaic cells

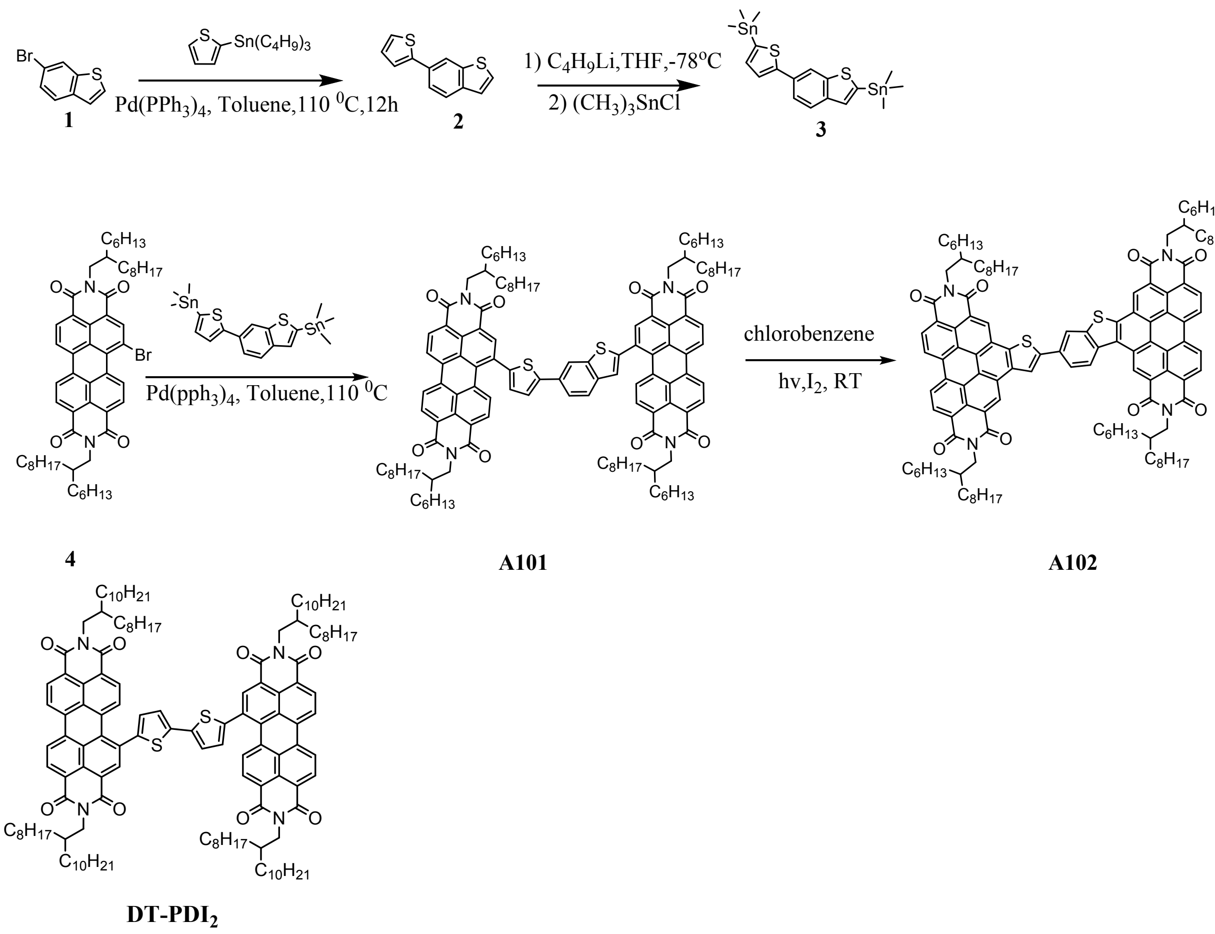
Organic solar cells were fabricated with the structure of ITO/PEDOT:PSS/active layer/Ca/Al. The patterned indium tin oxide (ITO) glass with a sheet resistance of 15 Ω sq^{-1} was pre-cleaned in an ultrasonic bath of acetone and isopropanol, and treated in an ultravioletozone chamber (Ultraviolet Ozone cleaner, Jelight Company, USA) for 15 min. A thin layer of poly (3,4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT:PSS) was spin-coated onto the ITO glass and baked at 150 °C for 15 min. The PBDB-T:**A101**/**A102** mixture (20 $mg{\cdot}mL^{-1}$ in total in CB) was spin-coated on the PEDOT:PSS layer to form a photosensitive layer. The calcium layer (ca.20 nm) and the aluminum layer (ca. 80 nm) were then evaporated onto the surface of the photosensitive layer under vacuum (ca. 4×10^{-6} mbar) to form the negative electrode. The active area of the device was 4 mm^2. The thicknesses of the active layer were detected by Alpha-atepD-120stylus profilometer, Kla-Tencor.

The *J*-*V* curve was measured using a Keithley 2400 source-measure unit. Photocurrent was measured under AM 1.5 G illumination at 100 $mW{\cdot}cm^2$ using a Newport Thermal Oriel 91159A solar simulator. Light intensity is calibrated with a Newport oriel PN 91150V Si-based solar cell. The EQE spectrum was measured using an Oriel Newport system (Model 66902).

