

Supporting information

Nonfullerene acceptor as solid additive realizing a record efficiency of 17.74% in quasi-layered all-polymer solar cells

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Device Fabrication

The patterned indium tin oxide (ITO) coated glass substrates (15 Ω per square) were cleaned via sequential sonication in detergent, de-ionized and ethanol and then blow-dried by high-purity nitrogen. All pre-cleaned ITO substrates were treated by oxygen plasma for 1 minute to improve their work function and clearance. Subsequently, poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT: PSS, purchased from H.C. Starck co. Ltd.) solution was spin-coated on ITO

substrates at 5000 rpm for 40 s and dried at 150 °C for 15 min in atmospheric air. Then ITO substrates coated with PEDOT: PSS films were transferred into a high-purity N₂-filled glove box. Polymer donor PM6 and polymer acceptor PY-IT were purchased from Solarmer Materials Inc. The layered donor and acceptor layers were spin coated from 7 mg/ml PM6 chlorobenzene solution at 1200 rpm for 40 s, then spin coated the 7 mg/ml PY-IT chloroform solution or 7 mg/ml PY-IT:L8-BO chloroform solution at 2000 rpm for 30 s on the top of the PM6 layers. Then thermally annealed at 95 °C for 5 min. Interfacial layer of PNDIT-F3N was deposited by spin-coating solution in methanol (0.5 mg/ml) at 2000 rpm for 30 s. PNDIT-F3N was dissolved in methanol with the addition of 0.25 vol% acetic acid to prepare a 0.5 mg/ml solution. The PNDIT-F3N solution was spin-coated onto the active layers at 2000 rpm for 30 s. Finally, 100 nm Ag layer was deposited by thermal evaporation through a shadow mask under the vacuum of 5×10⁻⁴ Pa conditions. The active area is approximately 3.8 mm², defined by the overlapping area of ITO anode and Ag cathode.

Device Measurement

The current-voltage (*J-V*) curves of all PSCs were measured in a high-purity nitrogen-filled glove box using a Keithley 2400 source meter. AM 1.5G irradiation at 100 mW cm⁻² was provided by An XES-40S2 (SAN-EI Electric Co., Ltd.) solar simulator (AAA grade, 70×70 mm² photobeam size), which was calibrated by standard silicon solar cells (purchased from Zolix INSTRUMENTS CO. LTD). The ultraviolet-visible (UV-Vis) absorption spectra of films were obtained using a Shimadzu UV-3101 PC spectrometer. The contact angles of PM6, PY-IT and PY-IT:L8-BO films were measured based on water and EG. The surface energy of films was calculated according to the contact angles by using Wu model. According to the surface energy of films, the interfacial energy between various films can be evaluated by the following equation:

$$\gamma_{AB} = \gamma_A + \gamma_B - \frac{4\gamma_A^d \gamma_B^d}{\gamma_A^d + \gamma_B^d} - \frac{4\gamma_A^p \gamma_B^p}{\gamma_A^p + \gamma_B^p}$$

Here, γ_{AB} is the interfacial energy between material A and B; γ_A and γ_B are the surface energy of the pure materials; superscripts *d* and *p* represent the dispersion and polar components calculated by using the contact angles.

The external quantum efficiency (EQE) spectra of PSCs were measured in air conditions by a Zolix Solar Cell Scan 100. The photoluminescence (PL) spectra of the active layer based on the various ETLs were measured by a fluorescence spectrophotometer (FLS 1000). Transient photovoltage (TPV) and transient

photocurrent (TPC) were conducted with the PaioCarrier measurement system (FLUXiM AG, Switzerland). A high-power white LED is utilized as the light source for TPV and TPC measurements. The integrated power of the LED is 72 mW cm⁻², and the spectrum distribution is mainly in the wavelength range of 440-470 nm and 540-630 nm, and the peak values are located at 460 nm and 550 nm. Femtosecond time-resolved transient absorption (TA) spectra measurement was performed using a commercial fs-TA spectra system. Grazing incidence wide angle X-ray scattering (GIWAXS) measurements were accomplished at PLS-II 9A U-SAXS beamline of the Pohang Accelerator Laboratory in Korea.

