

Electronic Supplemental Information:

Realizing the Efficiency-Stability Balance of All-polymer Photovoltaic Blends

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PM6-b-PY-IT: In a dry 25 mL flask, Pd₂(dba)₃ (1.0 mg) and P(*o*-tol)₃ (1.5 mg) were added to a solution of Y5-I-C20-Br (131.7 mg, 0.066 mmol) and 2,5-bis(trimethylstannyl)thiophene (27.2 mg, 0.066 mmol) in 6 mL degassed toluene under argon and stirred vigorously at 110 °C for 5 hours. Then the pre-prepared PM6 block was added to the reaction system by syringe. The new reaction system was stirred vigorously at 110 °C for additional 24 hours. Then the mixture was poured into methanol (100 mL) and precipitation occurred. The dried precipitates were purified by Soxhlet extractor with methanol, acetone, hexane, and dichloromethane each for 5 hours, and chloroform for 2 hours as a final, respectively. The chloroform fraction was concentrated and precipitated with methanol, black solids was obtained and dried. The obtained crude polymer was dissolved in warm chloroform and then the solution was quickly filtered through a pre-prepared wet silica gel column (80-100 mesh) with chloroform. The collected chloroform solution was concentrated and precipitated in methanol to get PM6-b-PY-IT as a dark solid (90 mg, 41%). $M_n = 23.8$ kDa, $M_n = 44.0$ kDa, and $\bar{D} = 1.85$.

Characterization

Molecular weights of polymers were measured by high temperature gel permeation chromatography (GPC) using monodispersed polystyrene as the standard and 1,2,4-trichlorobenzene as the eluent at 150 °C. UV-vis absorption spectra were recorded by Ultra-Violet Visible Scanning Spectrophotometer (Shimadzu 1700). AFM measurements were obtained by using a Dimension Icon AFM (Bruker) in a tapping mode. The grazing incidence X-ray scattering (GIWAXS) measurement was carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The incident angle was 0.2°. The samples for GIWAXS/GISAXS measurements were fabricated on silicon substrates using the same recipe for the devices.

Solar cell fabrication and characterization

Solar cells were fabricated in a conventional device configuration of

ITO/PEDOT:PSS/active layers/PDINN/Ag. The ITO substrates were first scrubbed by detergent and then sonicated with deionized water, acetone and isopropanol subsequently, and dried overnight in an oven. The glass substrates were treated by UV-Ozone for 30 min before use. PEDOT:PSS (Heraeus Clevis P VP AI 4083) was spin-cast onto the ITO substrates at 4000 rpm for 30 s, and then dried at 150 °C for 15 min in air. The PM6:PY-IT blends (1:1 weight ratio), were dissolved in chloroform (the concentration of PM6 was 7 mg mL⁻¹ for all blends), with 1-chloronaphthalene (1% vol) as additive, and stirred overnight in a nitrogen-filled glove box. The blend solution was spin-cast at 2200 rpm for 30 s onto PEDOT:PSS films followed by a temperature annealing of 95°C for 5 min. The PM6-b-PY-IT was dissolved in chloroform based on a 12 mg mL⁻¹ with 1-chloronaphthalene (1% vol) as additive, and stirred overnight in a nitrogen-filled glove box. The solution was spin-cast at 2000 rpm for 30 s onto PEDOT:PSS films followed by a temperature annealing of 95°C for 5 min. A thin PDINN layer was coated on the active layer, followed by the deposition of Ag (evaporated under 5×10⁻⁴ Pa through a shadow mask). The optimal active layer thickness measured by a Bruker Dektak XT stylus profilometer was about 100 nm. The current density-voltage (*J-V*) curves of all encapsulated devices (by Epoxy) were measured using a Keithley 2400 Source Meter in air under AM 1.5G (100 mW cm⁻²) using a Newport solar simulator, where the applied voltage varies from -1.3V to 0.5V. The light intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement to bring spectral mismatch to unity). The scan speed is about 0.5V/s, and devices were scanned for several times to exclude the effect of burn-in loss. Optical microscope (Olympus BX51) was used to define the device area (5.9 mm²). EQEs were measured using an Enlitech QE-S EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300W lamp source.