Space charge limited current (SCLC) mobility measurements

The mobility of hole-only or electron-only of the OSCs device was achieved by fabricated the architecture ITO/PEDOT:PSS/active layer/Au for holes or ITO/TiO_x/active layer/Al for electrons. The mobility was extracted by fitting the current density-voltage curves using the Mott-Gurney relationship (SCLC). The active layer and electrodes were prepared the same as the solar cells condition. Au (80 nm) and Al (80 nm) cathodes were thermal evaporated in glove box at a chamber pressure of ~ 4.0×10^{-6} mbar.

The charge carrier mobility was determined by fitting the dark current to the model of a single carrier SCLC according to the equation: $J = 9\varepsilon_0\varepsilon_r\mu V^2/8d^3$, where J is the current density, d is the film thickness of the active layer, μ is the charge carrier mobility, ε_r is the relative dielectric constant of the transport medium, and ε_0 is the permittivity of free space. $V = V_{app} - V_{bi}$, where V_{app} is the applied voltage, V_{bi} is the offset voltage.



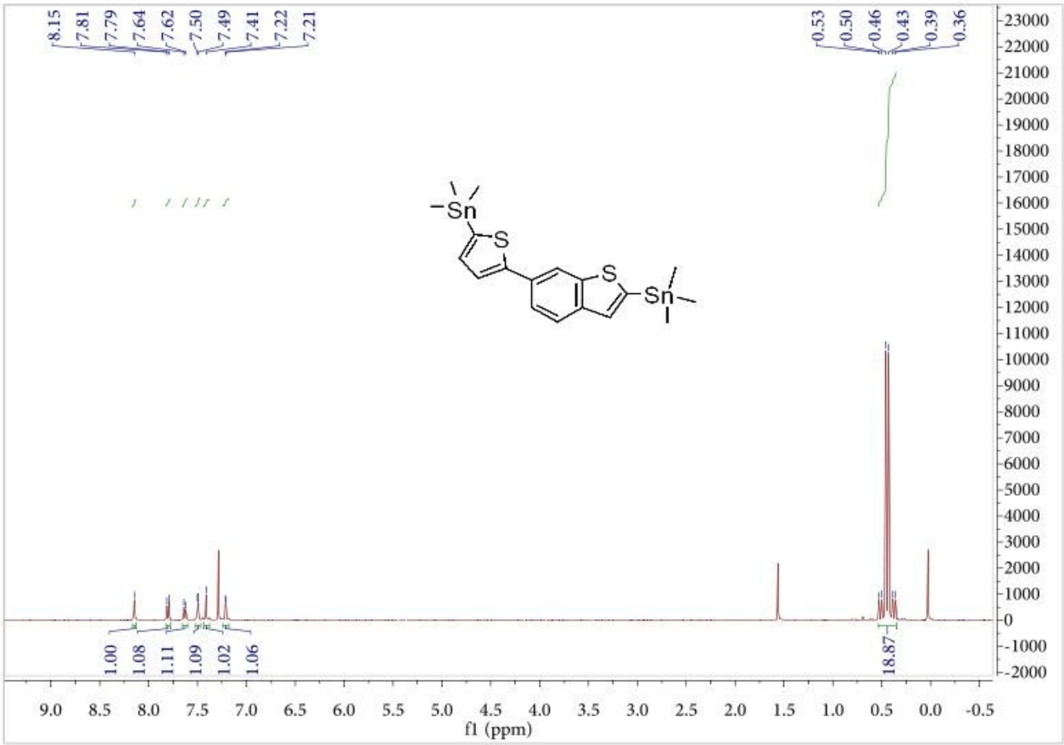
Scheme S1. Synthesis of **A101**, **A102** and **DT-PDI$_2$**.

6-(thiophen-2-yl)benzo[b]thiophene (2): 2.11 g (9.9 mmol) 6-bromobenzo[b]thiophene (1) and tributyl(thiophen-2-yl)stannane (3.88 g, 10.4 mmol) were added into round-bottom flask in 30 mL of toluene. Pd(PPh$_3$)$_4$ (40 mg, 0.035 mmol) were added in the above solution. Then the solution was filled and vacuumed with nitrogen for 3 times to remove oxygen, and heated at 110 °C for 24 h with stirring. After cooled to room temperature, the reaction mixture was added into 70 ml saturated KF solution with stirring overnight to quench tin reagent. The mixture was extracted by chloroform three times and the organic phase was concentrated by rotary evaporation and purified by column chromatography on silica gel with dichloromethane and petroleum ether as eluent. The white powder product was obtained (2.14 g, 100% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.14 (d, *J* = 0.7 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.66 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.47 (d, *J* = 5.4 Hz, 1H), 7.40 (dd, *J* = 3.6, 1.0 Hz, 1H), 7.37-7.30 (m, 2H), 7.13 (dd, *J* = 5.1, 3.6 Hz, 1H).

