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Supporting Information

Efficient Ternary Small Molecular Solar Cells by Synergistically Optimized Photon Harvesting and Phase Separation

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1. Detailed Experimental Section

Photovoltaic Device Fabrication

The patterned indium tin oxide (ITO) coated glass substrates (sheet resistance 15 Ω/square) were cleaned consecutively in ultrasonic baths containing acetone, detergent, de-ionized water and ethanol, respectively. The cleaned ITO coated glass substrates were blow-dried by high pure nitrogen gas and then treated by UV-ozone for 10 minutes in order to further increase the work function of ITO coated glass substrates. The poly-(3,4-ethylenedioxythiophene):poly-(styrenesulphonicacid) (PEDOT:PSS) (purchased from H.C. Starck co. Ltd.) thin films were fabricated on the cleaned

ITO coated glass substrates by spin-coating method at 5000 round per minute (RPM) for 40 s, and then annealed at 150 °C for 10 minutes in air environment. The electron donor materials SMPV1, DIB-SQ and electron acceptor materials $PC_{71}BM$ (purchased from Luminescence Technology Corp and used as received) were dissolved in chloroform to generate 20 mg/ml blend solutions. The doping weight ratios of DIB-SQ are 0, 5 wt%, 10 wt%, 15 wt%, 20 wt%, 30 wt%, 50 wt%, 100 wt% in electron donors (SMPV1 and DIB-SQ) and the weight ratio of donors to acceptor was kept constant as 1:1 ($SMPV1_{1-x}$:DIB-SQ_x:$PC_{71}BM_1$, x represents DIB-SQ doping ratio in donors). The blend solutions were spin-coated on PEDOT:PSS films at 900 RPM for 30 s in a high purity nitrogen-filled glove box to fabricate the active layers. The thickness of the active layers is ~90 nm, which is measured by Ambios Technology XP-2 stylus Profiler. After that, the semiconducting conjugated polyelectrolyte poly[9,9-bis(3'-(N,N-dimethylamino)-propyl-2,7-fluorene) -alt-2,7-(9,9-dioctylfluorene)] (PFN) was dissolved in methanol to prepare 0.2 mg/ml solution with addition of 0.25 vol% acetic acid, and then the PFN solutions were spin-coated on the top of active layers at 3000 RPM for 30 s. The cathode of Al (100 nm) film was deposited on the PFN film by thermal evaporation under 10^{-4} Pa and the thickness was monitored by a quartz crystal microbalance. The active area is about 3.8 mm^2, which is defined by the vertical overlap of ITO anode and Al cathode.

Space Charge-Limited Current (SCLC) Device Fabrication

The structure of electron-only devices is Al/LiF/active layer/ LiF/Al. The structure of hole-only devices is ITO/PEDOT:PSS/active layer /MoO_3/Ag. The fabrication conditions of the active layer films are the same with those for preparing solar cells. The charge carrier mobility was estimated by using the Mott-Gurney square law,[1, 2]

$$J = \frac{9}{8}\varepsilon_r\varepsilon_0\mu\frac{V^2}{L^3}$$

where J is the current density, ε_0 is the permittivity of free space (8.85×10^{-14} F/cm), ε_r is the dielectric constant of the blend material, μ is the hole mobility, V is the voltage drop across the device and L is the active layer thickness. The ε_r parameter was assumed to be 3, which is a typical value for organic materials.

Film Fabrication and Characterization

i) Absorption spectra measurement: The used materials of the active layer, SMPV1, DIB-SQ and $PC_{71}BM$, were dissolved in chloroform with a concentration 10 mg/ml, respectively. The SMPV1:DIB-SQ blend solutions with various DIB-SQ doping ratios (0, 5 wt%, 10 wt%, 15 wt%, 20 wt%, 30 wt%, and 50 wt% and 100 wt%) and neat $PC_{71}BM$ solutions were spin-coated on cleaned quartz substrate at 900 RPM for 30 s in glove box. The thickness of thin films is around 70 nm. The chemical structure and normalized absorption spectra of used materials are shown in Fig. S1.

ii) Photoluminescence (PL) and time-resolved transient photoluminescence (TRTPL) spectra measurement: The SMPV1:DIB-SQ blend solutions with various DIB-SQ doping ratios were spin-coated on cleaned class substrate at 900 RPM for 30 s in glove box and the thickness of thin films is around 70 nm.

iii) X-Ray diffraction (XRD), atomic force microscopy (AFM) and transmission electron microscopy (TEM) measurement: The films for XRD, AFM and TEM characterization were prepared under the same conditions compared with those of active layers for solar cells. The active layer films prepared on PEDOT:PSS coated ITO substrates were floated in deionized water and then picked up by using 400-mesh copper TEM grids for TEM measurement.

