

Balancing Photovoltaic Parameters to Enhance Device Performance of Fluorene-Fused Heptacyclic Small-Molecule Acceptors through Variation of Terminal Groups and Polymer Donors

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Experimental Section

Instruments and Measure Methods

¹H NMR, ¹³C NMR, and ¹⁹F NMR spectra were measured with Bruker AVANCE 400 spectrometer. Molecular mass was determined by flight mass spectrometry (MALDITOF MS) using a Bruker Aupoflex-III mass spectrometer. Ultraviolet-visible (UV-vis) absorption spectra were measured on Perkin Elmer Lamada 25 spectrometer with a dilute CHCl₃ solution (10⁻⁵ M). PL Thermal gravimetric analysis (TGA) was performed under nitrogen at a heating rate of 20 °C min⁻¹ with TGA Q50 analyzer. Differential scanning calorimetry (DSC) analysis was measured on a DSC instrument (DSC Q10) in a temperature range from 25 to 300 °C under N₂ with a heating rate of 5 °C min⁻¹. The cyclic voltammetry (CV) was measured on an electrochemistry work station (CHI830B, Chenhua Shanghai) with a Pt slice electrode (coated with a small acceptor film), a Pt ring, and a Ag/AgCl electrode as the working electrode, the auxiliary electrode and the reference electrode respectively, in a 0.1 M tetrabutylammonium hexafluorophosphate acetonitrile solution. The potentials were calibrated using a ferrocene/ferrocenium (Fc/Fc⁺) redox couple as an internal standard, whose redox potential is supposed at -4.8 eV relative to zero vacuum level. The HOMO/LUMO energy levels were obtained from the equation HOMO/LUMO = -(E_{ox/red}-E_{Fc/Fc⁺} + 4.8) (eV), where the redox potential (E_{Fc/Fc⁺}) of Fc/Fc⁺ was determined to be 0.59 V versus Ag/AgCl in this study. Therefore, the above equation can be simplified as HOMO/LUMO = -(E_{ox/red} + 4.21) (eV).

Preparation and Performance Test of PSCs

The solar cell devices with an inverted structure of ITO/ZnO/polymer:SMA/MoO₃/Al were fabricated and characterized in an N₂-filled glovebox, where polymer means PBDB-T or PBDB-TF using as donor and

DTCFO-ICF and **DTCFO-ICCI** were used as an SMA. 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 mixed solution containing polymer donor and SMA. The total concentration of the mixed solution was various according to the different donor:acceptor systems. Subsequently, a MoO₃ layer (~5 nm) and an Al layer (~100 nm) were evaporated through a shadow mask and form a top anode. The active area of the devices was defined by a shadow mask. The thicknesses of the active layer were controlled by varying the spin-coating speed 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 2602 Source Meter. The incident light intensity was calibrated using a standard Si solar cell. The external quantum efficiency (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 hole only device configuration (ITO/PEDOT:PSS/active layer/MoO₃/Al) for hole mobility and an electron only device configuration (ITO/ZnO/active layer/PFN-Br/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 $\ln(JL^3/V^2) \approx 0.89(1/E_0)^{0.5} (V/L) + \ln(9\epsilon_0\epsilon_r\mu/8)$.

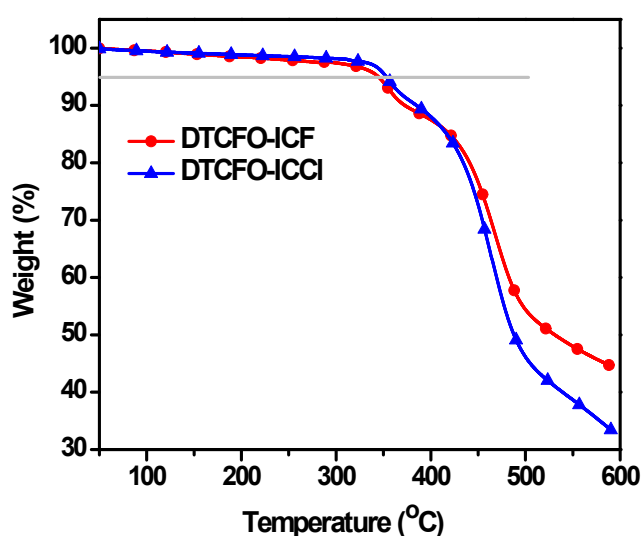


Fig. S1. TGA plots of **DTCFO-ICF** and **DTCFO-ICCI**.

