Supporting Information

Molecular Interactions Regulation by Adding a Third Component with High Miscibility Suppresses the Energetic Disorder and Reduces Energy Loss for Efficient Ternary Solar Cells

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Experimental details

Material

The D18 (68 to 80 kDa) were purchased form Derthon Optoelectronic Materials Science & Technology Co., LTD. and L8-BO were purchased form Volt-amp Optoelectronics Tech Co., LTD. Other solvents and reagents were purchased from commercial sources (Sigma-Aldrich and TCI) and used without any further treatment. The compound PBTz-Cl (18 to 32 kDa) was synthesize in our own laboratory.

Device fabrication and characterization

Binary and ternary OSC devices were fabricated with a structure of indium tin oxide (ITO)/PEDOT:PSS/activelayer/PDIN/Ag. The ITO-coated glass substrates were ultrasonic cleaned with conductive glass cleaning solution, deionized water, acetone and ethanol, and dried in the oven at 60 ° C overnight. After the substrates were cleaned by oxygen plasma for 15 min, poly(styrene sulfonate)-doped poly(ethylene-dioxythiophene) (PEDOT:PSS) (Bayer Baytron 4083) thin films was spin-coating onto the ITO at 3000 rpm for 30s and annealing at 150 °C for 20 min then transferred to a N₂-glovebox. The donor and acceptor were dissolved in chloroform concentration 4mg/ml for donor with a D:A ratio of 1:1.4, and stirred at 100 °C for 4h, and cooling to 40 °C for spin-coating. The blend solution was spin-coated at 3000 rpm for 30 s onto the top of activelayer. Finally, a 100 nm of Ag was deposited onto the active layer under vacuum at a pressure of ca. 2×10^{-4} Pa. The effective area of one cell is 0.0516 cm².

Measurements and Instruments:

Cyclic voltammetry (CV)

Cyclic voltammetry measurements were conducted using a Metrohm Autolab PGSTAT302N electrochemical workstation, employing platinum electrodes, at a scan rate of 50 mV s⁻¹. The reference electrode used was Ag/Ag+ in a nitrogen-saturated solution containing 0.1M tetrabutylammonium hexafluorophosphate dissolved in acetonitrile. Potentials were calibrated with respect to the ferrocene/ferrocenium (Fc/Fc+) redox couple, using ferrocene as an internal standard. To prepare the samples

for analysis, they were dissolved in chloroform and subsequently deposited onto the electrode.

UV-Vis absorption

The UV-vis-NIR spectra of pure and blend films on a quartz substrate were obtained by using UV-3600 Plus UV-Vis-NIR spectrometer at room temperature (ca. 25°C).

J-V and EQE measurement

The *J-V* characteristics of the devices were obtained by using a Keithley 2400 sourcemeasurement unit, and measurements were taken under illumination from a solar simulator (Oriel model 91192) that emitted AM 1.5G spectrum. The intensity of illumination from the solar simulator was determined by employing a monocrystalline silicon reference cell (Hamamatsu S1133), which had a KG-5 visible color filter and had been previously calibrated by the National Renewable Energy Laboratory (NREL). To assess the external quantum efficiency (EQE) values of the organic solar cell (OSC) devices, an integrated system from Enlitech in Taiwan, China, was utilized. This system was equipped with a lock-in amplifier and a current preamplifier, and measurements were taken under short-circuit conditions. The OSC devices were subjected to monochromatic light emitted by a 75 W xenon lamp. The intensity of light at each specific wavelength was calibrated using a silicon photodiode.

Highly sensitive EQE and External Electroluminescence quantum efficiency (EQE_{EL}) measurements

Highly Sensitive EQE (s-EQE) was measured by using an integrated system (PECT-600, Enlitech), where the photocurrent was amplified and modulated by a lock-in instrument. EQE_{EL} measurements were performed by applying external voltage/current sources through the OSCs (REPS, Enlitech).

AFM characterization

The surface morphology of each blend film was analyzed using atomic force microscopy (AFM) measurements conducted on a Dimension Icon Scanning Probe Microscope system.