Active Layers and Devices Characterization

The ultraviolet-visible (UV-Vis) absorption spectra of films were obtained by using a Shimadzu UV-3101 PC spectrometer. The current density-voltage (*J-V*) curves of all solar cells were measured in air environment by using a Keithley 2400 source meter. AM 1.5G irradiation at 100 mW/cm^2 provided by an ABET Sun 2000 solar simulator. The external quantum efficiency (EQE) spectra of solar cells were measured by a Zolix Solar Cell Scan 100. The PL spectra of films were measured by a Perkin Elmer LS-55 spectrophotometer. The TRTPL spectra were obtained by using a FluoroCube-01-NL and FluoroCub-NL from Jobin Yvon. The XRD patterns of blend films were collected using a Bruker D8 Advance X-Ray diffractometer. The morphology of the blend films with different DIB-SQ doping ratio in donors was investigated by AFM (multimode

Nanoscope IIIa) operated in tapping mode. TEM images of active layers were obtained by using a JEOL JEM-1400 transmission electron microscope operated at 80 kV bias.

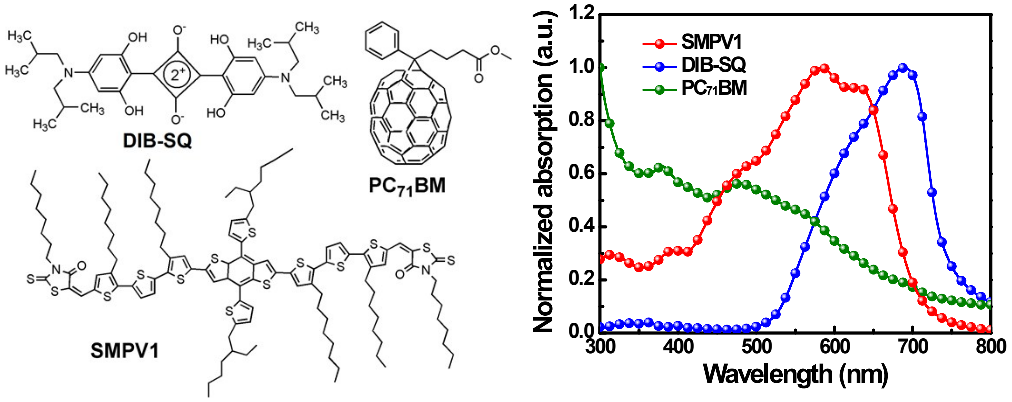

Fig. S1 The chemical structure and absorption spectra of used materials

2. Additional Experimental Results

The relative changes of photovoltaic parameters dependence on DIB-SQ doping ratio in donors are depicted in Figure S2. The V_{oc} of ternary solar cells is kept constant at 0.92 V, which is equal to the V_{oc} of binary solar cells with SMPV1:$PC_{71}BM$ as the active layers. Both J_{sc} and FF of ternary solar cells show an increase and then decrease tendency along with the increase of DIB-SQ doping ratio in donors. The optimized J_{sc} and FF of ternary solar cells were obtained simultaneously when the DIB-SQ doping ratio increased to 10 wt%. As a result, the PCE of ternary solar cells have been continuously increased along with DIB-SQ doping ratios up to 10 wt% and then decreased for the further increase of DIB-SQ doping ratio in donors.

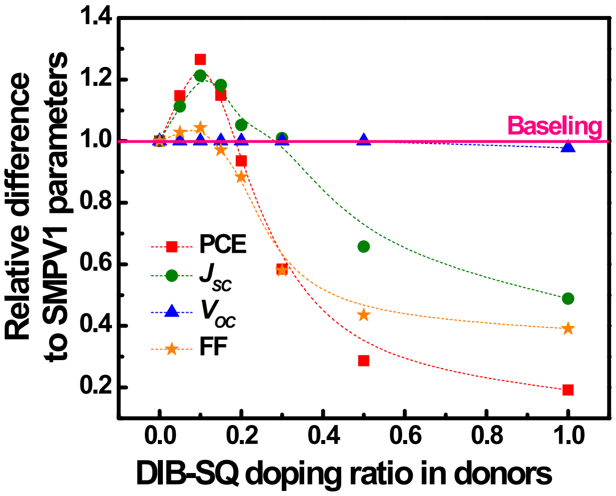

Fig. S2 Relative difference of photovoltaic parameters to the solar cells with SMPV1:PC$_{71}$BM as the active layer dependence on DIB-SQ doping ratios in donors. The photovoltaic parameters of binary SMPV1:PC$_{71}$BM are chosen as reference and set to 100%. All other device data are normalized to that reference.