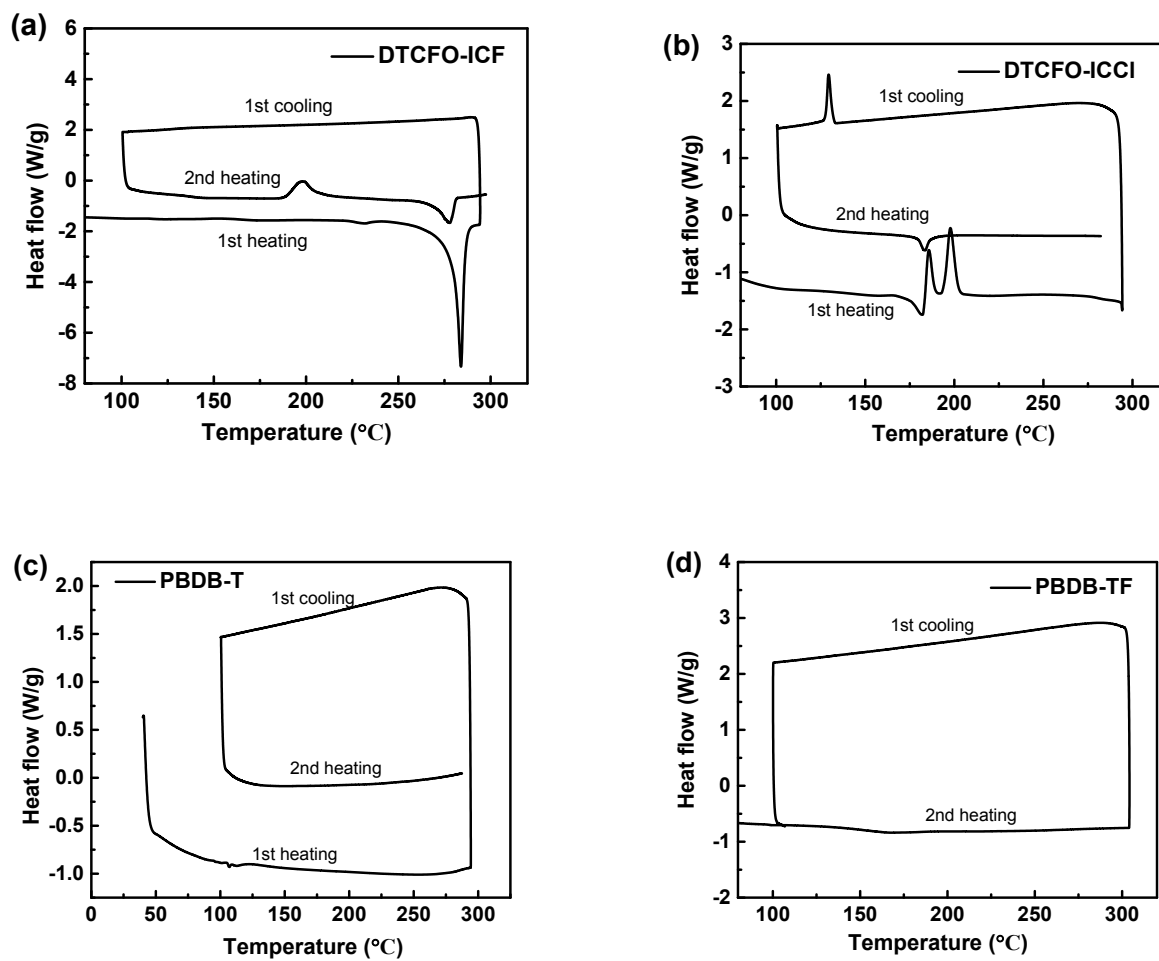


Fig. S2. DSC heating and cooling traces of the DTCF-based SMAs and donor polymers.

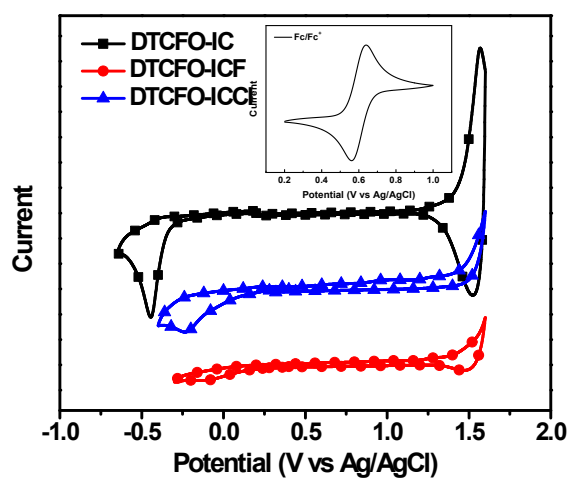


Fig. S3. CV curves of these DTCF-based SMA films on platinum electrode and Fc/Fc⁺ (see the inserted figure) versus Ag/AgCl.