GIWAXS measurements

The thin films were characterized using Grazing Incidence Wide Angle X-ray

Scattering (GIWAXS) at beamline 7.3.3 of Lawrence Berkeley National Lab. A 2-D detector (Pilatus 1M) with a pixel size of 172 μ m was used to record the scattering signal. The X-ray energy employed was 10 keV. The samples were approximately 15 mm long in the direction of the X-ray beam, were positioned, and the detector was located at 300 mm from the center of the sample. The distance was calibrated using a silver behenet standard. An incidence angle of 0.16° was selected to optimize the signal-to-background ratio. To replicate the device conditions, thin film samples were prepared on silicon wafers covered with PEDOT:PSS. The data collected was subsequently processed and analyzed using the Nika software package.

Contact Angle measurement

Contact angles were measured by a JY-PHa contact Angle tester.

Charge carrier mobility measurement

The hole and electron mobilities were assessed using the space-charge limited current (SCLC) method, employing distinct device structures. For hole mobility measurement, the structure consisted of ITO/PEDOT:PSS/active layer/Ag, while electron mobility was evaluated with ITO/ZnO/active layer/Ag. The active layers for both types of devices were applied using spin-coating under identical conditions as those used for fabricating solar cells. Current-voltage (J–V) curves spanning from -4 to 4 V were acquired utilizing a Keithley 2400 source-measure unit under dark conditions.The mobilities were obtained by fitting J-V curves with the formula of:

$$J = 9/8\varepsilon_o\varepsilon_r\mu V^2 L^{-3}$$

where J is the current density, L is the thickness of the active layer, μ is the mobility, ε_0 is the vacuum dielectric constant, ε_r is the relative dielectric constant of the transport medium, $V(V_{app}-V_{bi})$ is the internal voltage, where V_{app} is the applied voltage and V_{bi} is the built-in voltage.

TPC and TPV Measurement

The transient photocurrent and transient photovoltage characteristics were measured by Paios (Fluxim AG, Switzerland) with all-in-one characterization platform. TPC and TPV measurement were used absolute light intensity measurement type. In the TPV measurement, the light-pulse intensity is 100%, offset light intersity is 0%, and settling time is 1 μ s, light-pulse length is 10 μ s and the follow-up time is 10 ms. In the TPC measurement, the light-pulse intensity is 100%, offset light intersity is 0%, and settling time is 5 μ s, light-pulse length is 5 μ s, the follow-up time is 50 μ s and offset voltage is 0 V.

Femtosecond transient absorption measurement

The Transient absorption (TA) spectra were collected by a home-built TA system described briefly as below. The fs laser out from an amplifier (800 nm, 1 KHz, Legend Elite F 1K HE+II, COHERENT) was used as the light source. The output from amplifier (800 nm) or the frequency doubled (400 nm) were employed as the pump light. For the pump light, pump "on" and "off" were regulated by a mechanical chopper (500 Hz, MC2000B-EC, THORLABS) in the pump beam. The supercontinuum white light generated by a 3 mm thick sapphire plate was used as the probe light, which was then collected by a spectrometer (300 nm-1100 nm, Omni- λ 200i, Zolix). The delay between the probe light and the pump light is controlled by a mechanical delay stage.



Figure S1 The cyclic voltammetry curves of D18, D18:PBTz-Cl, PBTz-Cl and L8-BO.



Figure S2 Steady-state photoluminescence spectra of films excited at 550 nm.



Figure S3 The *J-V* curves of solar cells devices with a range of PBTz-Cl weight ratios from 0 to 20 wt%.



Figure S4 The statistical PCE of 22 devices for both D18:L8-BO based binary and D18:PBTz-Cl:L8-BO based ternary devices.



Figure S5 Thermal stability of devices under annealing at 100°C.



Figure S6 AFM images of D18:L8-BO, D18:PBTz-Cl:L8-BO and PBTz-Cl:L8-BO films (a-c) without-annealing and (d-f) with annealing at 100°C for 60 minutes.



Figure S7 *J-V* curves in dark of hole-only devices of D18:L8-BO, D18:PBTz-Cl:L8-BO, and PBTz-Cl:L8-BO devices.



Figure S8 *J-V* curves in dark of electron-only devices of D18:L8-BO, D18:PBTz-C1:L8-BO, and PBTz-C1:L8-BO devices.



Figure S9 The *J-V* curves of organic solar cells devices based on D18, PBTz-Cl neat films and D18:PBTz-Cl blend film.



