

## Electronic Supplementary Information

### Effect of conjugated polymer electrolyte with diverse acid derivatives as the cathode buffer layer on the photovoltaic properties

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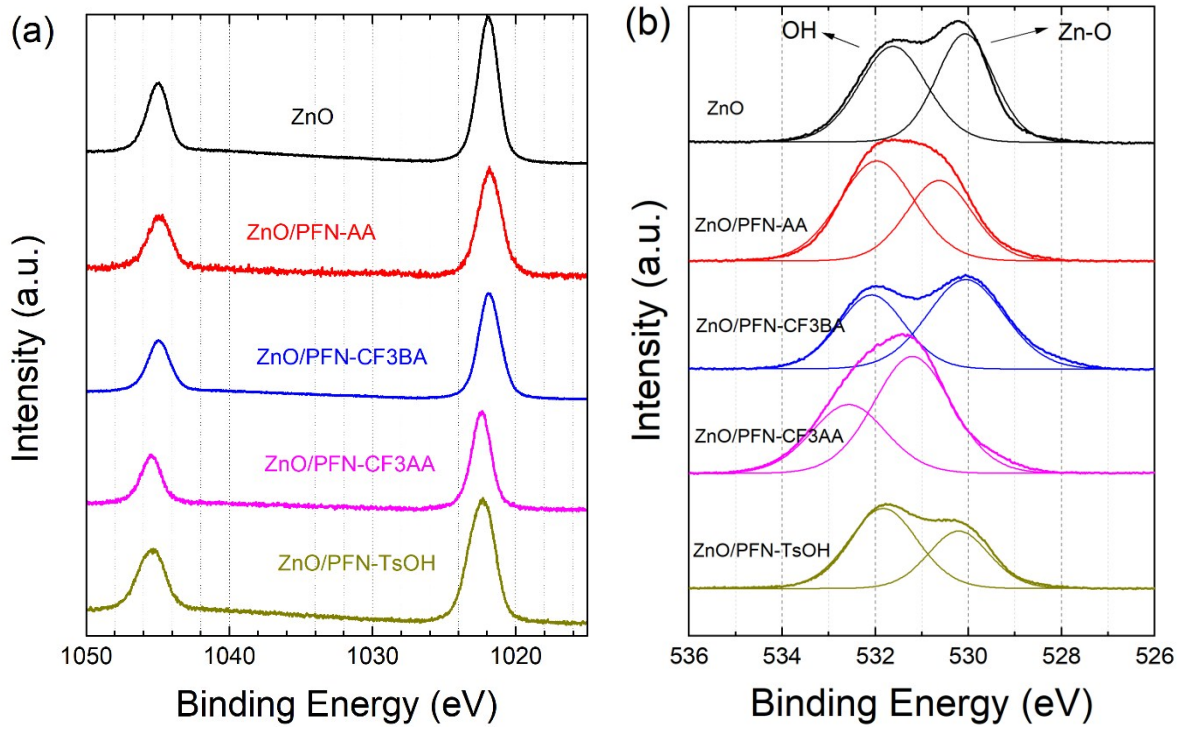
### Experimental

**Measurements.** The thickness of the ZnO and the active layer were measured using an Alpha-Step IQ surface profiler (KLA-Tencor Co.). X-ray photoelectron spectroscopy (XPS) is recorded using Al K $\alpha$  X-ray line (15 kV, 300 W) (Thermo Electron Co., MultiLab 2000). Atomic force microscopy (AFM) images were captured using a Bruker (NanoScope V) AFM in the tapping mode. The water contact angles of the substrates were measured using KRUSS Model DSA 100. Kelvin probe microscopy (KPM) measurements (KP technology Ltd. Model KP020) were performed on the ZnO layers, with and without **V-OH**, and the work function of the samples was estimated by measuring the contact potential difference between the sample and the KPM tip at ambient condition. The KPM tip was calibrated against a standard reference gold surface, with a work function of 5.1 eV. The