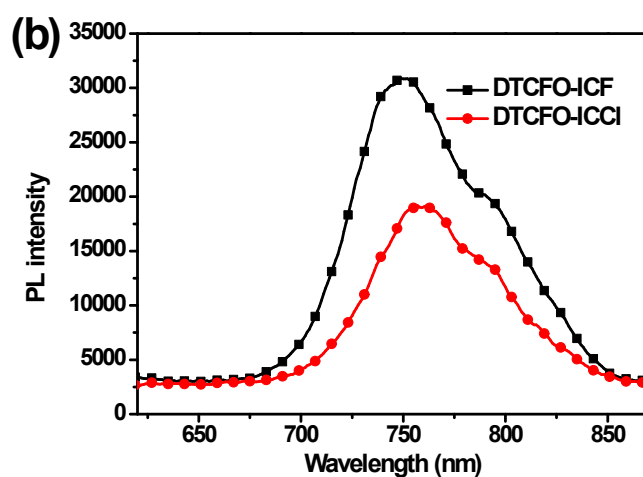
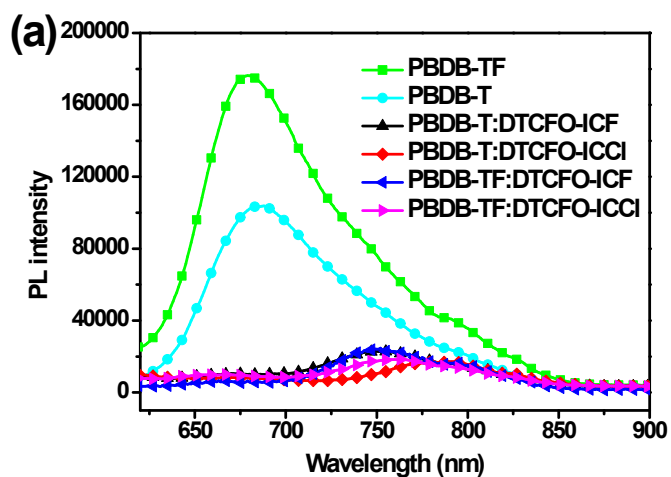


Fig. S4. The PL spectra of the pure polymer donors and blend films (a) and two pure SMAs (b).

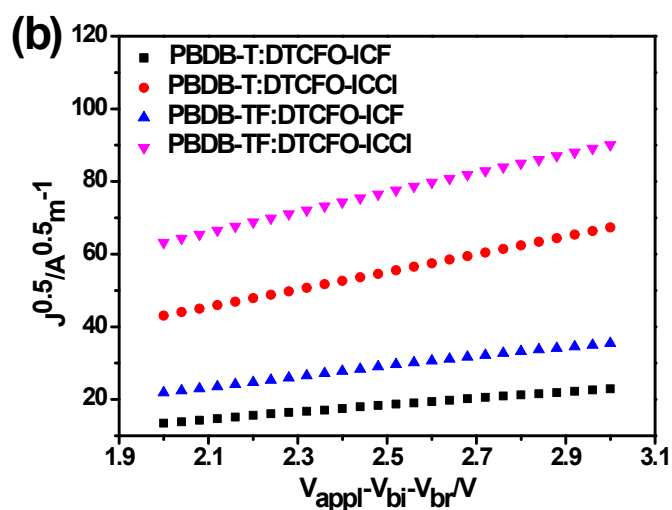
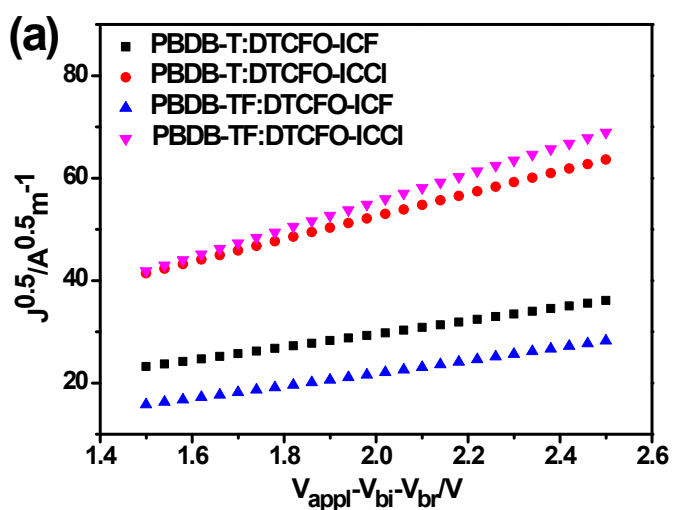


Fig. S5. The J - V plots for measuring the hole (a) and electron (b) by using SCLC method.

