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Supporting Information

Enhancing Small-Area and Module Device Performance in Organic Photovoltaics through Insulating Polymer-Induced Manipulation of Active Layer Morphology

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Materials and Methods

Materials: Chlorobenzene (Sigma-Aldrich, 99.8%), chloroform (Sigma-Aldrich, \geq 99%), 1-Chloronaphthalene (Sigma-Aldrich), 1,8-Diiodooctane (TCL, 98%), 1,3,5-Trichlorobenzene (TCL, 99%), 2,2,2,-Trifluoroethanol (Sigma-Aldrich, 99.5%), Polystyrene (Sigma-Aldrich), Isopropyl Alcohol (Sigma-Aldrich) were purchased from commercial sources and used without further purification. PM6, Y6BO, L8BO, BTP-eC9, Y6 and PDINN were purchased from Solarmer Material Inc. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate [PEDOT:PSS] (Clevious P VP AI 4083 H. C. Stark, Germany), ITO purchased from Libo Technology Company, Molybdenum trioxide (MoO₃) and ZnO were purchased from Alfa Aesar company.

Device Fabrication:

Small-area devices: The forward structured device ITO/PEDOT:PSS/active layer/PDINN/Ag was used, with an ITO sheet resistance of 15 Ω . The ITO was ultrasonically cleaned in cleaning solution, deionized water, acetone, and isopropanol for 15 min each, and the pre-cleaned substrate was processed in a UV ozone chamber for 15 min. Spin coat PEDOT: PSS solution onto ITO substrate at a speed of 5000 rpm to form a hole transport layer, and anneal at 150 °C for 10 minutes. The blend solution of PM6:Y6BO(1:1.2, 25 mg/ml in total, 0.5% 1-CN), and PM6:BTPeC9(1:1.2, 25 mg/ml in total, 0.5% DIO) in chlorobenzene. PM6:Y6(1:1.2, 15 mg/ml in total, 0.5% 1-CN) and PM6:L8BO(1:1.2, 15 mg/ml in total, 8mg/ml TCB) in chloroform. Meanwhile, PS was pre-dissolved in CB(CF) and formulated into four different concentrations of 0.05 mg/ml, 0.1 mg/ml, 0.25 mg/ml and 0.5 mg/ml, which were added to the active layer solution. The prepared films of PM6:Y6, PM6:Y6BO and PM6:BTP-eC9 were then treated with thermal annealing at 96 °C for 8 min and PM6:L8BO was then treated with thermal annealing at 100 °C for 10 min. The electron transport layer, prepared in a nitrogen-filled glove box, was obtained by dissolving 1 mg/ml of PDINN in a solution of isopropanol and 2,2,2-trifluoroethanol (8:2 mixing ratio) and spin-coated at 3000 rpm for 30 s. Finally, a 120 nm Ag electrode was evaporated onto the electron transport layer through a mask plate.

Module devices: Module devices with ITO/PEDOT:PSS/active layer/PDINN/Ag

structure were fabricated according to the following procedure. ITO layer of the ITO glass substrates (8 Ω , maximum transmittance of about 89%) is laser etched by a 1064 nm nano-sec beam (3 W) to form isolated cells. Then the ITO glass substrates were sequential cleaned by ultrasonication in acetone, detergent, deionized water, and isopropyl alcohol for 15 min each and then dried under a dry oven. The precleaned substrates were treated in an ultraviolet-ozone chamber for 15 min, then a ~20 nm thick PEDOT:PSS (Clevious P VP AI 4083 H. C. Stark, Germany) thin film was deposited onto the ITO surface by spin-coating and baked at 150 °C for 15 min. Active layers were prepared by following the same procedure as fabricating small area devices. A ~5 nm thick of PDINN (same as small area) was spin-coated on the top of the active layer. A 532 nm nano-sec laser beam (2 W) is used for P2 scribing to expose the top ITO layer for later series connection. Then, module devices were brought into an evaporating chamber and a 150 nm thick silver layer was thermally evaporated on the PDINN layer at a base pressure of 1×10^{-6} mbar. P3 scribing is carried out with the same 532 nm nano-sec beam (2 W). The module device is composed of 8 sub-cells, in which each sub-cell has an active area of 2.2 cm², the total active layer area for the efficiency test is 17.6 cm².

