## **Electronic Supplementary Information**

# Mitigating Efficiency Loss in Thick-Film Organic Solar Cells via Suppressing Charge Recombination and Energetic Disorder

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#### Materials

PTzBI-dF, L8-BO, and PFN-Br were sourced from Volt-Amp Optoelectronics Tech. Co., Ltd, China. The aqueous dispersion of poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) (PEDOT:PSS, P VP Al 4083) was obtained from Heraeus, Germany. All solvents and chemicals were supplied by Sigma-Aldrich.

#### **Device fabrication**

Conventional organic solar cells (OSCs) were fabricated with the structure ITO/PEDOT:PSS/Active layer/PFN-Br/Ag (Figure S1). Patterned ITO substrates (15  $\Omega/\Box$ ) underwent ultrasonic cleaning with detergent, deionized water, and isopropanol for 30 minutes each, followed by drying at 55 °C overnight. After vacuum plasma treatment for 120 seconds, PEDOT:PSS (~35 nm) was spin-coated at 3000 rpm for 30 s and baked at 150 °C for 15 minutes in air. The active layer PTzBI-dF:L8-BO (1:1.2, wt:wt) was dissolved in chloroform (12 mg mL<sup>-1</sup>) and stirred at 50 °C for 10 hours in a nitrogen-filled glove box. A certain volume ratio of DBE (or CN, or DIO) was added as additive. For thicker active layers, a higher concentration (~20 mg mL<sup>-1</sup>) was used, with spin-coating speeds between 1500 and 600 rpm to achieve thicknesses of 200-400 nm, followed by thermal annealing at 100 °C for 5 minutes. The PFN-Br layer (~5 nm) was coated at 2000 rpm from a 0.5 mg mL<sup>-1</sup> solution in methanol. Finally, silver electrodes (100 nm) were deposited in a thermal evaporation chamber under a vacuum of  $2 \times 10^{-7}$  mbar. The effective area was 0.0516 cm<sup>2</sup>, further defined as 0.04 cm<sup>2</sup> using a non-refractive mask. The devices were encapsulated by epoxy resin and glass sheet and exposed to UV for curing.

#### Hole-only and electron-only devices fabrication

Hole-only and electron-only devices were structured as ITO/PEDOT:PSS/Active layer/MoO<sub>x</sub>/Ag and ITO/ZnO/Active layer/PFN-Br/Ag, respectively. For the hole-only device, a MoO<sub>x</sub> layer (~10 nm) by thermal evaporation was used to replace the PFN-Br. For the electron-only device, the ZnO was used to replace the PEDOT:PSS. A ZnO electron transport layer (~30 nm) was spin-coated at 4000 rpm for 60 s from a ZnO precursor solution (zinc acetate dihydrate, 0.1 g mL<sup>-1</sup> in ethylene glycol monomethyl

ether with 2.8 vol% ethanolamine), followed by annealing at 200 °C for 1 hour in air. The other functional layers were fabricated using methods similar to those described above.

Charge mobilities were calculated using the Mott-Gurney equation:  $J = 9\varepsilon_0\varepsilon_r\mu V^2/8d^3$ , where J is the space charge limited current,  $\varepsilon_0$  is the vacuum permittivity (8.85 × 10<sup>-12</sup> F m<sup>-1</sup>),  $\varepsilon_r$  is the permittivity for active layers,  $\mu$  is the charge mobility, and d is the thickness of active layers. The effective voltage (V) was obtained by the equation  $V = V_{appl} - V_{bi} - V_s$ , where the built-in voltage ( $V_{bi}$ ) and the voltage drop ( $V_s$ ) were deducted from the applied voltage ( $V_{appl}$ ) of devices. Hole and electron mobilities were integrated from the slope of the  $J^{1/2} \sim V$  curves.

