Supporting Information

Achieving 15.81% and 15.29% efficiency of all-polymer solar cells based on layer-by-layer or bulk heterojunction structure

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Experimental section

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, 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 nitrogen-filled glove box. Polymer donor PM6 and polymer acceptor PY-IT were purchased from Solarmer Materials Inc. The BHJ active layers were spin coated from 14 mg/ml chloroform solution (PM6:PY-IT=1:1, without or with 1 vol% CN) at 2400 rpm for 30 s. For LbL active layer, the donor layers were spin coated from 7 mg/ml PM6 chlorobenzene solution at 800 rpm for 40 s, then the acceptor layers were spin coated from 7 mg/ml PY-IT chloroform solution (without or with 1 vol% CN) at 1400 rpm for 30 s on the top of the PM6 layers. Then the active layers were thermally annealed at 95 °C for 5 min. PNDIT-F3N was dissolved in methanol with the addition of 0.25 vol% acetic acid to prepare a 0.5 mg/ml solution and then spin coated at 2000 rpm for 30 s on the active layers. Finally, 100 nm Al 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 mm^2, defined by the overlapping area of ITO anode and Al 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 mm^2 photobeam size), which was calibrated by standard silicon solar cellsa (purchased from Zolix INSTRUMENTS CO. LTD). The absorption spectra of films were obtained by using a Shimadzu UV-3101 PC spectrometer. The external quantum efficiency (EQE) spectra of all-PSCs were measured in the air conditions by a Zolix Solar Cell Scan 100. The reflection spectra measurement of all devices was performed on a commercial QE measurement system (QE-RT3011, Enlitech) by using an integrating sphere. The absorption spectra of active layers in cells were calculated by subtracting the parasitic absorptions (1-R_1) from the total absorption (1-R_2) in all-PSCs, where R_1 is the reflection spectrum of the special device with configuration of ITO/PEDOT:PSS/PMMA/ PNDIT-F3N/Al, R_2 is the reflection spectra of all-PSCs with configuration of ITO/PEDOT:PSS/Active layers/PNDIT-F3N/Al. The PMMA layer in the special device is used to simulate the optical path in real all-PSCs because PMMA has negligible photon harvesting in the whole spectral range. Photoluminescence (PL) spectra of films were measured by a HORIBA Fluorolog®-3 spectrofluorometer system. Transient photovoltage (TPV) and transient photocurrent (TPC) were conducted with the Paioscarrier measurement system (FLUXiM AG, Switzerland). A high-power white LED is utilized as 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. 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.

Additional experimental results

The Mw and Mn of polymer PM6 are 98 and 41 kDa. The Mw and Mn of polymer PY-IT are 15 and 33 kDa.

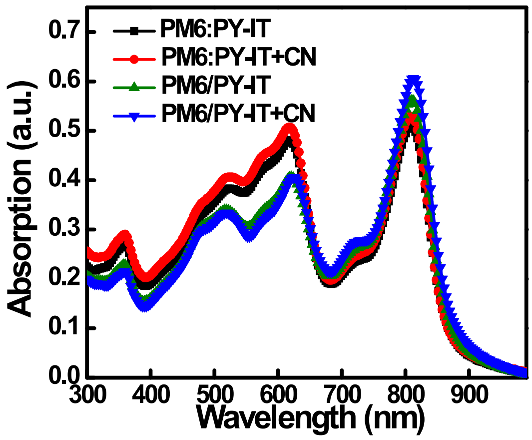
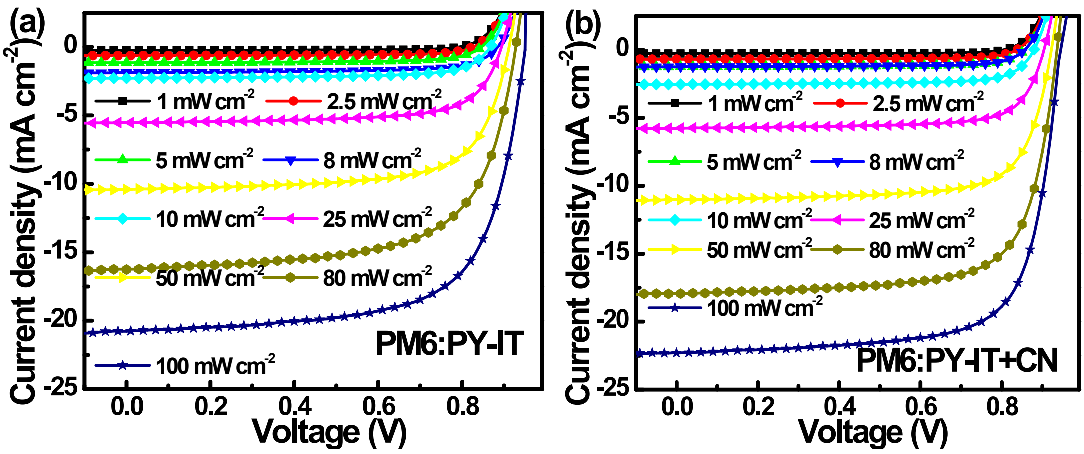


Figure S1. Absorption spectra of PM6 and PY-IT blend films processed without or with additive.