Device Characterization: The current-voltage (J-V) curves were measured with Keithley 2400 Source under the illumination of AM 1.5 G irradiation (100 mW cm⁻²) using a 150 W solar simulator (DM-40S3, SAN-EI ELECTRIC, Japan) in a glove box at room temperature. The light intensity was determined by a 2×2 cm² standardized mono silicon cell (Oriel PN 91150V, Newport, USA.) calibrated by the National Renewable Energy Laboratory (NREL). The external quantum efficiency (EQE) measurement was conducted on a TRACQ-BASIC System using a lock-in amplifier with a monochromator and 500 W xenon lamp. A calibrated silicon detector (PRL-12, Newport, USA) with a known photoresponse was utilized as a reference. The J-Vcurves were measured along the reverse scan direction from 1.0 to -0.1 V, yielding identical results. The scan speed and dwell times were fixed at 0.015 V s⁻¹ and 20 ms, respectively.

SCLC mobility measurements: The electron-only devices were fabricated with

ITO/ZnO/PM6:Y6BO/PDINN/Ag structures and hole-only devices were fabricated with ITO/PEDOT:PSS/PM6:Y6BO/MoOx/Ag structures. The thickness of the active layer is ~120 nm. The space charge limited current (SCLC) mobility was calculated

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

according to the Mott-Gurney square law, $8L^3$, where J is the current density, is the relative dielectric constant of the transport medium component, is the vacuum permittivity, μ is the electron or hole mobility, V is the effective voltage (V=Vappl-Vbi), and L is the thickness of the active layer.

Measurements and instruments

Jph-Veff Measure the current voltage (J-V) curve in a room temperature glove box using a Keithley 4200 digital source meter under light (AM 1.5G) and dark conditions. Effective voltage (Veff) range: -1.5V to 1.5V, integration time is 0.2 s. AFM measurements were performed using a Dimension Icon AFM instrument (Bruker) in the tapping mode. The GIXD characterization of the thin-films was performed at the Advanced Light Source (ALS) on beamline 7.3.3 (Lawrence Berkeley National Laboratory, LBNL). The incidence angle was 0.16°, and the beam energy was 10 keV. Samples were prepared under device conditions on the Si/PEDOT:PSS substrates.

Transient absorption spectroscopy (TAS)

For femtosecond transient absorption spectroscopy, the fundamental output from Yb:KGW laser (1030 nm, 220 fs Gaussian fit, 100 kHz, Light Conversion Ltd) was separated into two light beams. One was introduced to NOPA (ORPHEUS-N, Light Conversion Ltd) to produce a certain wavelength for pump beam (here we use 550 and 750 nm, 30 fs pulse duration), the other was focused onto a YAG plate to generate white light continuum as the probe beam. The pump and probe overlapped on the sample at a small angle of less than 10°. The transmitted probe light from the sample was collected by a linear CCD array.

Transient photovoltage (TPV) and photocurrent (TPC) measurements

The background illumination was provided by the LED light source, and pulsed light was provided by an arbitrary wave generator (AFG322C, Tektronix). The

photovoltage traces were registered by the oscilloscope (AFG322C, Tektronix). The photocurrent traces were registered with the resistance of 50 Ω , switching open-circuit mode to short-circuit mode. The integrated TPC signal provides a measure of the total charge generated by the LED light source. The exponential fitting was used to process the *V*-*t* curves measuring from the TPV signal to obtain the lifetime of carriers. The total charge generated by LED was obtained from the integrated TPC signal. Empirically, the differential capacitance values are found to follow the exponential

dependence on the open-circuit voltage given by
$$C = \frac{\Delta Q}{\Delta V_0} = C_0 \exp(\gamma V_{oc}) + D$$
[C is

the differential capacitance (F), ΔQ is the total charge generated by a pulse (C), ΔV_0 is the TPV magnitude (V), C_0 is the exponential capacitance prefactor (F), γ is the capacitance exponential constant (V⁻¹), D is the effectively fixed capacitance (F)], so the charge-carrier density as a function of V_{oc} is given by treating the device as a parallel-plate capacitor and integrating with respect to voltage, as

$$n = \frac{1}{Aed} \int_{-\infty}^{v_{oc}} C_0 exp(\gamma V) dV$$
[*n* is the bulk charge-carrier density (m⁻³), *A* is the area

of the device (m^2) , d is the thickness of the active layer (m)]. Then, the recombination

rate coefficient can be determined, which is defined by $k(n) = \frac{1}{\tau(n) \cdot n}$.