Trimethyl(5-(2-(trimethylstannyl)benzo[b]thiophen-6-yl)thiophen-2-yl)stannane (3): Compound 2 (2.0 g, 9.25 mmol) were dissolved in 70 mL of dry THF under argon protection. Then 8.14 mL of n-butyllithium (20.35 mmol, 2.5 M in hexane) was injected dropwise in 5 minutes at -78 °C. The mixture was stirred for 2 h with removing acetone bath in room temperature. After cooled down to -78 °C again. The 22 mL of chlorotrimethylstannane (1.0 M in hexane, 22 mmol) was added dropwise and the mixture was stirred overnight at the room temperature. Then, the mixture was poured into water and extracted with chloroform three times, the combined organic phase was concentrated by rotary evaporation. The pure product was obtained by recrystallization using methanol as a light-grey powder (2.62 g, yield 52.3%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.80 (d, J = 8.3 Hz, 1H), 7.63 (d, J = 8.3 Hz, 1H), 7.50 (d, J = 3.2 Hz, 1H), 7.41 (s, 1H), 7.24-7.16 (m, 1H), 0.55-0.34 (m, 18H).

A101: The compound 3 (434 mg, 0.8 mmol) and 5-bromo-2,9-bis(2-hexyldecyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (1.54g, 1.68 mmol) were mixed in 30 mL of toluene. When the flask was purged by argon for three times, 27 mg catalyst of $Pd(PPh_3)_4$ was added, and then the mixture was bubbled with nitrogen again. The solution was heated to 105 °C and stirred for 24 h under argon protection. Subsequently, the reactant was poured into water and extracted with chloroform three times. The organic layer was combined and purified by column chromatography on silica gel (eluent: dichloromethane) to get reddish brown solid (Yield: 1.26 g, 83.4 %).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.60 (m, 7H), 8.55 (dd, J = 17.8, 7.3 Hz, 4H), 8.38 (d, J = 8.2 Hz, 1H), 8.29 (dd, J = 15.2, 8.2 Hz, 2H), 8.21 (d, J = 8.0 Hz, 1H), 8.08 (s, 1H), 7.86 (d, J = 8.3 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.56 (s, 1H), 7.49 (d, J = 3.6 Hz, 1H), 4.07 (d, J = 11.5 Hz, 8H), 1.98 (s, 4H), 1.28 (m, 96H), 0.90-0.70 (m, 24H). MALDI-TOF (m/z) [M] = 1890.4 (Calcd for $C_{124}H_{152}N_4O_8S_2$: 1889.1).

A102: (200 mg, 0.106 mmol) and I_2 (54 mg, 0.212 mmol) were dissolved in 100 mL of chlorobenzene. The reaction mixture was irradiated with a 500 W halogen lamp for 12 hours. Then saturated sodium sulfite solution was added to quench remaining I_2. The organic phase was combined and dried under reduced pressure to obtain crude product, which was purified by column chromatography (eluent:CH_2Cl_2) to afford A102 as a dark red solid (185 mg, 93%).The target product was characterized by ^{1}H NMR spectroscopy and mass spectrometry, the ^{1}H NMR spectra of ring-fused A102 was broad and complex in the aromatic region. MALDI-TOF (*m/z*) [*M*] = 1886.8 (Calcd for $C_{124}H_{148}N_4O_8S_2$: 1885.7).