SCLC Measurements

The electron and hole mobility were measured by using the method of space-charge limited current (SCLC) for electron-only devices with the structure of ITO/ZnO/active layer/PNDIT-F3N/Ag and ITO/PEDOT:PSS/active layers/MoO_x/Ag for hole-only

devices. The charge carrier mobility was determined by fitting the dark current to the model of a single carrier SCLC according to the equation: $J = 9\epsilon_0\epsilon_r\mu V^2/8d^3$, where J is the current density, d is the film thickness of the active layer, μ is the charge carrier mobility, ϵ_r is the relative dielectric constant of the transport medium, and ϵ_0 is the permittivity of free space. $V = V_{\text{app}} - V_{\text{bi}}$, where V_{app} is the applied voltage, V_{bi} is the offset voltage. The carrier mobility can be calculated from the slope of the $J^{1/2} \sim V$ curves.

The Analysis of J_{ph} vs V_{eff} relationships

The definition of J_{ph} is the current density under illumination (J_{L}) minus the dark current density (J_{D}), and V_0 refers to the voltage value when $J_{\text{ph}} = 0$. Accordingly, $V_{\text{eff}} = V_0 - V_{\text{appl}}$, where V_{appl} represents applied voltage, has a clear meaning. Importantly, when V_{eff} reaches a high value ($> 2\text{V}$) it is normally believed that generated excitons are fully collected, in which J_{ph} is equal to saturated current density (J_{sat}). Then, we can calculate $J_{\text{SC}}/J_{\text{sat}}$ and $J_{\text{max}}/J_{\text{sat}}$ to describe exciton dissociation (η_{diss}) and charge collection (η_{coll}) efficiency. J_{max} is the J_{ph} at the maximal output point.

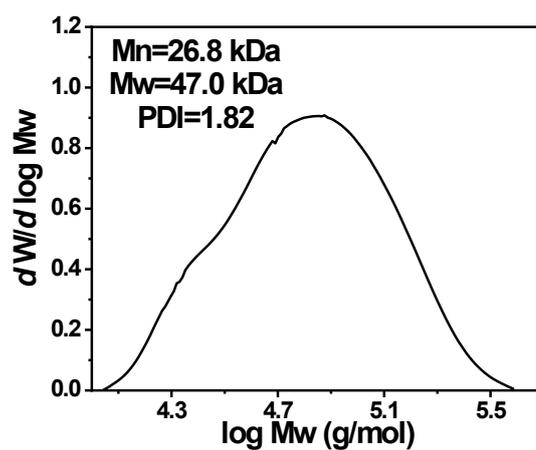


Figure S1. GPC curves of one pot synthesized PM6-b-PY-IT.

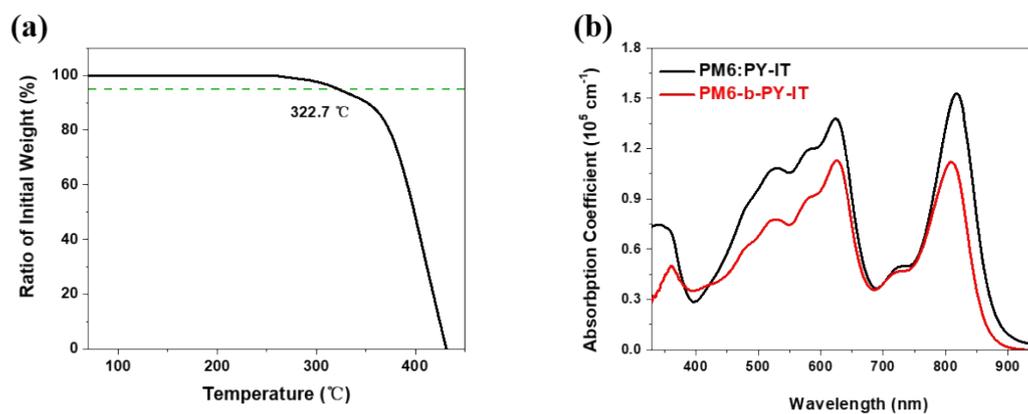


Figure S2. (a) TGA curves of PM6-b-PY-IT. (b)

