Supporting Information:

Materials

PM6 was purchased from Solarmer Material Inc. PY-DT and PNDIT-F3N were purchased from eFlexPV Limited. PEDOT:PSS (Clevios P VP 4083) was purchased from Heraeus Inc., Germany. All the other reagents and chemicals were purchased from Sigma Aldrich or Aladdin and used as received.

Device Fabrication

Solar cells were fabricated in a conventional device configuration of ITO/PEDOT:PSS/active layer/PNDIT-F3N/Ag. The ITO substrates were cleaned by detergent and then sonicated with deionized water, acetone and isopropanol subsequently, and dried overnight in an oven. The glass substrates were treated with UV-Ozone for 30 min before PEDOT:PSS was spin-casted on top at 5,000 rpm for 30 s, and then annealed at 150 °C on a hotplate for 10 min in air.

BC and SqP devices:

1) For the blend-casting (BC) devices, namely, PM6:PY-DT (BC), the PM6: PY-DT blend (1:1.2 weight ratio) was dissolved in toluene (the concentration of donor was 7 mg mL⁻¹ for all blends), with 1-chloronaphthalene (1% vol) as an additive, and stirred overnight in a nitrogen-filled glove box. The 95°C toluene blend solution was spin-casted at 2500 rpm for 30 s onto the PEDOT:PSS films followed by a thermal annealing of 95°C for 5 min.

2) For the sequentially processed (SqP) device, namely, PM6/PY-DT (SqP), PM6 was dissolved in toluene (the concentration of donor was 8 mg mL⁻¹), PY-DT was also dissolved in toluene (the concentration of donor was 12 mg mL⁻¹) but with 1-chloronaphthalene (2% vol) as an additive. Both solutions were stirred overnight in a nitrogen-filled glove box. The donor solution was spin-casted at 4000 rpm for 30 s onto the PEDOT:PSS films, then the acceptor solution was spin-casted at 4000 rpm for 30 s onto the donor films followed by a thermal annealing of 95°C for 5 min.

For all types of devices, a methanol with 0.5% vol acetic acid blend solution of PNDIT-F3N at a concentration of 0.5 mg mL⁻¹ was spin-coated onto the active layer at 2000 rpm for 30s. Around 100 nm of Ag was evaporated under 4×10^{-4} Pa through a shadow mask. Then the encapsulation was carried out.

Device Characterization

The current density-voltage (*J-V*) curves of all encapsulated devices were measured using a Keithley 2400 Source Meter under AM 1.5G (100 mW cm⁻²) using an Enlitech solar simulator. The light intensity was calibrated using a standard Si diode with KG5 filter to bring spectral mismatch to unity. Optical microscope (Olympus BX51) was used to define the device area (7.2 mm²). EQEs were measured using an Enlitech QE-S EQE system equipped with a standard Si diode. Monochromatic light was generated from a Enlitech 300W lamp source. The glass encapsulated devices were put under a white light-emitting diode array with 1-sun illumination in air for MPP tracking.

SCLC Measurements: The electron- and hole-mobilities were evaluated using the space-charge limited current (SCLC) method. The device architecture of the electron-only devices was ITO/ZnO/active layer/PNDIT-F3N/Ag and that of the hole-only devices was ITO/PEDOT:PSS/active layer/MoOx/Ag. The charge carrier mobilities were determined by fitting the dark current into the model of a single carrier SCLC according to the equation: $J = 9\varepsilon_0\varepsilon_{\eta}\mu V^2/8d^3$, 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. The V used in the equation is defined by: $V = V_{app} - V_{bi}$, where V_{app} is the applied voltage, V_{bi} is the built-in voltage. The carrier mobilities were calculated from the slope of the $J \sim V^2$ curves.

Film-depth-dependent light absorption and composition distribution

Film-depth-dependent light absorption was carried out with in-situ spectrometer (PU100, Shaanxi Puguang Weishi Co. Ltd.) equipped with a soft plasma-ion source. A 100 W power with an input pressure of ~10 Pa (oxygen) was used to generate soft ionic source. The surface of the target film is gradually etched by the soft ion source, without damage to the materials underneath. The absorption for the film during etching was insitu monitored by an spectrometer.

The distribution of the donor and acceptor materails along the vertical direction of the film was obtained from the film-depth-dependent spectra and the absorption of pure films. The exciton generation contour is numerically simulated upon inputting film-depth-dependent light absorption spectra into a modified optical transfer-matrix approach.

GIWAXS Measurements

GIWAXS measurement were 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 incidence angle is 0.2°. The samples for GIWAXS measurements are fabricated on silicon substrates using the same recipe for the devices.

TPV/TPC Measurements

In TPV measurements, the devices were placed under background light bias enabled by a focused Quartz Tungsten-Halogen Lamp with an intensity of similar to working devices, i.e., the device voltage matches the open-circuit voltage under solar illumination conditions. Photo-excitations were generated with an 8 ns pulses from a laser system (Oriental Spectra, NLD520). The wavelength for the excitation was tuned to 518 nm with a spectral width of 3 nm. A digital oscilloscope was used to acquire the TPV signal at the open-circuit condition. TPC signals were measured under shortcircuit conditions under the same excitation wavelength without background light bias.



Figure S1. (a) J_{SC} versus light intensity; (b) V_{OC} versus light intensity; (c) dark J-V curves of BC and SqP



Figure S2. AFM height images of (a) PM6 and (b) PY-DT neat films, as well as (c) BC and (d) SqP blend films.



Figure S3. Original spectra gained during the etching of (a) BC and (b) SqP films.

Device	Peak (Å ⁻¹)	d-spacing (Å)	CCL (Å)
BC	1.64	3.83	29.6
SqP	1.63	3.85	31.4