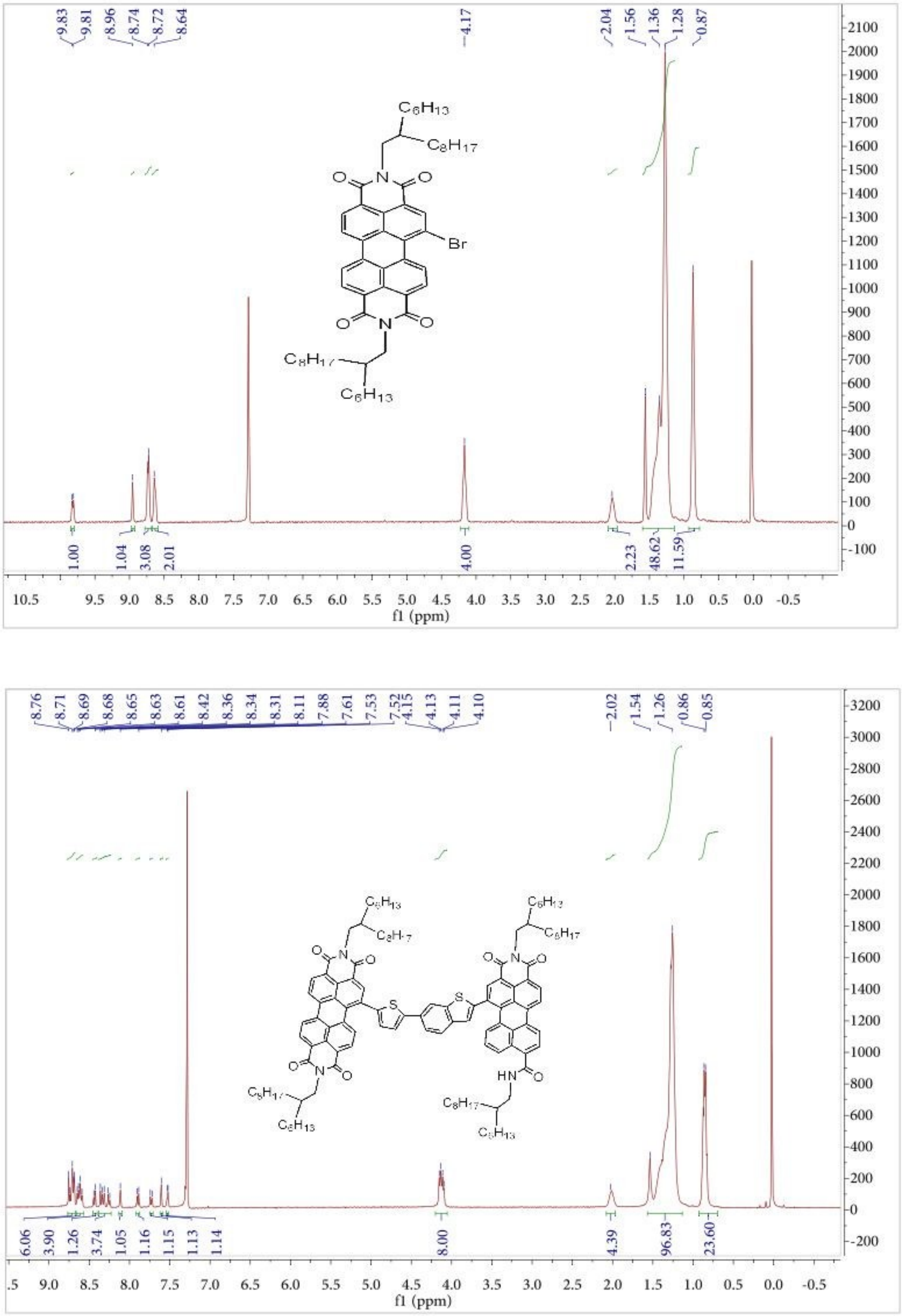
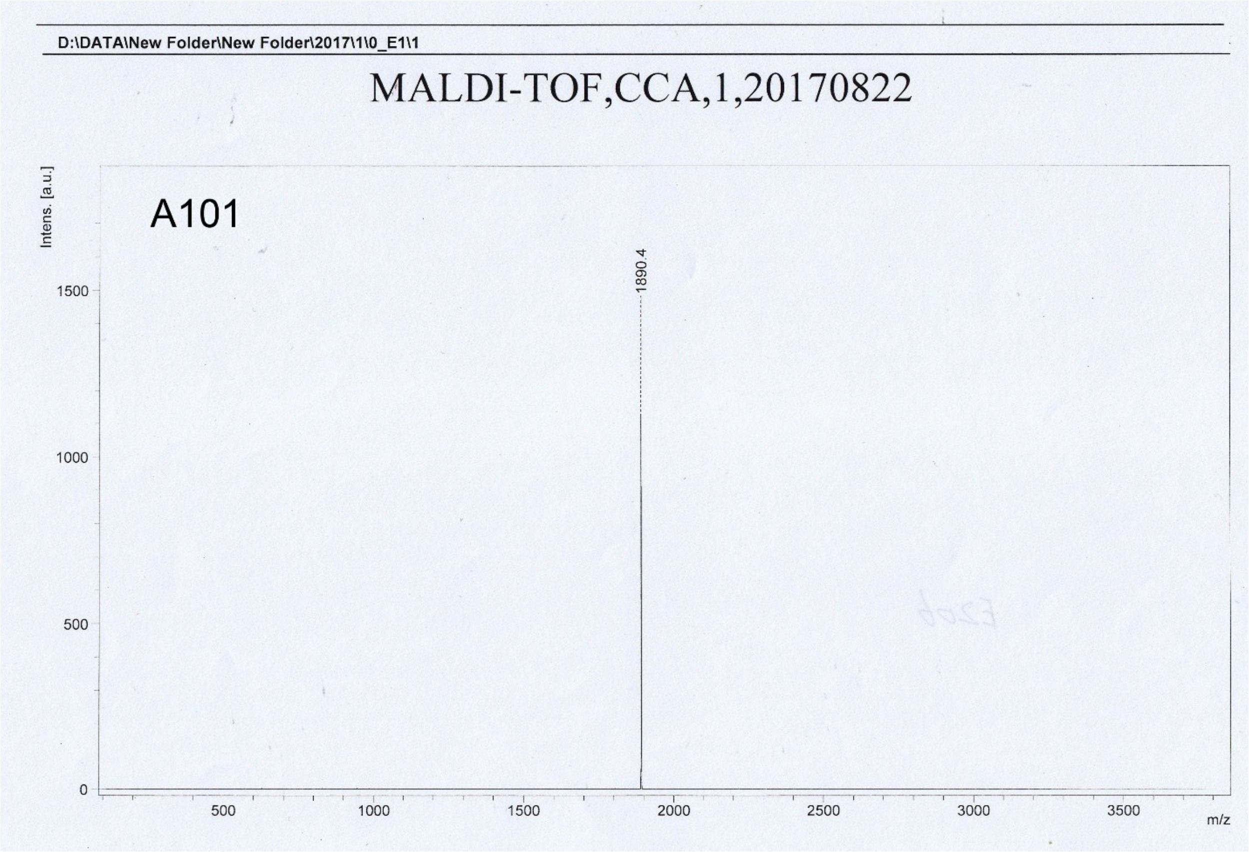


Figure S1. ^{1}H NMR spectra of synthesized acceptors and intermediates.