Table S1. Device parameters of all-PSCs.

Active layer	J_{sat} (mA cm^{-2})	$J_{ph}{}^{*}$ (mA cm^{-2})	$J_{ph}{}^{\&}$ (mA cm^{-2})	η_D (%)	η_C (%)
PM6:PY-IT	22.34	20.76	18.08	92.92	80.92
PM6:PY-IT+1% CN	23.19	22.29	19.35	94.61	82.01
PM6/ PY-IT	22.79	21.12	18.58	92.66	81.51
PM6/ PY-IT +1% CN	23.72	22.61	19.48	94.43	82.11



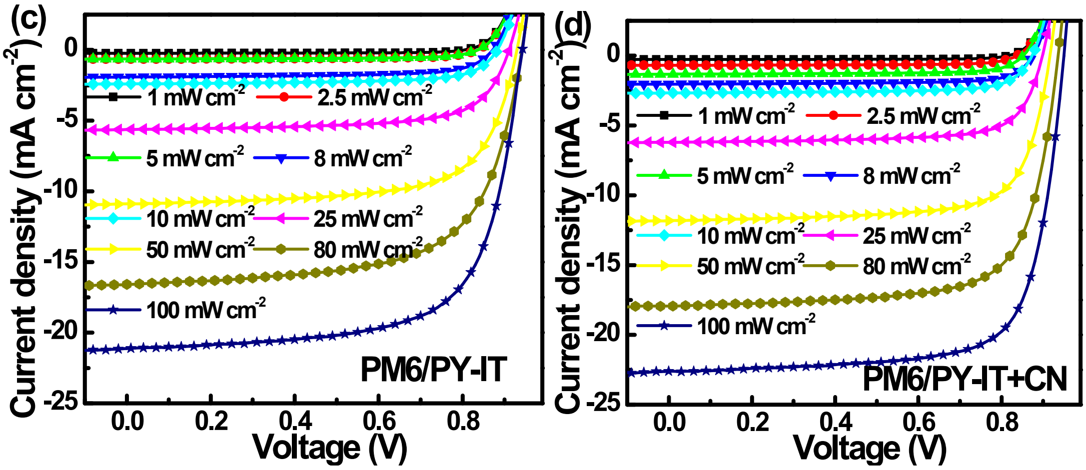


Figure S2. *J-V* curves of (a) PM6:PY-IT, (b) PM6:PY-IT+CN, (c) PM6/PY-IT, (d) PM6/PY-IT+CN all-PSCs under different light intensity (100, 80, 50, 25, 10, 8, 5, 2.5, 1 mW cm^{-2}), obtained from standard AM 1.5G (100 mW cm^{-2}) illumination with a set of neutral optical filters.

Table S2. The fitted parameters of all-PSCs processed with or without additives.

Active layer	R_{CT} (Ω)	R_{OS} (Ω)	CPE_T (nF)	CPE_P	τ (ns)
PM6:PY-IT	89.3	33.4	10.8	0.873	964.44
PM6:PY-IT+1% CN	53.0	31.5	17.1	0.901	906.30
PM6/ PY-IT	88.7	32.0	8.7	0.886	771.69
PM6/ PY-IT +1% CN	50.1	30.3	15.2	0.912	761.52

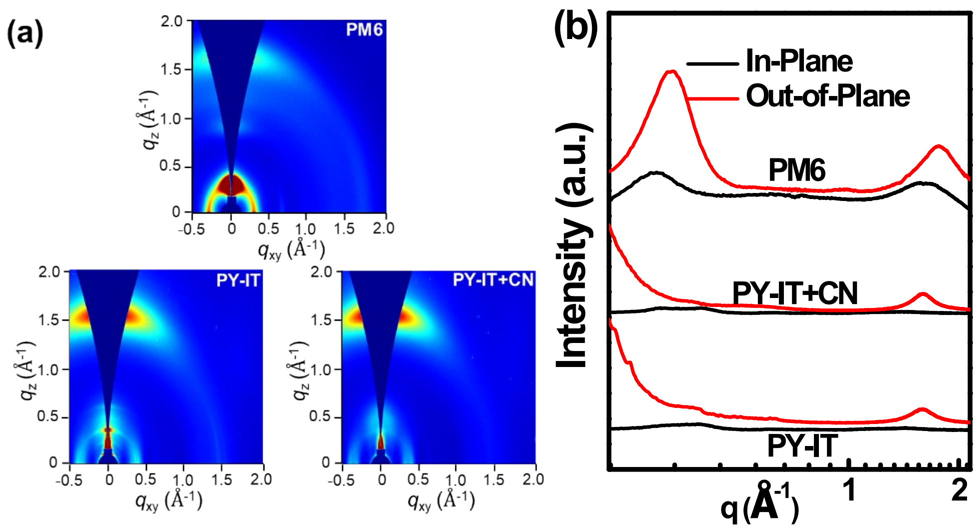


Figure S3. (a) The 2D-GIWAXS patterns of PY-IT films and PY-IT films with CN additive. (b) The in-plane (IP, black line) and out-of-plane (OOP, red line) profiles abstracted from 2D-GIWAXS patterns corresponding blend films.