Supporting Information

Exquisite Modulation of Electron Transporting Layer for High-Performance Fullerene-Free Organic Solar Cell with Inverted Structure

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Experimental Section

Materials. PBDB-TF, IT-4F and PFN-Br were purchased from Solarmer Material Inc.

Zinc acetate, dihydrate, potassium hydroxide and molybdenum trioxide (MoO₃) were

purchased from Alfa Aesar. All these solvents used here were commercially available

from Acros.

Device fabrication and characterization.

Preparation of the ZnO Nanoparticles (ZnO NPs): Zinc acetate dihydrate (13.5 mmol) was dissolved in methanol (125 mL) at 65°C. Then the solution of KOH in methanol (dissolving 23 mmol KOH in 65 mL methanol), was added into the zinc acetate dihydrate solution in 10 minutes. After 2h and 15 minutes stir, the synthesis was stopped, remaining the reaction flask stand for 2h. The white precipitate was separated

and rinsed with methanol at least twice to remove the reaction residues. Finally, the ZnO NPs were added into methanol, and stabilized by 2-methoxyethanol. PFN-Br was added in methanol with a concentration of 0.5 mg/ml. The solution was stable for a few months. The PFN-Br solution was condensed to 1 mg/mL to be mixed with ZnO emulsion. The ZnO:PFN-Br ETL solutions with different ratio were prepared by mixing ZnO emulsion and 1 mg/mL PFN-Br solution with different volume ratio. The PBDB-TF:IT-4F (wt/wt, 1:1) was dissolved in chlorobenzene (CB) with a concentration of 10 mg/ml with respect to the polymer. The solution was stirred at 25°C for at least 3 hours. 0.5 % 1,8-diiodooctane (DIO) (v/v, DIO/CB) was added 30 minutes prior to the spin coating process.

Device fabrication: Indium-tin-oxide (ITO) (12 Ω/\Box) substrates were sequentially cleaned with detergent, deionized (*DI*) water, acetone and isopropanol by sonication. The dried ITO substrates were treated with *UV*-ozone for 15 minutes, and then the solution of ETLs were spin-coated on top of ITO. Rotation speed can be tuned to change the thickness of ETLs. After spin coating, the ETL coated ITO substrates were transferred into N₂ glove box. Then the BHJ solution was spin-coated, followed by 100°C annealing for 10 minutes. After that, 10nm MoO₃ and 100 nm of Al cathode was thermally evaporated under high vacuum (ca. 3×10^{-4} Pa). The device area, as defined by the aperture area on mask, was 1.938 mm².

Characterization: *J-V* characteristics of solar cells were recorded with a Keithley 2400 Precision Source/Measure unit under standard AM 1.5G (100 mW/cm²) solar irradiation sourced by a XES-70S1 solar simulator (SANYOU Electric Co., Ltd., AAA grade, 70 mm×70 mm photo-beam size). A 20 mm ×20 mm single-crystal Si diode was used to calibrate the irradiation intensity from solar simulator. EQE spectra were measured by a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech, Taiwan). The light intensity at each wavelength was calibrated with a single-crystal Si photovoltaic cell. The UV-visible absorption spectroscopy were measured by a Perkin Elmer General TU-1901 UV-vis spectrophotometer. The UPS measurements were performed on the Bruker ESCALAB250Xi system. Contact angle characterization was performed on DSA100, Kruss. XRD analysis was carried on Rigaku MiniFlex 600. AFM was carried on Bruker MultiMode 8-HR. GIWAXS measurements were performed by using a XEUSS SAXS/WAXS system. Samples were prepared on Si substrates using blend solutions identical to those devices used. The wavelength of the X-ray beam is 1.54 Å, and the incident angle was 0.2°. Scattered X-rays were detected by using a Dectris Pilatus 300 K photon counting detector.



Figure S1. V_{OC} s and FFs of devices with varies BHJ materials fabricated in our preliminary experiments. The figure shows that without using our new-developed method, the V_{OC} and FF of inverted devices are all lower than normal devices.



Figure S2. SCLC plot of devices with structures of a) ITO/MoO₃/BHJ/MoO₃/Au and b) ITO/ZnO/BHJ/ZnO/Al. After spin coated on the studied ETLs with varies γ_{s} , the BHJs are prepared by ladlinh out the floating BHJ films in methonal: 2-methoxyethanol and put them on the ITO/MoO₃ or ITO/ZnO substrates to test SCLC curves.



Figure S3. AFM topological images of BHJs coated on ITO/ZnO:PFN-Br (a) and ITO/ZnO (b).

Table S1. Device parameters extracted from <i>J-V</i> characteristics of in Figure 4h.						
ETLs	$V_{\rm OC}$ [V]	$J_{\rm SC} [{ m mA/cm^2}]$	FF [%]	PCE [%]		
Device with fresh ZnO	0.85	20.13	73.42	12.56		
Device with fresh ZnO:PFN-Br	0.87	20.16	78.79	13.82		
Device with aged ZnO	0.58	18.57	42.99	4.63		
Device with aged ZnO:PFN-Br	0.87	20.14	78.09	13.68		



Figure S4. *J-V* curves of devices with different ETLs. The legends are the ratios of

ZnO/PFN-Br.

ratios of ZnO/PFN-Br	V _{oc} (V)	$J_{\rm sc}$ (mA/cm ²)	FF (%)	PCE (%)
100:0	0.85	20.13	73.42	12.56
97:3	0.87	20.03	77.30	13.47
90:10	0.87	20.16	78.79	13.82
70:30	0.83	19.40	68.81	11.08
0:100	0.72	17.05	40.73	5.00

 Table S2 Summary of device performance in Figure S4.