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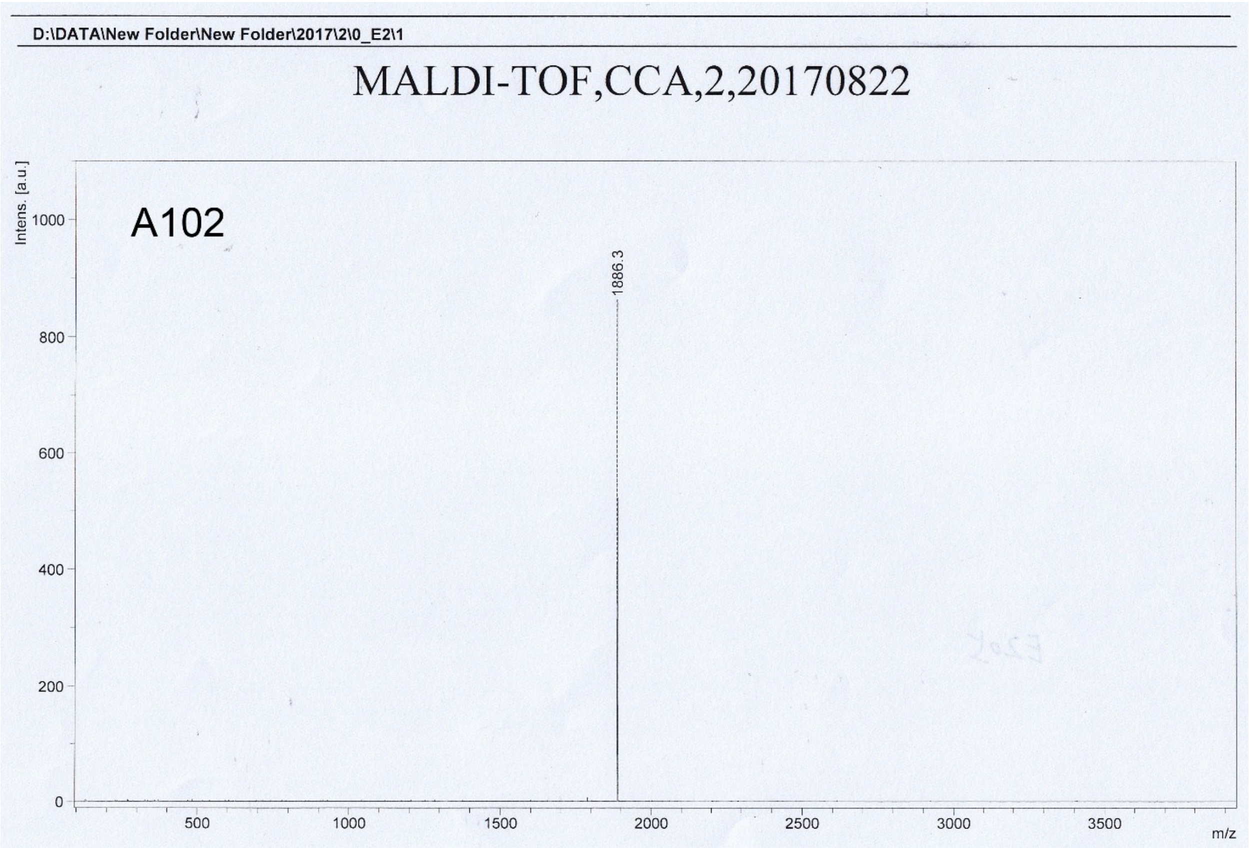

Figure S2. Mass spectra of synthesized acceptors.

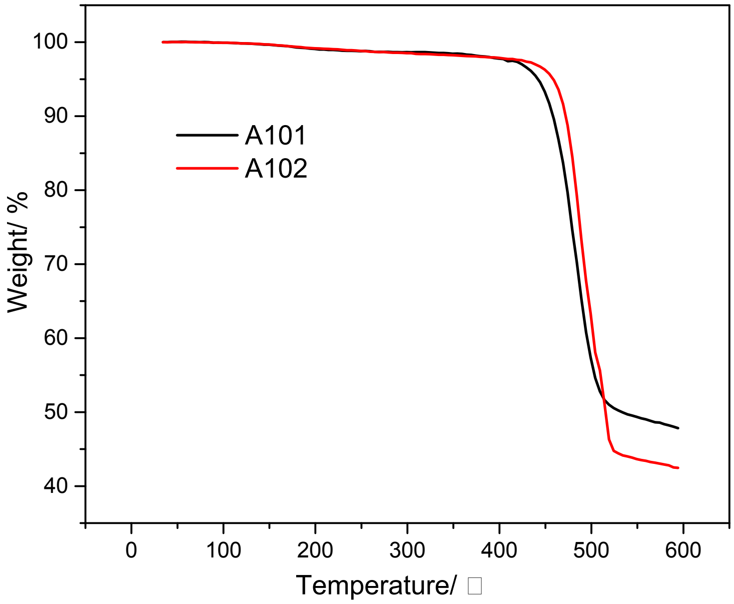

Figure S3. TGA curves of A101 and A102.

