Electronic Supplementary Information

Enhanced Efficiency in Polymer Solar Cells by Adding a **High-Mobility Conjugated Polymer**

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Experimental Section

Materials The high-mobility polymer Nalkyl-diketopyrrolo-pyrrole- dithienylthieno [3,2-b] thiophene (DPP-DTT) was synthesized by the method reported before.²⁵ The molecular weights, M_p/M_w, are 125,500/349,000, measured at 160°C using 1,2,4-trichlorobenzene as eluent against polystyrene standards. Polythieno[3,4-b]- thiophene-benzodithiophene (PTB7), poly[4.8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b;4,5-b']dithiophene-2,6-diyl-alt-(4-(2ethylhexyl)-3-fluorothieno[3,4-b]thiophene-)-2-carboxylate-2-6-diyl)] (PBDTTT-EFT), [6,6]-phenyl C_{71} -butyric acid methyl ester (P C_{71} BM) and the high mobility polymer poly[2,5-bis(alkyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione-alt-5,5'-di(thiophene-2-yl)-2,2'-(E)-2-(2-(thiophen-2-yl)vinyl) thiophene] (PDVT-10) were purchased from 1-Materials Inc. The poly(3,4-ethylenedioxythiophene):polystyrene sulphonic acid (PEDOT:PSS) (CLEVIOS™ PH 500) was purchased from Heraeus, Germany.

Device fabrication

OPVs were prepared by solution process with the device structure shown in Figure 1a. A high mobility polymer (DPP-DTT or PDVT-10) was added as an additive in PTB7/PC₇₁BM (1:1.5 weight ratio) blend with the mixed solvent of chlorobenzene (CB) and 1,8-diiodoctane (DIO) (97:3 volume ratio). $PTB7/PC_{71}BM$ solar cells with various DPP-DTT addition amounts (DPP-DTT weight percentages relative to PTB7 are 0.5%, 1%, 2.5% and 5%) and the control devices of PTB7/PC71BM and DPP-DTT/PC71BM were fabricated at the same conditions. Patterned ITO/glass with a sheet resistance of 15 Ω/cm^2 was used as the substrates. The ITO substrates were cleaned by acetone, isopropyl alcohol and deionized water and then treated with O₂ plasma. A ~40 nm poly(3,4–ethylenedioxy thiophene):poly(styrenesulfonate) (PEDOT:PSS) layer was spin coated on ITO and annealed at 150°C for 1 h. Then the active layer was spin-coated on the PEDOT:PSS layer from the PTB7(+DPP-DTT)/PC₇₁BM precursors (concentrations are 0.05 mg-0.5 mg/ml, 10 mg/ml and 15 mg/ml for DPP-DTT, PTB7 and PC₇₁BM, respectively) at 1500rpm for 60s in a N₂-filled glovebox, followed by slow drying process. Before electrode deposition, methanol was spin coated onto the active film at 2500 rpm for 60 seconds. After that, a 20 nm thick Ca layer and a 100 nm Al electrode were sequentially deposited on the active layer by thermal evaporation. The area of the active layer defined by the overlap of the Al and ITO electrodes of the device was 12.0 mm². All of the OPVs were encapsulated with glass caps in the glove box and then tested in air. The devices with the additions of PDVT-10 were prepared at the same conditions as mentioned above. The addition precentages relative to PTB7 in the experiments are 0.5, 1.0, 2.5, and 5.0 wt.%, respectively.

We prepared the OPVs based on PBDTTT/PC₇₁BM at exactly the same fabriation condition of PTB7/PC₇₁BM -based OPVs. The additions of DPP-DTT and PDVT-10 at different levels were carefully controlled and 3 devices were prepared for each condition.