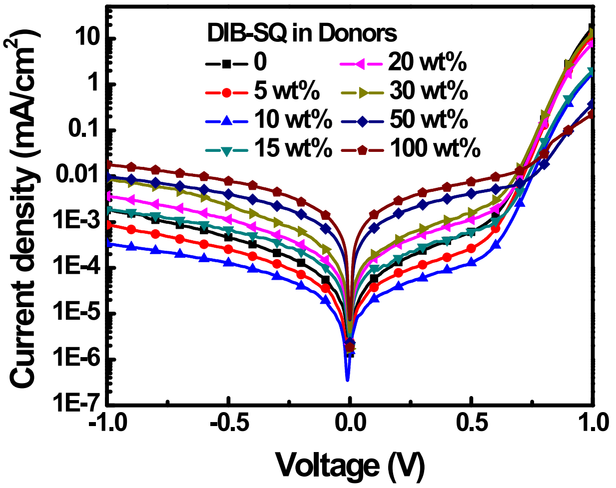

Fig. S3 The *J-V* curves of all cells with different DIB-SQ doping ratio in donors in dark condition.

As described in Fig S4, the ternary solar cells with 10 wt% SQ doping ratio exhibit the relatively high EQE values in the in the whole wavelength region (300-800) compared to that of SMPV1:PC$_{71}$BM-based solar cells. The calculated J_{sc} values of

SMPV1:$PC_{71}BM$-based cells and the ternary solar cells with 10 wt% DIB-SQ doping ratio in donors are 9.21 mA/cm^2 and 11.10 mA/cm^2, which are very close to the values obtained from *J-V* curves, suggesting that the presented experimental results are reliable.

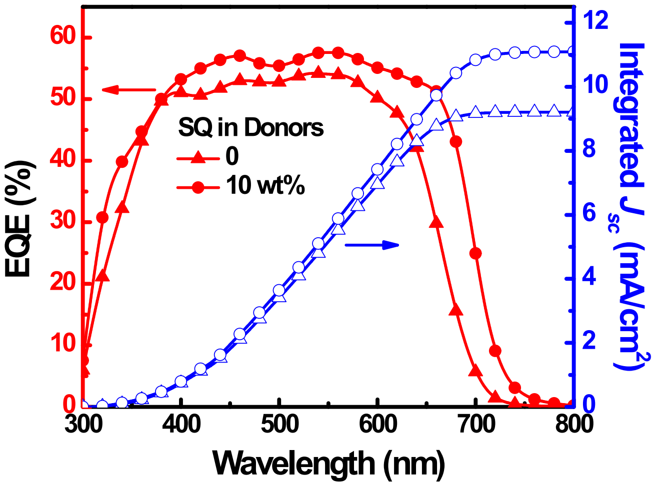

Fig. S4 the EQE spectra of SMPV1:$PC_{71}BM$ solar cells and the optimized ternary solar cell with 10 wt% DIB-SQ doping ratio in donors, the integrated J_{sc} dependence on the spectral range.

Table S1 The detailed parameters of XRD patterns of active layers with different DIB-SQ doping ratio in donors

DIB-SQ in Donors [wt%]	2-Theta	d(Å)	Height	FWHM	XS(Å)
0	4.31	20.49	16757	1.38	58.7
5	4.31	20.47	13293	1.46	55.8
10	4.31	20.47	12444	1.14	74.1
15	4.29	20.58	10383	-	-
20	4.26	20.74	9018	-	-
30	4.33	20.41	8493	-	-
50	4.34	20.34	7943	-	-
100	8.11	10.90	7751	-	-