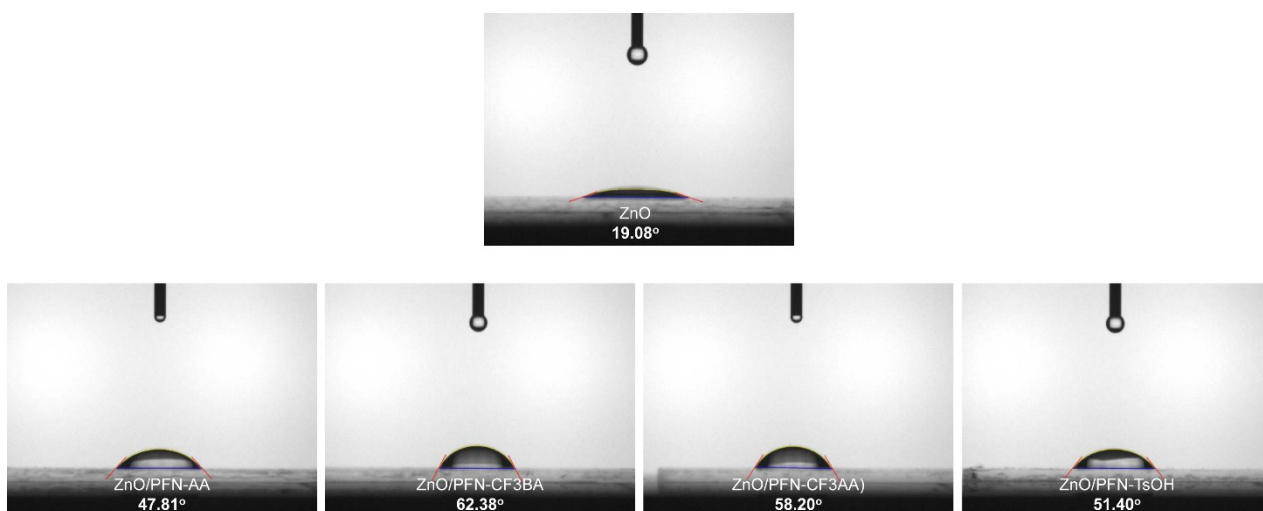
current density-voltage measurements were performed under simulated light (AM 1.5G, 1.0 sun condition, Peccell Technology, Model PEC-L01) from a 150 W Xe lamp, using a KEITHLEY Model 2400 source-measure unit. A calibrated Si reference cell with a KG5 filter certified by National Institute of Advanced Industrial Science and Technology was used to confirm 1.0 sun condition. Non-modulated impedance spectroscopy was performed using an impedance analyzer (WonATech., Zcon™ Impedance Monitor). A 50 mV voltage perturbation was applied over a constant applied bias, 0 ~ 1.0 V, in the frequency range between 1 Hz and 1.0 MHz under the dark condition with the device for a current density - voltage (J-V) characteristics. The incident photon-to-electron conversion efficiency (IPCE) spectra were measured by a 150 W Xe lamp (Abet Technology Model LS150), monochromator (Oriel Cornerstone 130 1/8 m), and source-measure unit (KEITHLEY Model 2400). All the measurements were performed at room temperature under ambient atmosphere.

**Fabrication of PSCs.** To fabricate the inverted type organic photovoltaic (OPV) with the device structure: [ITO/ZnO (25 nm) with or without PFN + acid derivative/active layer (PTB7-Th:PC<sub>71</sub>BM, 70 nm)/MoO<sub>3</sub> (3 nm)/Ag (100 nm)], a ZnO layer was deposited on an ITO substrate by the sol-gel process. Zinc acetate dihydrate (0.1 g) and 0.025 mL of ethanolamine were dissolved in 1 mL of methoxyethanol and stirred for 12 hours at 60 °C. A thin film of ZnO sol-gel precursor was spin coated at 4000 rpm for 60 s then cured at 200 °C for 10 min. The active layer was spin-cast from a mixture of PTB7-Th and PC<sub>71</sub>BM (obtained by dissolving 10 mg of PTB7-Th and 15 mg of PC<sub>71</sub>BM in 1 mL of chlorobenzene with 3% (v/v) 1,8-diiodooctane (DIO)) and rotated at 1800 rpm for 120 s. The active solution was filtered through a 0.45 μm membrane filter before spin coating. Successive layers of MoO<sub>3</sub> and Ag were thermally evaporated through a shadow mask, with a device area of 0.09 cm<sup>2</sup> at 2 x 10<sup>-6</sup> Torr.

