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Supporting information

Conjugated side-chain optimization of indacenodithiophene-based nonfullerene acceptors for efficient polymer solar cells

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Experimental section

Analytical instruments

Nuclear magnetic resonance (NMR) spectra were measured with Bruker AVANCE 400 spectrometer. Ultraviolet-visible (UV-Vis) absorption spectra were measured on PerkinElmer Lamada 25 spectrometer. Molecular mass was determined by flight mass spectrometry (MALDITOF MS) using a Bruker Aupoflex-III mass spectrometer. Thermal gravimetric analysis (TGA) was performed under nitrogen at a heating rate of 20 °C min with TGA Q50 analyzer. The electrochemical cyclic voltammetry (CV) was recorded on a electrochemistry work station (CHI830B, Chenhua Shanghai) with a Pt slice electrode (coated with a polymer film), a Pt ring, and an Ag/AgCl electrode as the working electrode, the auxiliary electrode and the reference electrode respectively, in a 0.1 mol L tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution. Atomic force microscopy (AFM) measurement was carried out on a Dimension 3100 (Veeco) Atomic Force Microscope in the tapping mode.

PSC Device Preparation and Performance Measurement

The devices with an inverted structure of ITO/ZnO/Active layer/MoO₃/Al were fabricated and

characterized in an N₂-filled glovebox, where the active layer comprised with polymer donor PBDB-T and small molecule acceptors IDT-PhIC, IDTV-PhIC, m-IDTV-PhIC, and IDTV-ThIC. The indium tin oxide (ITO) patterned glass was cleaned with ultrasonic treatment in detergent, deionized water, acetone, ethanol, and isopropyl alcohol sequentially, and dried in an ultraviolet-ozone chamber for 15 min. The ZnO layer was deposited by spin-coating on top of a pre-cleaned ITO-coated glass substrate. And then, the active layer was spin-coated on the ZnO layer from a blend solution. The materials were dissolved in CB or CF or DCB. The device was transferred to a glove box, where the above prepared blend solution was then spin-coated on ZnO surface as the active layer. Here, it should be noted that a certain amount of DIO or CN was added to use as a process additive if necessary. Subsequently, a MoO₃ layer (~10 nm) and an Al layer (~100 nm) were evaporated though a shadow mask and form a top anode. The active area of the devices was defined ~ 0.04 cm² by a shadow mask. The thicknesses of the active layer were controlled by varying the spin-coating speed and blend concentration and measured on an Ambios Technology XP-2 surface profilometer. Photovoltaic performance of solar cells was tested under illumination condition with an AM 1.5G (100 mW cm⁻²), and the current density-voltage (J-V) characteristics were measured by a computer controlled Keithley 2450 Source Meter. The EQE was measured by using a Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd.). The light intensity at each wavelength was calibrated by a standard single-crystal Si solar cell.

The charge mobility was measured by the space charge-limited current (SCLC) method with a holeonly device configuration (ITO/PEDOT:PSS/Active layer/MoO₃/Al) for hole mobility and an electrononly device configuration (ITO/ZnO/Active layer/Ca/Al) for electron mobility. Both hole and electron mobilities were extracted by fitting measured *J-V* curves using the empirical Mott-Gurney formula in single carrier SCLC device with the equation of $ln(JL^3/V^2) \approx 0.89(1/E_0)^{0.5} (V/L) + ln(9\varepsilon_0\varepsilon_r\mu/8)$.



Fig. S1 TGA curves of these NFAs under nitrogen atmosphere at a heating rate of 20 °C min⁻¹.



Fig. S2 CVs of IDT-PhIC, IDTV-PhIC, *m*-IDTV-PhIC, and IDTV-ThIC films on platinum electrode in acetonitrile solution containing 0.1 mol L⁻¹ Bu_4NPF_6 at a scan rate of 0.1 V s⁻¹.



Fig. S3 Simulated electron distributions of HOMO/LUMO energy levels by DFT calculations for simplified molecules of **IDT-PhIC**, **IDTV-PhIC**, *m*-**IDTV-PhIC**, and **IDTV-ThIC**.