Hole-only and electron-only devices were fabricated for measuring hole and electron mobilities in PTB7+DPP-DTT/PC₇₁BM blend films, PTB7+PDVT-10/PC₇₁BM blend films and PBDTTT+PDVT-10/PC₇₁BM blend films. Hole-only devices with the structure of ITO/PEDOT:PSS/blend layer/Au were prepared by spin coating the PEDOT:PSS and PTB7+DPP-DTT/PC₇₁BM (or PTB7+PDVT-10/PC₇₁BM or PBDTTT+PDVT-10/PC₇₁BM) films consequently on ITO glass substrates in the glovebox. The average thickness of the PTB7+DPP-DTT/PC₇₁BM (or PTB7+PDVT-10/PC₇₁BM or PBDTTT+PDVT-10/PC₇₁BM) films was characterized to be 250nm under atomic force microscopy (AFM, Digital Instruments). Then Au top electrodes were deposited by thermal evaporation through a shadow mask. Electron-only devices with the structure of ITO/ZnO/blend layer/Al were prepared by spin coating ZnO precursor solution consisting of 0.5M zinc acetate dehydrate in a 2-methoxyethanol at 3000rpm for 30s, followed by thermal annealing on a hotplate at 200 °C for 30 min in dry air, and spin coating PTB7+DPP-DTT/PC₇₁BM (or PTB7+PDVT-10/PC₇₁BM) films on ZnO layer. Then Al top electrodes were deposited by thermal shadow mask.

Device Characterization

The *J-V* characteristics of the OPVs were measured by using a Keithley 2400 source meter under the illumination of 100 mW/cm² (Newport 91160, 300 W, solar simulator equipped with an AM 1.5 filter). The light intensity was calibrated with a standard silicon solar cell. The EQE spectra of the devices were measured with a standard system equipped with a xenon lamp (Oriel 66902, 300W), a monochromator (Newport 66902), a Si detector (Oriel 76175_71580), and a dual channel power meter (Newport 2931_C). The Impedance (real and imaginary parts) of the OPVs were characterized by an impedance analyzer (HP 4294) under different bias voltages.

The surface morphology of the active layers of the OPVs was characterized under an AFM (Digital Instruments). The absorption spectra of $PTB7/PC_{71}BM$ and DPP-DTT chlorobenzene solutions were characterized with a UV-VIS spectrophotometer (UV-2550, Shimadzu, Japan).

The space charge limited currents (SCLCs) of the hole-only devices and electron-only devices were characterized by the semiconductor parameter analyzer (Agilent 4156C) in the glovebox. The current density as a function of bias voltage was fitted (least-square fitting) with the Murgatroyd equation:⁴⁵

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu e^{0.89\beta \sqrt{(V-V_b)/d}} \frac{V^2}{d^3}, \qquad (1)$$

where ε_r is the relative permittivity of the organic blend (taken as 3.5), ε_0 is the permittivity of free space, V is the applied voltage, μ is the carrier mobility. μ , β and V_b are fitting parameters.

GIXD characterization PTB7+DPP-DTT/PC₇₁BM films coated on SiO₂/Si substrates were characterized with Grazing Incidence X-Ray Diffraction (GIXD, Regaku 9KW SmartLAB). Each peak was fitted with the Lorentz function:

$$I = I_b + \frac{2A}{\pi} \frac{w}{4(q - q_p)^2 + w^2},$$
(2)

where I is the intensity, I_b is the background intensity, A is the peak area, w is the half-width and q_p is the peak position.

Impedance measurement The impedance of the OPVs was characterized by using the impedance analyzer HP4294. Figure S6a shows Nyquist plots of the OPV with 1wt.% DPP-DTT additive at different bias voltages. Each curve only contains a semicircle that can be described by the carrier diffusion-recombination model.⁴² The impedance decreases with the increase of the bias voltage due to the decreased thickness of charge accumulation region at the heterojunction. Figure S6b shows the Nyquist plots of different devices under the same bias voltage of 0.7V that is close to the V_{oc} of the devices. It is notable that the radius of the impedance circle increases with the increasing amount of DPP-DTT, which can be attributed to the increase of the heterojunction thickness in the ternary device. The cascade band structure of the ternary device shown in Fig 1b tends to separate the electrons and holes to the two lower energy sides, which leads to longer distance between them. So the effective thickness of the heterojunction increases with the increase of DPP-DTT amount and consequently results in an increased impedance of the heterojunction. Similar case for PBDTTT+PDVT-10/PC₇₁BM can be found in Figure S9.

Figures:



Figure S1. Normalized light absorption of PTB7/PC₇₁BM chlorobenzene solutions added with different weight percentage of DPP-DTT and a DPP-DTT solution. All curves are normalized at the absorption peak at \sim 680nm.



Figure S2. The normalized PCEs of the OPVs based on $PTB7/PC_{71}BM$ with and without the addition of DPP-DTT as a function of the active layer thickness.



Figure S3. Fitting curves (red line) of GIXD out-of-plane diffraction patterns (black curve) of different polymer films. (a) $PC_{71}BM$; (b) PTB7.