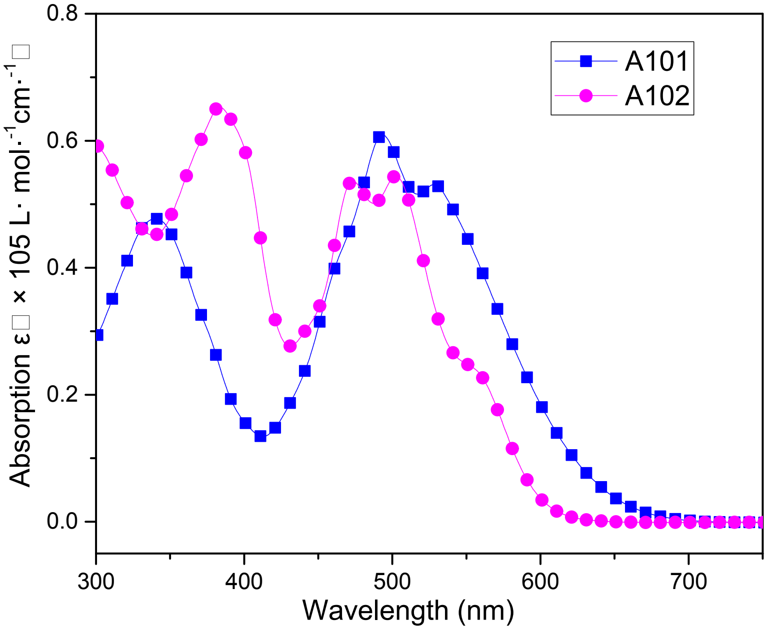

Figure S4. The optical absorption spectra of **A101** and **A102** in $CHCl_3$ solution.

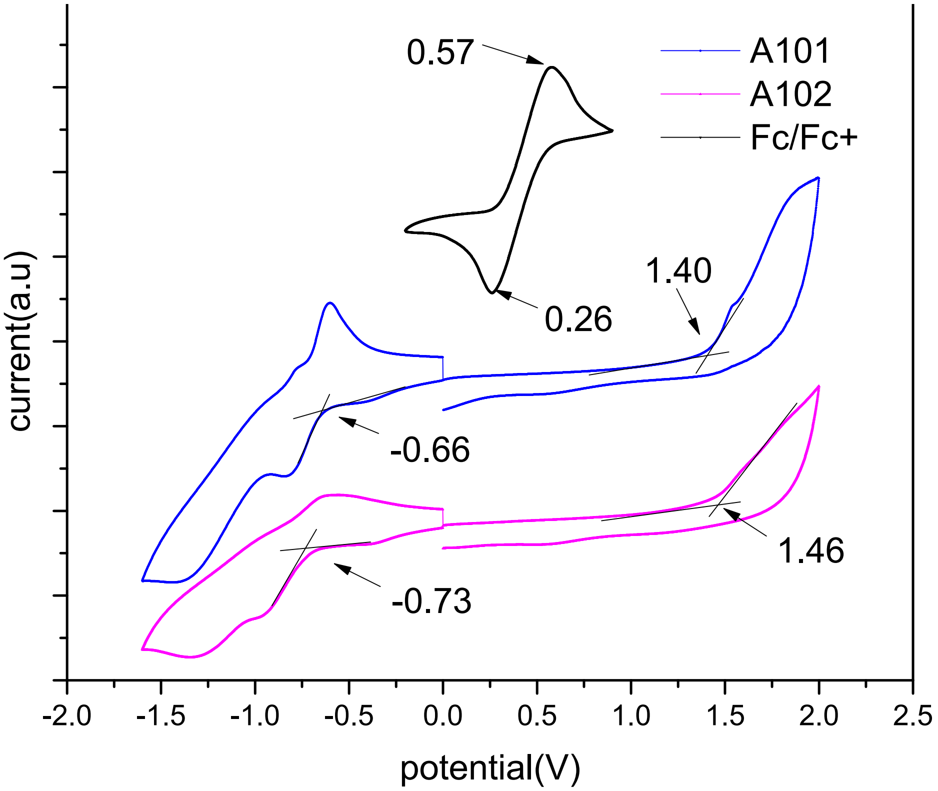

Figure S5. Cyclic voltammetric graph of synthesized acceptors(Acetonitrile, 0.1 M $[nBu4N]^+[PF6]^-$, 50 mVs^{-1}) with Fc/Fc$^+$ as the reference.