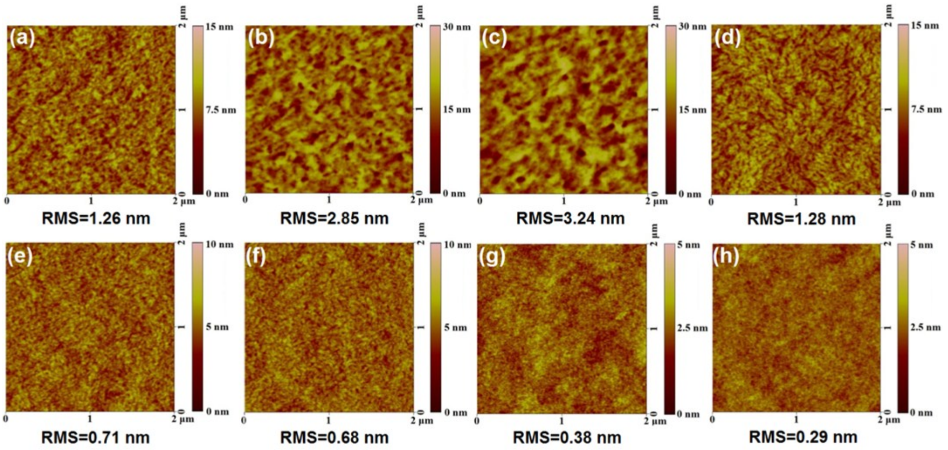

Fig. S5 The surface topography of active layers with (a) 0, (b) 5 wt%, (c) 10 wt%, (d) 15%, (e) 20 wt%, (f) 30 wt%, (g) 50 wt% and (h) 100 wt% DIB-SQ in donors .

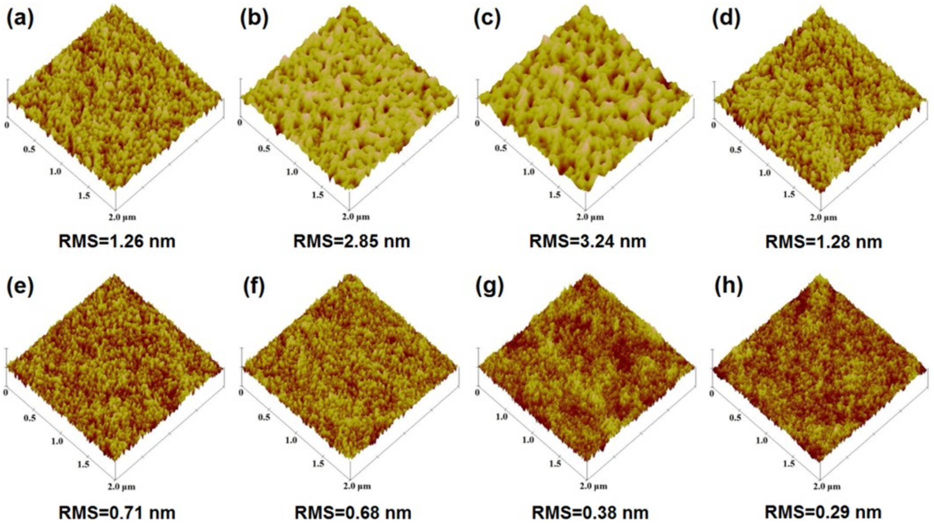

Fig. S6 The 3D surface topography of active layers with (a) 0, (b) 5 wt%, (c) 10 wt%, (d) 15%, (e) 20 wt%, (f) 30 wt%, (g) 50 wt% and (h) 100 wt% DIB-SQ in donors .

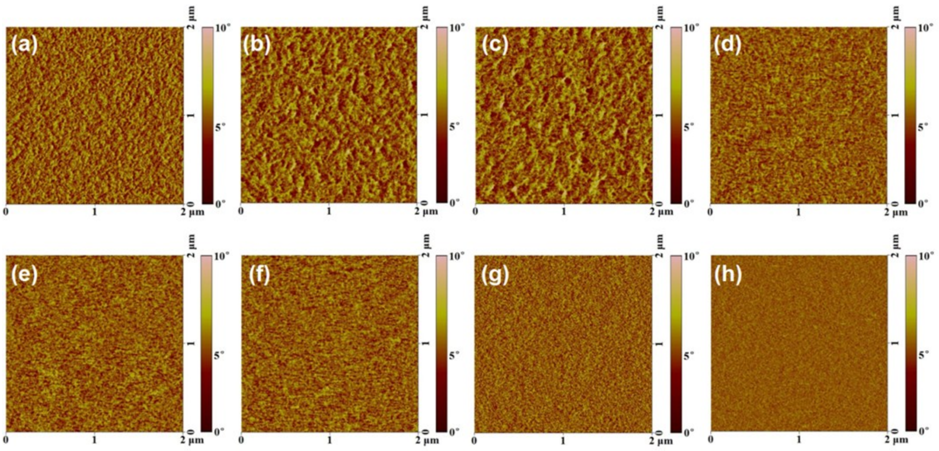

Fig. S7 The phase images of active layers with (a) 0, (b) 5 wt%, (c) 10 wt%, (d) 15%, (e) 20 wt%, (f) 30 wt%, (g) 50 wt% and (h) 100 wt% DIB-SQ in donors .

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2. H. Cha, D. S. Chung, S. Y. Bae, M.-J. Lee, T. K. An, J. Hwang, K. H. Kim, Y.-H. Kim, D. H. Choi and C. E. Park, *Adv. Funct. Mater.*, 2013, **23**, 1556-1565.