Charge mobility measurement by SCLC method:

The structure of electron-only devices is ITO/ZnO/active layer/ PNDIT-F3N /Al. The fabrication conditions of the active layer films are the same as those for the QLA-PSCs. The charge mobilities are generally described by the Mott-Gurney equation (1):

$$J = \frac{9}{8} \epsilon_r \epsilon_0 \mu \frac{V^2}{L^3} \quad (1)$$

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 used materials, μ is the charge mobility, V is the applied voltage and L is the active layer thickness. The ϵ_r parameter is assumed to be 3, which is a typical value for organic materials. In organic materials, charge mobility is usually field dependent and can be described by the disorder formalism, typically varying with electric field, $E=V/L$, according to the equation (2):

$$\mu = \mu_0 \exp\left[0.89\gamma \sqrt{\frac{V}{L}}\right] \quad (2)$$

where μ_0 is the charge mobility at zero electric field and γ is a constant. Then, the Mott-Gurney equation can be described by (3):

$$J = \frac{9}{8} \epsilon_r \epsilon_0 \mu_0 \frac{V^2}{L^3} \exp\left[0.89\gamma \sqrt{\frac{V}{L}}\right] \quad (3)$$

In this case, the charge mobilities were estimated using the following equation (4):

$$\ln\left(\frac{JL^3}{V^2}\right) = 0.89\gamma \sqrt{\frac{V}{L}} + \ln\left(\frac{9}{8} \epsilon_r \epsilon_0 \mu_0\right) \quad (4)$$

The details of the materials are as follows:

The Mw of polymer PM6 and PY-IT are 98 and 15 kDa.

PM6: Poly[(2,6-(4,8-bis(5-(2-ethylhexyl-3-fluoro)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)]

PY-IT: Poly[2,2'-((2Z,2'Z)-((12,13-bis(2-octyldodecyl)-3,9-diundecyl-12,13-dihydro[1,2,5]thiadiazolo[3,4e]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]-indole-2,10-diyl)bis(methanylylidene))bis(5-methyl-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene)) dimalononitrile-co-2,5-thiophene]

L8-BO: 2,2'-((2Z,2'Z)-((12,13-bis(2-ethylhexyl)-3,9-(2-butyloctyl)-12,13-dihydro[1,2,5]thiadiazolo[3,4-e]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile

PNDIT-F3N: Poly[(9,9-bis(3'-(N,Ndimethylamino)propyl)-2,7-fluorene)-alt-5,5-bis(2,2'-thiophene)-2,6-naphthalene-1,4,5,8-tetracarboxylic-N,N'-di(2-ethylhexyl)imide]

Additional experimental results

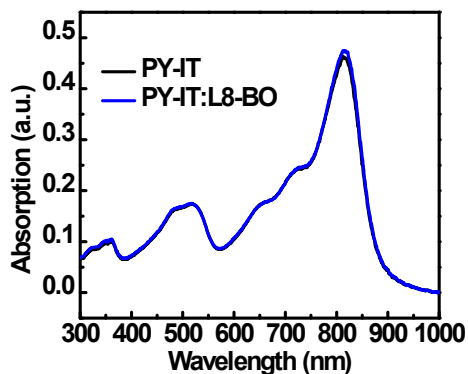


Figure S1. The absorption spectra of pure PY-IT and PY-IT:L8-BO fillms.

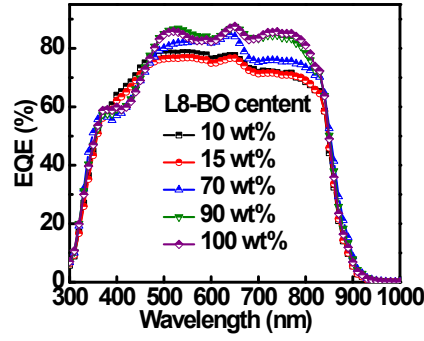


Figure S2. The EQE spectra of QLA-PSCs with L8-BO as third component in PY-IT layer.

Table S1. Contact angles and surface energy (γ) of individual films, and interfacial energy (γ_{XY}) between two films.

| Film (X) | Contact angle H ₂ O (deg) | Contact angle EG (deg) | γ (mN m ⁻¹) | γ^d (mN m ⁻¹) | γ^p (mN m ⁻¹) | Film (Y) | γ_{XY} (mN m ⁻¹) |
|-------------|--------------------------------------|------------------------|--------------------------------|----------------------------------|----------------------------------|----------|-------------------------------------|
| PM6 | 105.11 | 72.73 | 31.16 | 30.38 | 0.78 | / | / |
| PY-IT | 100.21 | 69.84 | 29.31 | 22.08 | 7.23 | PM6 | 3.32 |
| PY-IT:L8-BO | 97.99 | 60.64 | 36.96 | 34.55 | 2.41 | PM6 | 1.11 |