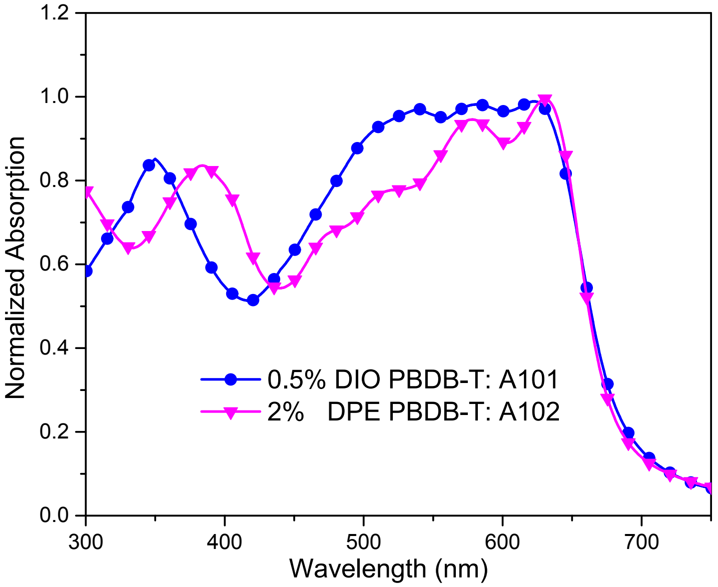

Figure S6. The optical absorption spectra of PBDB-T:**A101**/**A102** in blend films.

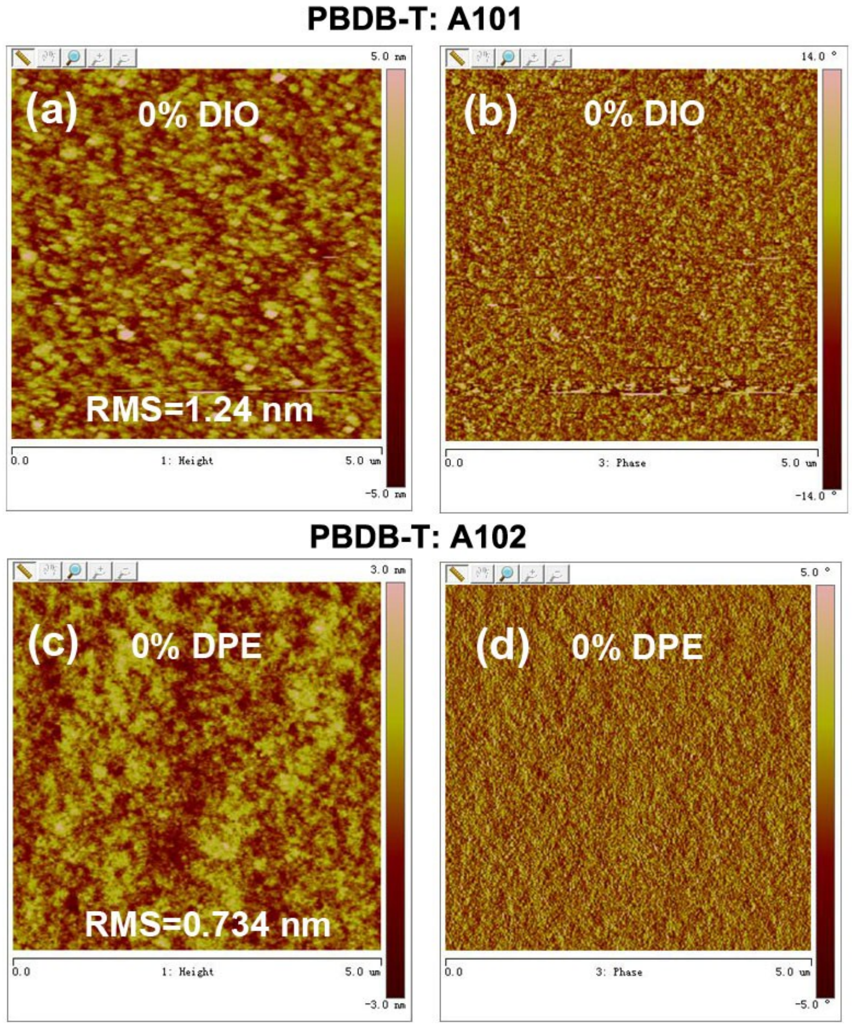

Figure S7. Atomic force microscopy (AFM) height (left) and phase (right) images (5×5 μm) of the blend films of (a) and (b) **PBDB-T:A101** and (c) and (d) **PBDB-T:A102** without additive.