### Instruments and characterizations

Ultraviolet-visible-near infrared (UV-vis-NIR) absorption spectra were obtained using a SHIMADZU UV-3600 spectrophotometer. J-V curves were recorded with a Keithley 2400 source meter under 100 mW cm<sup>-2</sup> AM 1.5G solar simulation (Enlitech SS-F5) using a forward scan from -0.2 V to 1.2 V (step: 0.02 V, dwell time: 1 ms). Light intensity was calibrated with an NREL-certified silicon solar cell, ensuring a range of 0.99-1.01 sun. Dark J-V curves were measured under identical conditions without illumination. Light intensity dependence was examined using a solar simulator with an intensity range of 10%-100%. EQE spectra were acquired using a commercial QE measurement system (Enlitech QE-R3011). Charge transport properties were analyzed with Keithley 236 sourcemeter in a dark chamber. Transient photocurrent (TPC) and transient photovoltage (TPV) measurements were performed using a mode-locked Ti:sapphire oscillator (SpectraPhysics Spitfire Ace, 580 nm, 120 fs pulse width, 1 kHz repetition rate). TPC signals were recorded with a Tektronix TDS 3052C oscilloscope (50  $\Omega$  resistor), while TPV signals were obtained on a 1 M $\Omega$  resistor under LED illumination. Bias was applied using SR570 Specifications. Temperature-dependent mobility characterization was conducted using an Agilent B1500 system within a probe state (Lake Shore), the chamber could be cooled down by evaporating the liquid

nitrogen. The space charge limited current (SCLC) method was employed to determine charge mobilities. The contact angle measurement was carried out by using JEM 2100F (Guangzhou Beituo Science and Technology Co., Ltd.) equipment. The Brucker Vertex 70 Fourier-Transform infrared (FTIR) spectrometer performed the FTPS measurements. The number of cycles is 256, and the voltage after amplification is 6 V.



**Figure S1.** Energy diagram of the concerned components used in polymer solar cells (PCSs)



**Figure S2** (a) *J-V* curves for PTzBI-dF:L8-BO based OSCs incorporating varied contents of DBE additive. (b) Fill factor histogram for the optimized DBE content; (c) dark *J-V* characteristics and (d) EQE spectrum for pristine PTzBI-dF:L8-BO and optimized OSCs.



**Figure S3** Photovoltaic parameters for OSCs based on PTzBI-dF:L8-BO incorporating varied additives.



**Figure S4** Contact angles of pristine PTzBI-dF and L8-BO, and PTzBI-dF:L8-BO blends without and with DBE additive. The measurements were performed by using deionized water (H<sub>2</sub>O) and ethylene glycol (EG) as wetting liquids.



**Figure S5** *J-V* curves for pristine and optimized PTzBI-dF:L8-BO based OSCs at different thicknesses.



**Figure S6** Photocurrent of OSCs based on active layers of (a) PTzBI-dF:L8-BO and (b) PTzBI-dF:L8-BO blends with DBE additive against effective bias ( $V_{eff}$ ) at series of light intensity.



Figure S7 TPV for PTzBI-dF:L8-BO based OSCs without and with DBE additives.



**Figure S8** Bias-dependent photocurrent decay kinetics measured on PTzBI-dF:L8-BO based OSCs without and with DBE additives.



**Figure S9** *J-V* characteristics of holy-only and electron-only devices based PTzBIdF:L8-BO without and with DBE additives measured at different temperature.



Figure S10 The measured FTPS-EQE spectrum for thick film and thick film\_DBE devices.

<b>F</b> :1	T	Location	Energy	Intensity	Area	FWHM
Film	1 ype	(nm)	(eV)	(A. U.)	(A. U.)	(nm)
	Gaussian	725.25	1.71	0.57	55.8	152.5
L8-BO	Gaussian	809.89	1.53	0.78	62.6	84.2
	Gaussian	739.08	1.68	0.71	101.2	149.4
L8-BO_DBF	Gaussian	825.10	1.50	0.72	58.2	85.3
PTzBI-dF:L8-BO	Gaussian	488.35	2.54	0.36	6.5	57.4
	Gaussian	620.81	2.00	0.98	102.3	131.9
	Gaussian	725.00	1.71	0.44	19.0	92.3
	Gaussian	793.00	1.56	0.86	39.0	59.3
PTzBI-dF:L8- BO_DBE	Gaussian	504.34	2.46	0.34	5.2	76.7
	Gaussian	625.57	1.98	0.98	50.8	119.7
	Gaussian	723.00	1.72	0.49	10.5	70.7
	Gaussian	799.00	1.55	0.97	33.5	78.8

 Table S1 Optical features obtained from the UV-vis-NIR absorption spectra.

