Supporting Information

Layer-by-Layer-Processed All-Polymer Solar Cells with Enhanced Performance Enabled by Regulating the Microstructure of PYIT-OD Upper Layer

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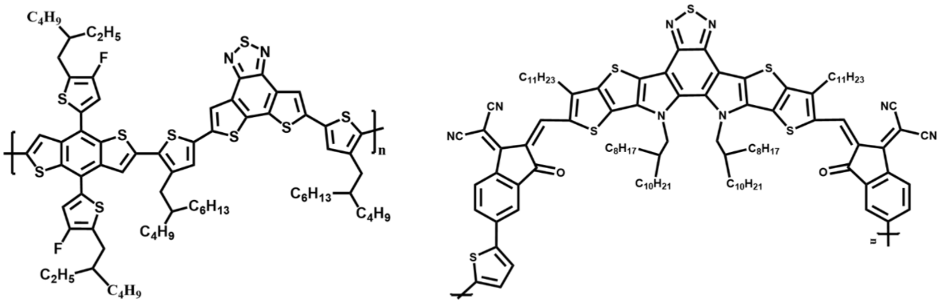
Experimental details

Materials: The D18 polymer and the non-fullerene polymer acceptor PYIT-OD were purchased from Derthon Optoelectronics Materials Science Technology Co. LTD. Other reagents and solvents were purchased from commercial sources (Sigma-Aldrich and TCI) and used without any further treatment.

Device Fabrication: The solution-processed layer-by-layer solar cells devices were fabricated with a conventional structure of Indium tin oxide (ITO)/PEDOT:PSS/D18/L PYIT-OD/PDIN/Ag and the fabrication details are as follows: ITO coated glass substrates were cleaned prior to device fabrication by sonication in acetone, detergent, distilled water, and isopropyl alcohol. After being treated with an oxygen plasma for 20 min, 40 nm thick poly(styrene sulfonate)-doped poly(ethylene-dioxythiophene) (PEDOT:PSS) (Bayer Baytron 4083) layer was spin-casted on the ITO-coated glass substrates at 3000 rpm for 30 s, the substrates were subsequently dried at 150 ℃ for 10 min in air and then transferred to a N_2-glovebox. The donor and acceptor were dissolved in chloroform (CF) with the concentration of 5 mg/ml and 7 mg/ml separately. The D18 solution was stir at 100°C for 30 minutes, followed by stirring at 40°C for 2 hours. After the D18 has completely dissolved in CF, spin-coat at a fixed temperature of 40°C on the prepared substrate with PEDOT:PSS. The PYIT-OD solution was stir at 60°C for 1 hour, then spin-coat at room temperature. The spin-coating conditions are 4000 rpm for 40 seconds. PDIN layer was deposited by spin casting from 2mg/ml solution in methanol. Finally, Ag (~90nm) was evaporated with a shadow mask as the top electrode. The effective area was measured to be 0.0516 cm^2.

Measurements and Instruments: UV-vis-NIR spectra of pure and blend films on a quartz substrate were recorded at room temperature (ca. 25°C) using a UV-3600 Plus UV-Vis-NIR spectrometer. Photoluminescence spectra were recorded on a Horiba Nanolog fluorescence spectrophotometer. PCEs were determined from *J-V* characteristics measured by a Keithley 2400 source-measurement unit under AM 1.5G spectrum from a solar simulator (Oriel model 91192). Solar simulator illumination intensity was determined using a monocrystal silicon reference cell (Hamamatsu S1133, with KG-5 visible color filter) calibrated by the National Renewable Energy Laboratory (NREL). External quantum efficiency (EQE) values of the encapsulated devices were measured by using an integrated system (Enlitech, Taiwan, China) and a lock-in amplifier with a current preamplifier under short-circuit conditions. The devices were illuminated by monochromatic light from a 75 W xenon lamp. The light intensity was determined by using a calibrated silicon photodiode. Steady-state photoluminescence and were performed using a Fluorolog 3 spectrofluorometer (HORIBA Instruments Incorporated). The Transient absorption (TA) spectra were collected by a home-built TA system described briefly as below. The fs laser out from an amplifier (800 nm, 1 KHz, Legend Elite F 1K HE+II, COHERENT) was used as the light source. The output from amplifier (800 nm) or the frequency doubled (400 nm) were employed as the pump light. For the pump light, pump "on" and "off" were regulated by a mechanical chopper (500 Hz, MC2000B-EC, THORLABS) in the pump beam. The supercontinuum white light generated by a 3 mm thick sapphire plate was used as the probe light, which was then collected by a spectrometer (300 nm-1100 nm, Omni-λ200i, Zolix). The delay between the probe light and the pump light is controlled by a mechanical delay stage. The atomic force microscopy (AFM) measurements of the surface morphology of D18 films were conducted on a Dimension Icon Scanning Probe Microscope system.



D18 **PYIT-OD**

Figure S1 Chemical structures of D18 and PYIT-OD.