Active layer (D:A, by weight)	Solvent	Additive	V _{oc}	$J_{ m sc}$	FF	PCE _{max} / _{ave} ^b
PBDB-T:IDT-PhIC (1:1)	СВ	-	0.93	9.99	54.66	5.11/4.94
PBDB-T:IDTV-PhIC (1:1)	CB	-	0.98	4.93	36.64	1.77/1.63
PBDB-T:IDTV-PhIC (1:1)	o-DCB	-	0.95	4.67	32.52	1.45/1.33
PBDB-T:IDTV-ThIC (1:1)	CB	-	0.90	1.62	33.73	0.49/0.49
PBDB-T: <i>m</i> -IDTV-PhIC (1:1)	CB	-	1.00	9.24	49.76	4.60/4.49
PBDB-T: <i>m</i> -IDTV-PhIC (1:1)	CF	-	0.95	7.19	37.66	2.58/2.41
PBDB-T: <i>m</i> -IDTV-PhIC (1:1)	o-DCB	-	0.75	5.06	35.15	1.33/1.12
PBDB-T:IDT-PhIC $(1:1)^a$	CB	-	0.91	9.94	51.59	4.70/4.55
PBDB-T: IDTV-PhIC $(1:1)^a$	CB	-	0.91	4.52	36.16	1.48/1.39
PBDB-T: IDTV-PhIC $(1:1)^a$	CF	-	0.91	5.40	33.87	1.67/1.61
PBDB-T:IDTV-ThIC $(1:1)^a$	CB	-	0.91	2.06	33.26	0.62/0.56
PBDB-T:IDTV-ThIC $(1:1)^a$	o-DCB	-	0.84	1.83	30.23	0.46/0.42
PBDB-T:IDTV-ThIC $(1:1)^a$	CF	-	0.86	2.49	28.52	0.61/0.60
PBDB-T: <i>m</i>-IDTV-PhIC (1:1) ^{<i>a</i>}	CB	-	0.98	10.09	52.34	5.19/5.10
PBDB-T: IDTV-PhIC $(1:1)^a$	o-DCB	1vol % DIO	0.56	2.25	34.76	0.44/0.31
PBDB-T:IDTV-ThIC $(1:1)^a$	CB	1vol % DIO	no	no	no	no
PBDB-T: <i>m</i>-IDTV-PhIC (1:1) ^{<i>a</i>}	CB	1vol % DIO	0.99	10.75	49.11	5.21/5.10
PBDB-T: <i>m</i>-IDTV-PhIC (1:1) ^{<i>a</i>}	CB	0.5vol %CN	0.99	10.08	52.82	5.29/5.26
PBDB-T: <i>m</i>-IDTV-PhIC (1:1) ^{<i>a</i>}	CB	1vol % CN	0.99	11.58	50.91	5.85/5.61
PBDB-T: <i>m</i> -IDTV-PhIC (1:1) ^a	CB	2vol % CN	1.00	10.41	49.98	5.23/5.18
PBDB-T: <i>m</i> -IDTV-PhIC (1:0.8) ^{<i>a</i>}	CB	1vol % CN	0.99	11.08	50.57	5.56/5.18
PBDB-T: <i>m</i> -IDTV-PhIC (1:1.5) ^a	CB	1vol % CN	0.98	10.71	48.50	5.06/4.88

Table S1 Photovoltaic performance of the PSCs based on PBDB-T:SMAs with different fabricated conditions. The devices were in inverted structure of ITO/ZnO/active layer/MoO₃/Al.

^{*a*} With the annealing temperature of 130 °C for 10 min. ^{*b*} Average PCE values are obtained from over 8 cells fabricated in parallel.



Fig. S4 AFM height images (a-d) and phase images (e-h) of the blend films based on **IDT-PhIC**, **IDTV-PhIC**, *m*-**IDTV-PhIC**, and **IDTV-ThIC**.