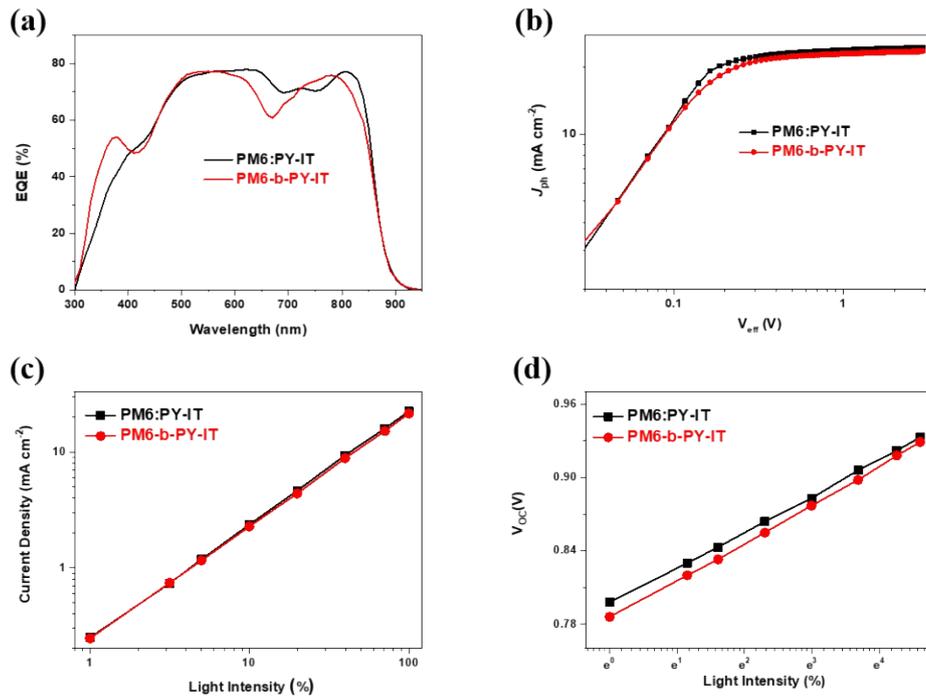


Figure S3. (a) EQE spectra of two devices. (b) J_{ph} - V_{eff} curves. (c) J_{SC} vs light intensity relationships. (d) V_{OC} vs light intensity relationships.

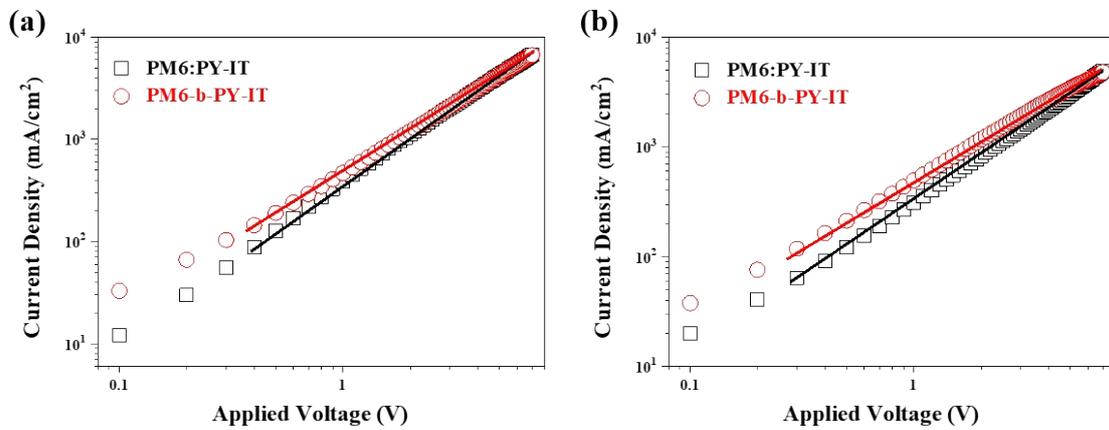


Figure S4. (a) Hole-only and (b) electron-only devices.

Table S1. The performance comparison.

Ref	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
This work	0.929	21.51	68.2	13.63

1	0.86	20.64	68	8.64
2	0.916	19.60	63.00	11.32
3	0.895	20.57	68.46	12.60
4	0.90	19.07	59	10.51

Reference

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