Supplementary Figures



Figure S1 Statistical values of devices with different PS concentrations (a) V_{oc} , (b) J_{sc} ,

(c) FF.



Figure S2 J_{sc} dependence on different light intensities at different concentrations of

PS



Figure S3 (a) carrier lifetime; (b) carrier concentration; (c) charge lifetime of the device at different charge densities; (d) non biphasic recombination coefficient of the



Figure S4 (a) photogenerated current density maps; (b) Carrier mobility (μ_e for electron mobility, μ_h for hole mobility); (c) density of electronic states (DoS) on the lowest unoccupied molecular orbitals derived from the capacitance spectra of the device in an exponential shape, with a total effective density of states *N* and characteristic energy E_t .



Figure S5 2D transient absorption spectra of (a)PM6, (b) Y6BO.



Figure S6 (a) 0.05PS 2D transient absorption spectrum and corresponding tangent plot, (b) 0.25 PS 2D transient absorption spectrum and corresponding tangent plot, (c) 0.50 PS 2D transient absorption spectrum and corresponding tangent plot.



Figure S7 charge-transfer time τ_1 , and exciton diffusion time τ_2 extracted from transient absorption spectra.



Figure S8 (a) 2D GIXD profiles of PM6, Y6BO, 0.05 PS, and 0.50 PS, and (b) outof-plane (solid line) and in-plane (dashed line) line-cut profiles of 2D GIXD data for PM6, Y6BO, 0.05PS, and 0.50 PS. (c) d-spacing (red symbols), CCL (blue symbols), and peak area (green symbols) of the pi-pi peaks and lamellar peaks.



Figure S9 AFM height map.



Figure S10 *J-V* curve of module components.



Figure S11 Normalized PCE of the device (a) under storage conditions, (b) under

illumination, (c) under heating at 85 °C.

Supplementary Tables

Table S1 Structure parameters for different blended films. Position, FWHM and peak

 area are available through multi-peak fitting and d-spacing, CCL can be calculated by

PS concentration	Lamellae	Lamellae	Lamellae	Lamellae	π-π	π-π	π-π	π-π
(mg/ml)	d-spacing	CCL	FWHM	Peak area	d-spacing	CCL	FWHM	Peak area
0	21.23	101.34	0.056	176.727	3.812	12.91	0.438	523.357
0.05	21.08	113.55	0.050	215.738	3.559	19.90	0.284	668.758
0.10	21.05	131.98	0.043	227.196	3.526	21.01	0.269	700.545
0.50	20.94	100.62	0.055	170.087	3.543	17.13	0.330	625.067

Scherrer Equation.

Table S2 The active layer is the photovoltaic parameter of PM6: Y6 device.

PS concentration (mg/ml)	$V_{ m oc}\left({ m V} ight)$	$J_{\rm sc}~({\rm mA/cm^2})$	FF (%)	PCE (%)
0	0.835	26.8	74.3	16.6
0.05	0.834	27.2	75.0	17.0
0.10	0.832	27.2	76.5	17.3
0.25	0.835	27.2	75.2	17.1
0.50	0.837	27.1	74.7	16.9

Table S3 The active layer is the photovoltaic parameter of PM6: L8BO device.

PS concentration (mg/ml)	$V_{ m oc}\left({ m V} ight)$	$J_{\rm sc}~({\rm mA/cm^2})$	FF (%)	PCE (%)
0	0.880	25.6	78.9	17.8
0.05	0.883	26.0	79.7	18.3
0.10	0.879	25.5	80.1	17.9
0.25	0.883	25.7	78.8	17.9
0.50	0.886	25.4	78.7	17.7

Table S4 The active layer is the photovoltaic parameter of PM6: BTP-eC9 device.

PS concentration (mg/ml)	$V_{ m oc}\left({ m V} ight)$	$J_{ m sc}~({ m mA/cm^2})$	FF (%)	PCE (%)
0	0.836	26.8	74.7	16.7
0.05	0.835	27.4	76.3	17.5

0.10	0.833	27.1	75.6	17.1
0.25	0.834	26.8	75.8	16.9
0.50	0.833	26.7	75.0	16.7