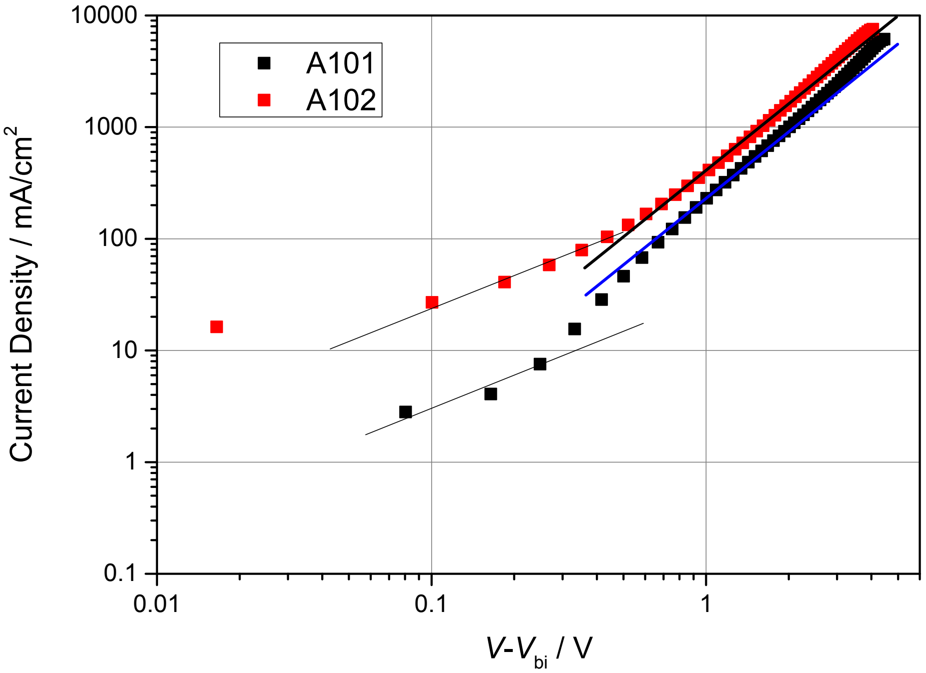

Figure S8. Current density-applied voltage (J-V) characteristics for hole-only device.

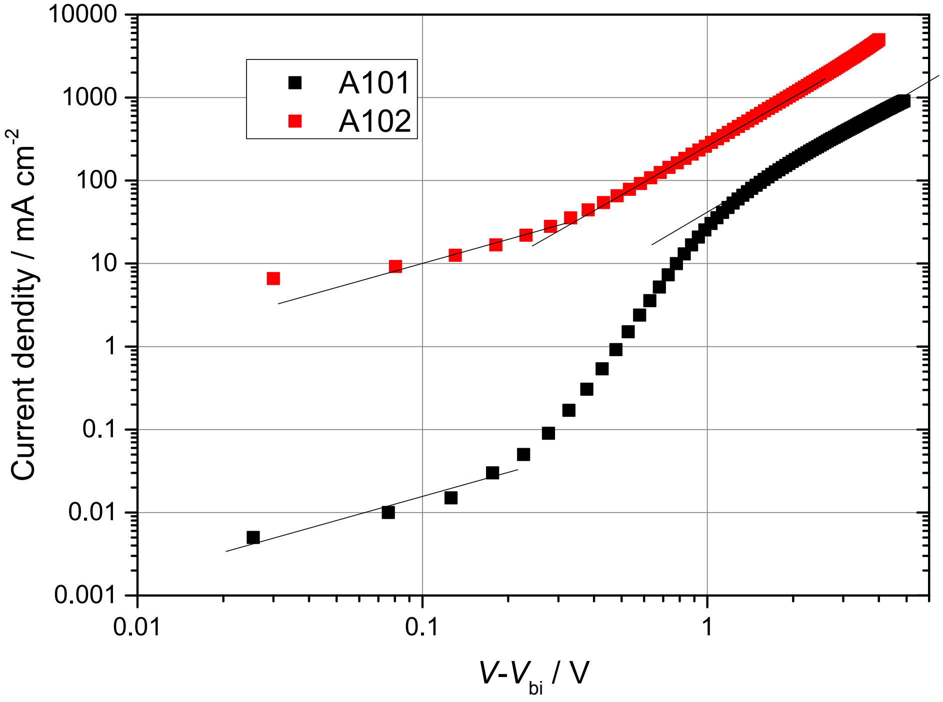

Figure S9. Current density-applied voltage (J-V) characteristics for electron-only device

Table S1: Effect of donor: acceptor ratio on photovoltaic performance of devices processed using CB as solvent, at r.t..

Devices	D:A	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
PBDB-T:A101	1:1	0.86	5.52	40.90	1.94
	1:1.5	0.88	5.49	45.97	2.22
	1.5:1	0.86	4.10	35.17	1.24
	1:2	0.85	4.33	41.29	1.52
PBDB-T:A102	1:1	0.95	7.91	40.43	3.04
	1:1.5	0.96	8.83	49.30	4.18
	1.5:1	0.93	5.60	36.29	1.89
	1:2	0.97	8.48	52.87	4.35

Table S2: Effect of additive on photovoltaic performance of devices processed at 1:1.5 ratio of donor: acceptor, CB solvent, at r.t..

Device	additive	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
PBDB-T:A101	no	0.87	5.52	46.21	2.22
	0.5% DIO	0.85	6.87	61.10	3.57
	1% DPE	0.86	5.86	64.73	3.26
	3%DPE	0.85	5.50	64.78	3.03
PBDB-T:A102	no	0.97	8.44	48.36	3.96
	0.5% DIO	0.97	8.68	51.98	4.38
	1% DPE	0.95	9.53	59.70	5.41
	2% DPE	0.96	9.66	60.88	5.65
	3% DPE	0.95	9.17	61.41	5.35
	5% DPE	0.99	8.51	60.71	5.12

Table S3. The photovoltaic performance of PBDB-T:A101/A102 under different thermal annealing temperature without solvent additive.

Device	annealing temperature (°C)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PBDB-T: A101	r.t.	0.87	5.52	46.21	2.22
	100	0.87	4.79	47.08	1.96
	120	0.88	4.50	46.75	1.85
PBDB-T: A102	r.t.	0.95	9.25	51.43	4.52
	80	0.96	8.68	53.85	4.49
	100	0.96	8.75	56.29	4.73
	120	0.96	8.71	56.21	4.70
	150	0.95	8.46	57.00	4.58