Table S2. The parameters of QLA-PSCs.

| L8-BO content [wt%] | $J_{ph}^{\&}$ [mA cm ⁻²] | J_{ph}^* [mA cm ⁻²] | J_{sat} [mA cm ⁻²] | η_D [%] | η_C [%] |
|---------------------|--------------------------------------|-----------------------------------|----------------------------------|--------------|--------------|
| 0 | 20.66 | 23.41 | 24.54 | 95.4 | 84.2 |
| 0.5 | 21.23 | 23.84 | 24.98 | 95.4 | 85.0 |
| 1 | 21.43 | 24.03 | 25.14 | 95.6 | 85.2 |
| 2 | 21.71 | 24.45 | 25.42 | 96.2 | 85.4 |
| 3 | 21.20 | 23.88 | 24.92 | 95.8 | 85.1 |

Table S3. The fitted parameters of QLA-PSCs according to the impedance spectroscopy.

| L8-BO content [wt%] | R_{OS} (Ω) | R_{CT} (Ω) | CPE_T (nF) | CPE_P | τ (ns) |
|---------------------|-----------------------|-----------------------|--------------|---------|-------------|
| 0 | 37.3 | 38.8 | 11.30 | 0.958 | 438 |
| 0.5 | 33.3 | 37.4 | 9.20 | 0.979 | 344 |

| | | | | | |
|---|------|------|------|-------|-----|
| 1 | 32.6 | 37.1 | 8.34 | 0.983 | 309 |
| 2 | 31.7 | 35.2 | 7.67 | 0.990 | 269 |
| 3 | 36.1 | 39.6 | 10.2 | 0.964 | 403 |

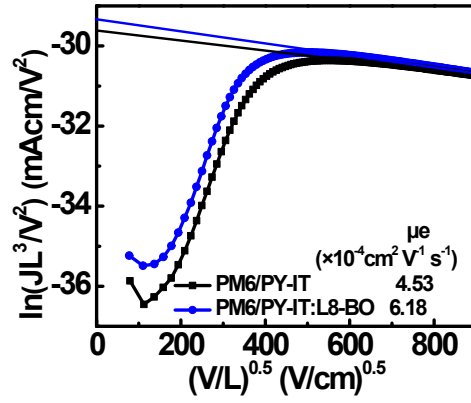


Figure S3. The $\ln(JL^3/V^2)$ versus $(V/L)^{0.5}$ curves of electron-only devices.