Film	Peak	$A_{\rm O}/A_{\rm A}$
L8-BO	١	1.37
L8-BO_DBE	١	1.01
DT-DL 4E.L 9 DO	L8-BO	1.95
P1ZBI-dF:L8-BO	PTzBI-dF	2.72
PTzBI-dF·L8-BO DBE	L8-BO	1.98
	PTzBI-dF	2.88

 Table S2 Optical features obtained from the UV-vis-NIR absorption spectra fitting.

**Table S3** Photovoltaic parameters for OSCs based on PTzBI-dF:L8BO incorporating varied contents of DBE additive.

Additive	V <sub>OC</sub> (V)	J <sub>SC</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
/	0.901	21.90	69.26	13.67
0.1 vol% DBE	0.874	23.43	76.05	15.58
0.3 vol% DBE	0.861	24.28	77.75	16.27
0.5 vol% DBE	0.859	22.63	77.66	15.10
0.7 vol% DBE	0.859	21.35	76.76	14.09
0.3% vol% DIO	0.868	20.91	74.98	13.61
0.3% vol% CN	0.876	21.33	76.93	14.38

**Table S4.** The NFPA hazard classification (Blue: Health hazard, Red: Flammable,Yellow: Reactive) from PubChem.

Additive	NFPA Hazard Classification
DBE	1
	0 0
1-CN <sub>CI</sub>	
	20
DIO	
	<b>N. A.</b>

**Table S5** Photovoltaic parameters for PTzBI-dF:L8-BO based OSCs without or with additive at different thicknesses.

Additive	Thickness (nm)	V <sub>OC</sub> (V)	$J_{\rm SC}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
/	100	0.901	21.90	69.26	13.67
	200	0.907	21.52	63.63	12.43
	300	0.900	23.08	55.65	11.56
0.3 vol% DBE	100	0.861	24.28	77.75	16.27
	200	0.887	23.79	74.43	15.71
	300	0.869	25.78	70.73	15.85
	400	0.846	23.30	54.00	10.65

DBE	$R_{\rm s}$ ( $\Omega  {\rm cm}^2$ )	$R_{\rm sh}$ ( $\Omega \ {\rm cm}^2$ )	$J_{\rm SC}$ (mA cm <sup>-2</sup> )	$J_{\rm sat}$ (mA cm <sup>-2</sup> )	P(E, T) (%)	α	п
/	1.95	$5.16 \times 10^{3}$	22.98	24.83	92.53	0.87	1.51
0.3 vol%	0.89	$3.29 \times 10^{4}$	25.88	26.70	96.94	0.99	1.17

 Table S6 Relative parameters obtained from corresponding graph.

Blend	Temperature (K)	Hole-only (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	Electron-only (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
	295	$1.55 \times 10^{-3}$	7.10 × 10 <sup>-4</sup>
	275	$1.05 \times 10^{-3}$	$6.80 \times 10^{-4}$
	255	$7.05  imes 10^{-4}$	6.61 × 10 <sup>-4</sup>
PTzBI-dF:L8-BO w/o DBE	235	$4.14 \times 10^{-4}$	$5.65 \times 10^{-4}$
	215	$2.09  imes 10^{-4}$	$3.82 \times 10^{-4}$
	195	$8.09  imes 10^{-5}$	$1.48 \times 10^{-4}$
	175	$2.30 \times 10^{-5}$	$7.34 \times 10^{-5}$
	295	$2.10 \times 10^{-3}$	$3.20 \times 10^{-3}$
	275	$1.65 \times 10^{-3}$	$3.02 \times 10^{-3}$
	255	$9.65  imes 10^{-4}$	$2.63 \times 10^{-3}$
PTzBI-dF:L8-BO with DBE	235	$6.94  imes 10^{-4}$	$2.22 \times 10^{-3}$
	215	$3.97 \times 10^{-4}$	$1.64 \times 10^{-3}$
	195	$1.83 \times 10^{-4}$	$1.06 \times 10^{-3}$
	175	$5.88 \times 10^{-5}$	$4.79 \times 10^{-4}$

**Table S7** SCLC mobility of single-carrier devices at different T determined by fittingsusing Mott-Gurney law based on various BHJs in this study