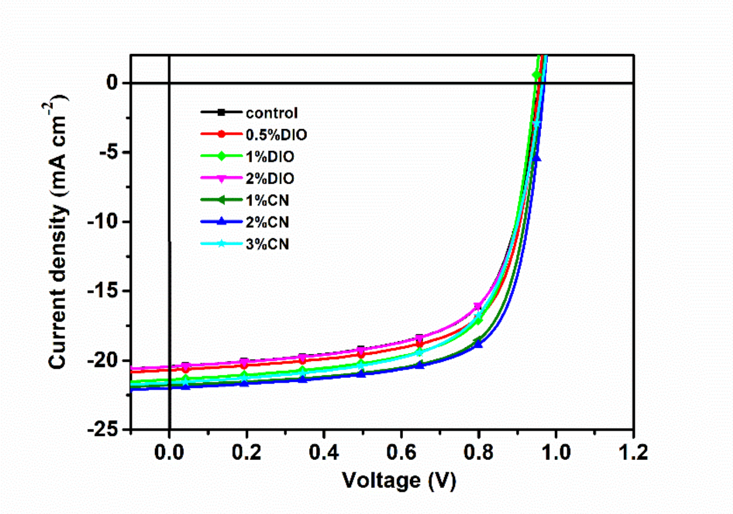


Figure S2 *J*-*V* curves of devices at different solvent additives concentration.

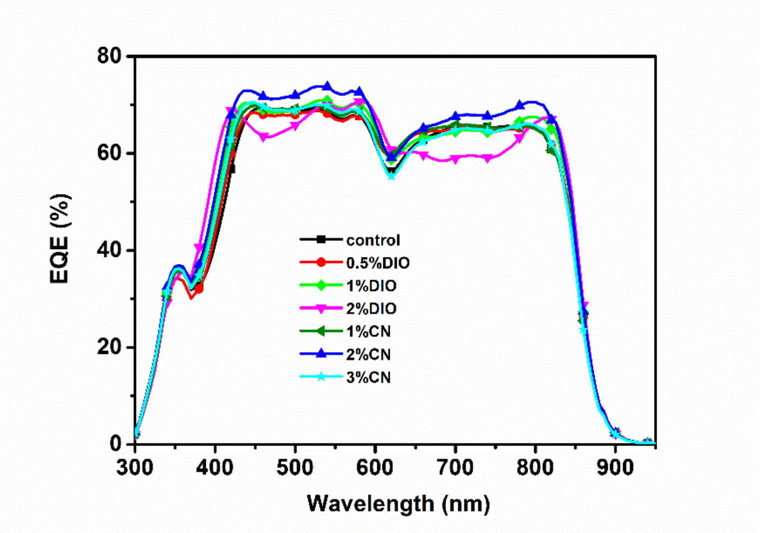


Figure S3 EQE curves of devices at different solvent additives concentration.

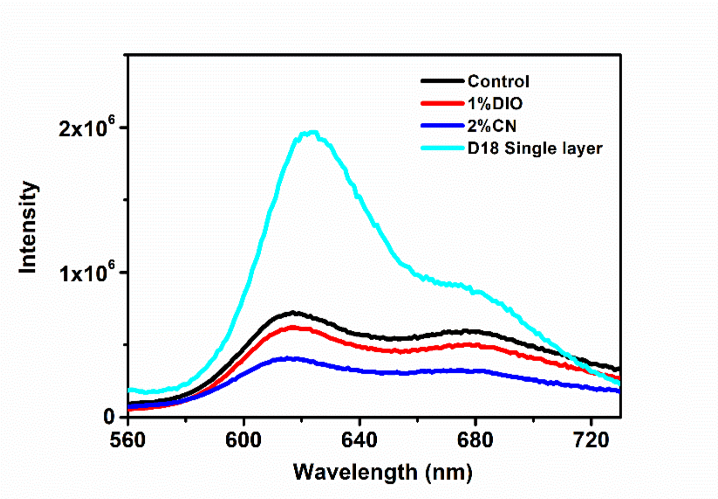


Figure S4 PL spectra of the pristine D18 film and the D18/PYIT-OD bilayer films.

Table S1 Photovoltaic parameters for D18/PYIT-OD-based all-PSCs

Condition	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF(%)	PCE(%)
Control	20.44	0.956	66.06	12.91
0.5%DIO	20.69	0.957	68.28	13.51
1%DIO	21.38	0.947	67.73	13.72
2%DIO	20.44	0.964	65.36	12.89
1%CN	21.78	0.963	70.55	14.80
2%CN	22.00	0.969	70.71	15.07
3%CN	21.59	0.965	65.01	13.54

Table S2 The parameters of exciton dissociation efficiency and G_{max} of devices obtained from different processing conditions

Devices	J_{ph}(mA cm^{-2})	J_{sat} (mA cm^{-2})	η_{diss}(%)	G_{max}(10^{28} m^{-3} s^{-1})
Control	5	23.12	89.3	
1% DIO	8	23.40	91.4	
2% CN	7	24.20	94.9	

Table S3 Summary of the fitting data for hole-only and electron-only devices.

Devices	μ_h (cm^2 V^{-1} s^{-1})	μ_e (cm^2 V^{-1} s^{-1})	μ_h/μ_e
Control		4.63	
1% DIO		6.93	
2% CN		8.18	