Figure S10 TRPL spectra of D18:L8-BO based binary film and D18:PBTz-Cl:L8-BO based ternary film.



Figure S11 AFM images of D18 and PBTz-Cl neat films, and D18:PBTz-Cl blend film.

Table S1 Photovolatic performance of solar cells devices with a range of PBTz-Cl

 weight ratios from 0 to 20 wt%.

D18:PBTz-Cl:L8-BO	$V_{OC}(\mathbf{V})$	J_{SC} (mA cm ⁻²)	FF (%)	PCE(%)
1:0:1.4	0.903	24.37	76.69	16.87
0.975:0.025:1.4	0.911	25.30	78.33	18.05
0.95:0.05:1.4	0.915	24.36	77.17	17.20
0.9:0.1:1.4	0.918	24.13	75.61	16.74
0.8:0.2:1.4	0.931	22.60	74.28	15.62
0:1:1.4	0.904	19.39	58.17	10.19

D18:PBTz-Cl:L8-BO J_{SC} (mA cm⁻²) FF (%) PCE(%) $V_{OC}(\mathbf{V})$ concentration 3.5 mg/ml 0.920 77.95 17.80 24.82 4 mg/ml 0.911 25.30 78.33 18.05 4.5 mg/ml 0.918 24.52 71.21 16.03

Table S2 Different concentration of D18:PBTz-Cl:L8-BO ternary organic solar cell atoptimal ratio of PBTz-Cl.

Table S3 Summary of the fitting data for hole-only and electron-only devices.

Active layer	$\mu_{ m e}$ (×10 ⁻⁴ cm ² V ⁻¹ s ⁻¹)	$\mu_{ m h}(imes 10^{-4}{ m cm}^2{ m V}^{-1}{ m s}^{-1})$	$\mu_{ m e}/\mu_{ m h}$
D18:L8-BO	4.39	2.71	1.61
D18:PBTz-Cl:L8-BO	7.42	5.58	1.33
PBTz-Cl:L8-BO	1.43	0.51	2.80

Table S4 J-V data of D18, D18:PBTz-Cl, PBTz-Cl films based devices.

Neat film	$V_{OC}(\mathbf{V})$	J_{SC} (mA cm ⁻²)	FF (%)	PCE(%)
D18	0.841	0.05	28.41	0.01
D18:PBTz-Cl	0.696	0.10	27.83	0.02
PBTz-Cl	0.765	0.08	28.13	0.02

Table S5 Summary parameters of exciton dissociation efficiency and charge collection

Active layer	$J_{ph}{}^a/J_{ph}{}^b (\mathrm{mA\ cm^{-2}})$	J_{sat} (mA cm ⁻²)	$\eta_{\rm diss}(\%)$	$\eta_{\rm coll}(\%)$
D18:L8-BO	23.96/21.83	25.00	95.84	87.32
D18:PBTz-Cl:L8-BO	25.61/23.68	26.58	96.35	89.08
PBTz-Cl:L8-BO	19.37/15.38	21.70	89.26	70.88

^aUnder short circuit condition. ^bUnder the maximal power output condition.

Active layer	τ_1 (ps)	τ_2 (ps)
D18:L8-BO	9.4	1402
D18:PBTz-Cl:L8-BO	8.9	1763
PBTz-Cl:L8-BO	0.8	321

Table S6 Lifetime data for the hole transfer process of binary and ternary films.

Table S7 GIWAXS data (out of plane direction) of D18, D18:PBTz-Cl and PBTz-Cl flims.

-OOP	qz (Å-1)	d-spacing (Å)	FWHM (Å ⁻¹)	CCL (Å)
D18	1.66	3.78	0.450	12.56
D18:PBTz-Cl	1.66	3.78	0.434	13.02
PBTz-Cl	1.56	4.03	0.451	12.53

Table S8 GIWAXS data (out of plane direction) of D18:L8-BO, D18:PBTz-Cl:L8-BO, and PBTz-Cl:L8-BO blend films.

-OOP	qz (Å-1)	d-spacing (Å)	FWHM (Å ⁻¹)	CCL (Å)
D18:L8-BO	1.73	3.63	0.314	18.00
D18:PBTz-Cl:L8-BO	1.71	3.67	0.304	19.34
PBTz-Cl:L8-BO	1.73	3.63	0.529	11.04