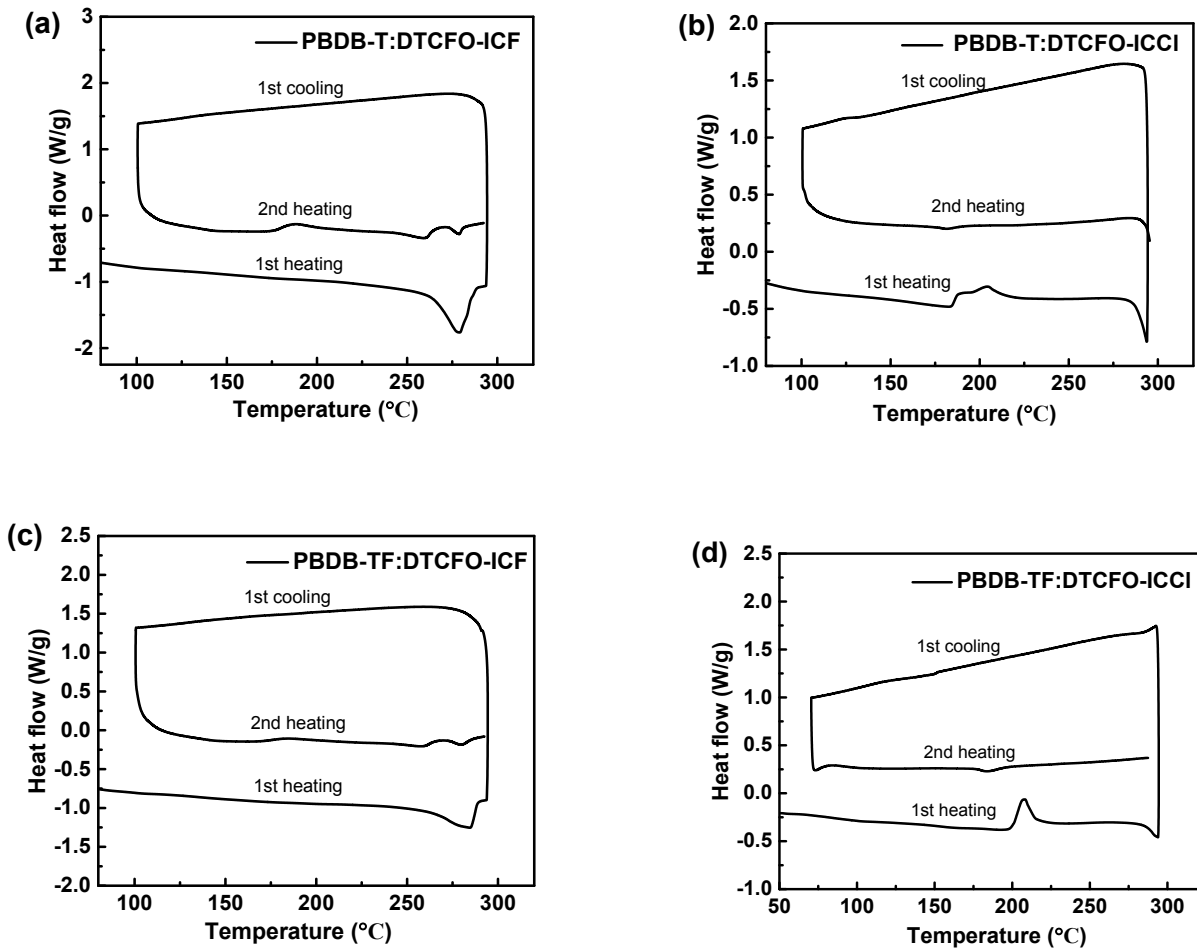


Fig. S6. DSC heating and cooling traces of the four donor:SMA blends.

Table S1. Best photovoltaic parameters of PSCs based on the previously reported fluorene-containing heptacyclic SMAs pairing with the specified polymer donor.