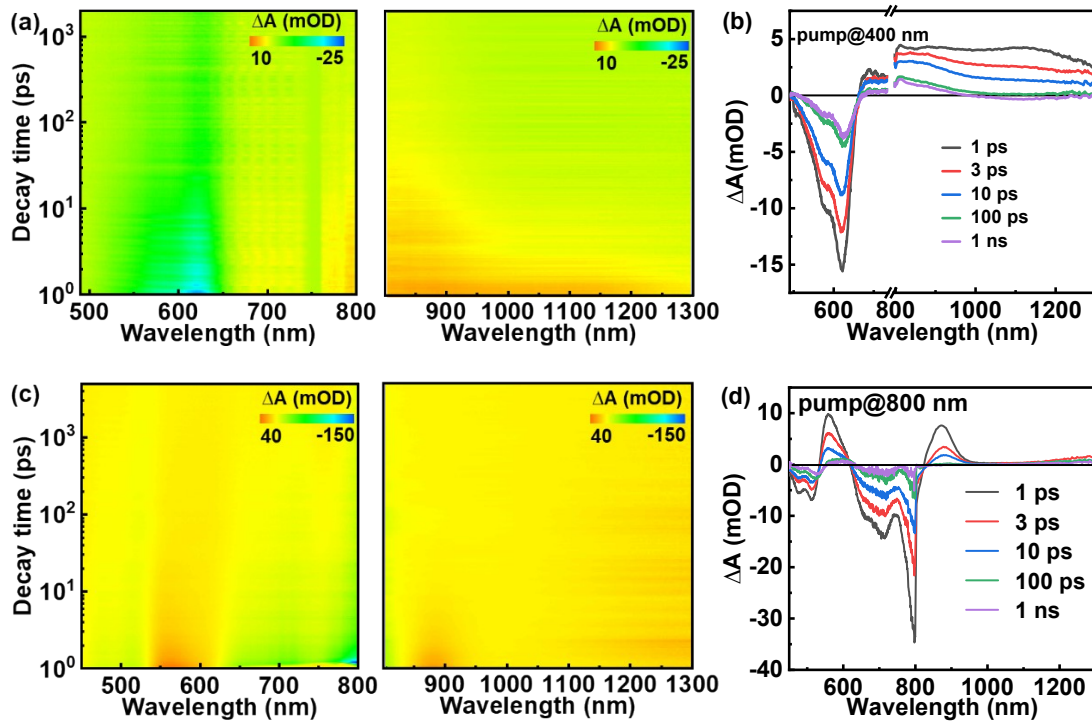


Figure S4. (a) 2D TA spectrum and (b) TA spectra at different probe delay times of PM6 pumped at 400 nm. (c) 2D TA spectrum and (d) TA spectra at different probe delay times of PY-IT pumped at 800 nm.

Table S4. Fitting parameters for the pump fluence-dependent TA decay curves.

| Probe at 900 nm | τ [ps] | k [$\times 10^9 \text{ s}^{-1}$] | γ [$\times 10^9 \text{ cm}^3 \text{ s}^{-1}$] | D [$\times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$] | L_D [nm] |
|--------------------|----------------|---|---|---|---------------|
| PY-IT | 1333 | 0.750 | 1.45 | 0.579 | 8.79 |
| PY-IT:L8-BO | 1361 | 0.735 | 1.51 | 0.603 | 9.06 |

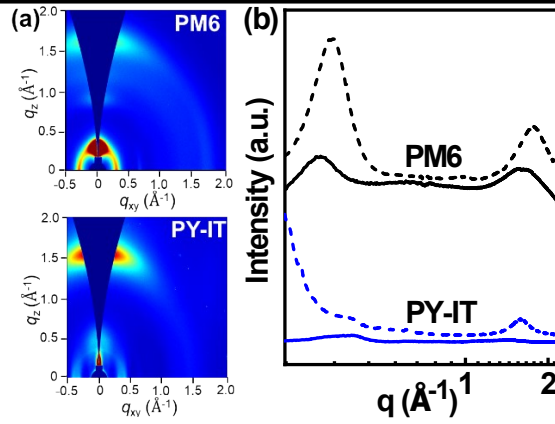


Figure S5. (a) The 2D-GIWAXS patterns of PM6 and PY-IT films. (b) The in-plane (solid lines) and out-of-plane (dotted lines) profiles abstracted from 2D-GIWAXS patterns corresponding films.

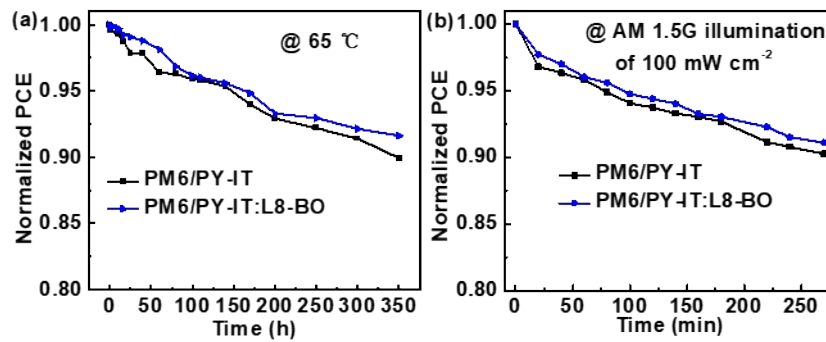


Figure S6. (a) Thermal stability under 65 °C and (b) light soak stability under AM 1.5G illumination of 100 mW cm⁻² condition of PM6/PY-IT and PM6/PY-IT:L8-BO based QLA-PSCs.

Table S5. The photovoltaic parameters of PM6/PY-IT, PM6/PY-IT:Y6 and PM6/PY-IT:BO-4F based QLA-PSCs.

| Solid additive | J_{sc} [mA cm ⁻²] | V_{oc} [V] | FF [%] | PCE (avg.±dev.) [%] |
|----------------|------------------------------------|-----------------|-----------|------------------------|
| w/o | 23.41 | 0.95 | 72.60 | 16.14 (16.01±0.12) |
| Y6 | 23.74 | 0.95 | 74.03 | 16.71 (16.54±0.15) |
| BO-4F | 23.85 | 0.95 | 74.10 | 16.79 (16.58±0.18) |

The average and error values of PCE are from 10 individual cells.