Figure S4. Fitting curves (red lines) of GIXD out-of-plane diffraction patterns (black line) of different polymer films. (a)-(e) PTB7+DPP-DTT/PC₇₁BM blend films with different DPP-DTT percentage. (f) DPP-DTT/PC₇₁BM.



Figure S5. AFM topography images of the PTB7/PC₇₁BM thin films added with DPP-DTT of different weight percentage: (a) 0% (b) 0.5% (c) 1% (d) 2.5% (e) 5%. (f) The surface roughness as a function of adding percentage of DPP-DTT.



Figure S6. (a) Impedance spectra of the OPV with 1 wt.% of DPP-DTT in PTB7/PC₇₁BM under different bias voltages; (2) Impedance spectra of the OPVs with different percentage of DPP-DTT introduced in PTB7/PC₇₁BM measured at the bias voltage of 0.7V.



Figure S7. (a) J–V characteristics of OPVs with different addition amount of PDVT-10 in PTB7/PC₇₁BM; (b) The PCEs of the devices with different PDVT-10 percentage.



Figure S8. Electron and hole mobilities calculated from the space charge limited currents (SCLCs) in PTB7/PC₇₁BM films with different addition amount of PDVT-10.



Figure S9. Electron and hole mobilities calculated from the space charge limited currents (SCLCs) in PBDTTT/PC₇₁BM films with different addition percentage of PDVT-10.



Figure S10. (a) Impedance spectra of the OPV with 0.5 wt.% of PDVT-10 added in PBDTTT/PC₇₁BM under different bias voltages; (2) Impedance spectra of the OPVs with different percentage of PDVT-10 introduced in PBDTTT/PC₇₁BM measured at the bias voltage of 0.8V. (c) Carrier lifetimes of different devices as functions of bias voltage.

Tables:

Addition Amount		J _{sc}	V _{oc}	FF	PCE	PCE
(wt.%)		(mA/cm ²)	(∨)	(%)	(%)	Enhancement
						(%)
0 wt.%	Average	14.4	0.745	70.7	7.58±0.13	/
(Control)						
0.5 wt.%	Average	16.0	0.740	68.2	8.08±0.12	6.6±1.3
	Best	16.0	0.742	68.8	8.17	7.8
1.0 wt.%	Average	15.8	0.762	69.2	8.33±0.13	9.9±1.8
	Best	16.2	0.763	68.8	8.51	12.3
2.5 wt.%	Average	15.3	0.749	68.0	7.79±0.06	2.8±0.8
	Best	15.8	0.746	66.6	7.85	3.6
5.0 wt.%	Average	14.8	0.740	67.8	7.42±0.06	-2.1±0.8
	Best	14.9	0.738	67.9	7.47	-1.5
100 wt.%	Average	9.16	0.675	43.3	2.68±0.04	/
	Best	9.55	0.656	44.1	2.78	

Table S1. Summary of photovoltaic performance of different devices based on $PTB7/PC_{71}BM$ and DPP-DTT additive.

Table S2. Surface roughness (RMS) of $PTB7/PC_{71}BM$ film as a function of DPP-DTT incorporated percentage.

DPP-DTT addition amount (W _{DPP-DTT} /W _{PTB7})%	Control	0.5 wt.%	1 wt.%	2.5 wt.%	5 wt.%
Surface roughness of film (nm)	1.40	1.33	1.32	1.14	1.07

PDVT-10		J _{sc}	V _{oc}	FF	PCE	PCE
Addition Amount		(mA/cm ²)	(V)	(%)	(%)	Enhancement
(wt.%)						(%)
0 wt.%	Average	0.786	17.11	65.1	8.75±0.213	/
(Control)						
0.2 wt.%	Average	0.763	17.82	68.6	9.33±0.05	6.6±0.6
	Best	0.768	17.57	69.7	9.40	7.4
0.5 wt.%	Average	0.780	18.73	69.0	10.08±0.05	15.2±0.6
	Best	0.777	18.74	69.6	10.14	15.9
1.0 wt.%	Average	0.765	18.03	65.5	9.03±0.18	3.2±2.4
	Best	0.776	18.10	66.1	9.28	6.1

Table S3. Summary of photovoltaic performance of different devices based onPBDTTT-EFT/PC71BM and PDVT-10 additive.