Active layer	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	Ref.
DTC-IC:PTB7-Th	0.87	14.35	53.9	6.92	1
FXIC-1:PTB7-Th	0.788	12.9	69.4	7.13	2
DTCFO-IC:PBDB-T	1.00	11.93	57.9	6.92	3
FDICTF:PBDB-T	0.94	15.81	66.0	10.06	4
FCO-2F:PM6	0.884	20.9	72.3	13.36	5
FDNCTF:PBDB-T	0.93	16.3	72.5	11.2	6
F-F:PBDB-T	0.88	17.36	71	10.85	7
F-Cl:PBDB-T	0.87	17.61	75	11.47	7
F-Br:PBDB-T	0.87	18.22	76	12.05	7

Table S2. Photovoltaic performance of the PSCs based on **DTCFO-ICF** and **DTCFO-ICCI** using different polymer donors under various fabricated conditions.

Active layer	TA	Solvent	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
PBDB-T: DTCFO-ICF = 1:0.8	130 °C 10 min	CF	0.78	15.98	48.2	6.00
PBDB-T: DTCFO-ICF = 1:1.0	130 °C 10 min	CF	0.81	15.52	54.1	6.80
PBDB-T: DTCFO-ICF = 1:1.5	130 °C 10 min	CF	0.82	13.91	50.9	5.81
PBDB-T: DTCFO-ICCI = 1:0.8	160 °C 10 min	CB	0.76	16.69	62.4	7.92
PBDB-T: DTCFO-ICCI = 1:1.0	160 °C 10 min	CB	0.76	16.86	64.3	8.24
PBDB-T: DTCFO-ICCI = 1:1.5	160 °C 10 min	CB	0.77	16.69	66.5	8.55
PBDB-T: DTCFO-ICCI = 1:2.0	160 °C 10 min	CB	0.79	14.86	64.9	7.62
PBDB-T: DTCFO-ICCI = 1:1.5	no	CB	0.81	14.67	60.1	7.14
PBDB-T: DTCFO-ICCI = 1:1.5	130 °C 10 min	CB	0.78	15.09	63.4	7.46
PBDB-T: DTCFO-ICCI = 1:1.5	200 °C 10 min	CB	0.71	11.86	47.4	3.99
PBDB-TF: DTCFO-ICF = 1:1.0	110 °C 10 min	CF	0.98	15.32	43.2	6.49
PBDB-TF: DTCFO-ICF = 1:1.0	110 °C 10 min	CB	0.95	11.07	40.4	4.38
PBDB-TF: DTCFO-ICF = 1:1.0	110 °C 10 min	CB:CF = 1:1	0.99	15.44	50.2	7.67
PBDB-TF: DTCFO-ICF = 1:1.0	110 °C 10 min	CB:CF = 3:2	0.91	12.12	47.6	5.25
PBDB-TF: DTCFO-ICF = 1:1.0	110 °C 10 min	CB:CF = 1:4	0.92	11.97	40.3	4.44
PBDB-TF: DTCFO-ICCI = 1:1.0	no	CB	0.92	13.45	62.1	7.68
PBDB-TF: DTCFO-ICCI = 1:1.0	110 °C 10 min	CB	0.93	13.51	66.1	8.31
PBDB-TF: DTCFO-ICCI = 1:1.0	130 °C 10 min	CB	0.89	14.18	54.4	6.87
PBDB-TF: DTCFO-ICCI = 1:1.2	110 °C 10 min	CB	0.93	18.80	63.1	11.03
PBDB-TF: DTCFO-ICCI = 1:1.5	110 °C 10 min	CB	0.90	20.05	60.8	10.97

Table S3. Photovoltaic performance of the PSCs based PBDB-TF:DTCFO-ICCI (1:1.2, by weight) under different spin-coating speeds. The fabricated conditions: TA 110 °C for 10 min; solvent CB; the total concentration of donor and acceptor: 15.5 mg mL⁻¹.

Active layer	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	Thickness	Spin-coating speed (rpm)
PBDB-TF:DTCFO-ICCI	0.93	18.80	63.1	11.03 (10.84)	60	3500
PBDB-TF:DTCFO-ICCI	0.93	18.15	62.5	10.57 (10.50)	69	3000
PBDB-TF:DTCFO-ICCI	0.93	18.62	60.5	10.47 (10.33)	82	2500
PBDB-TF:DTCFO-ICCI	0.93	18.37	56.9	9.66 (9.63)	93	2000

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