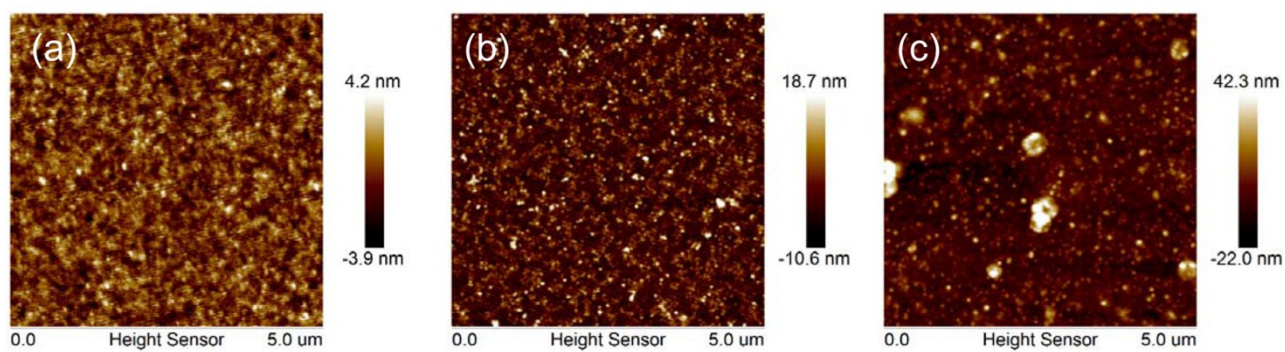
**Fabrication of electron-only devices.** Electron-only devices with the structure: [ITO/ZnO (25 nm) with or without PFN + acid derivative/PC<sub>71</sub>BM (60 nm)Al (100 nm)], have been fabricated to investigate the electron mobility.



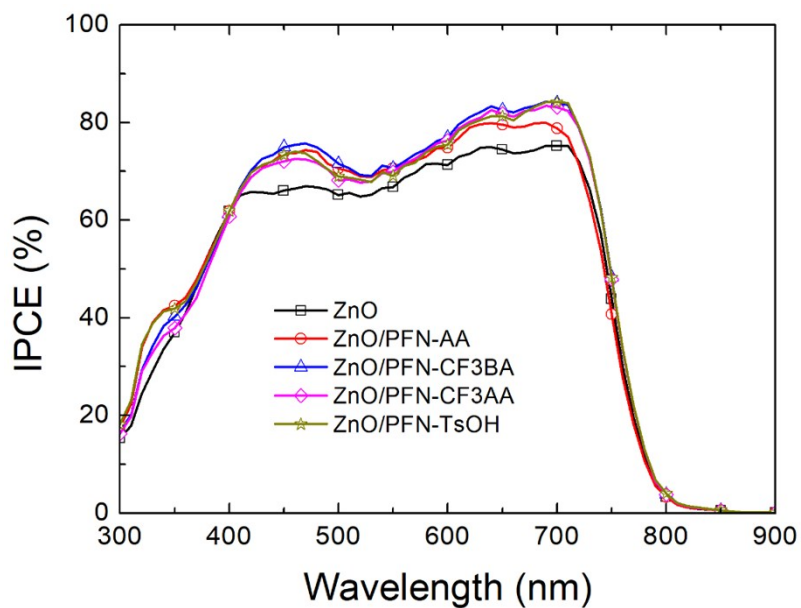
**Figure S1.** (a) Zn 2p and (b) O 1s spectra of ZnO and PFN-acids coated ZnO.



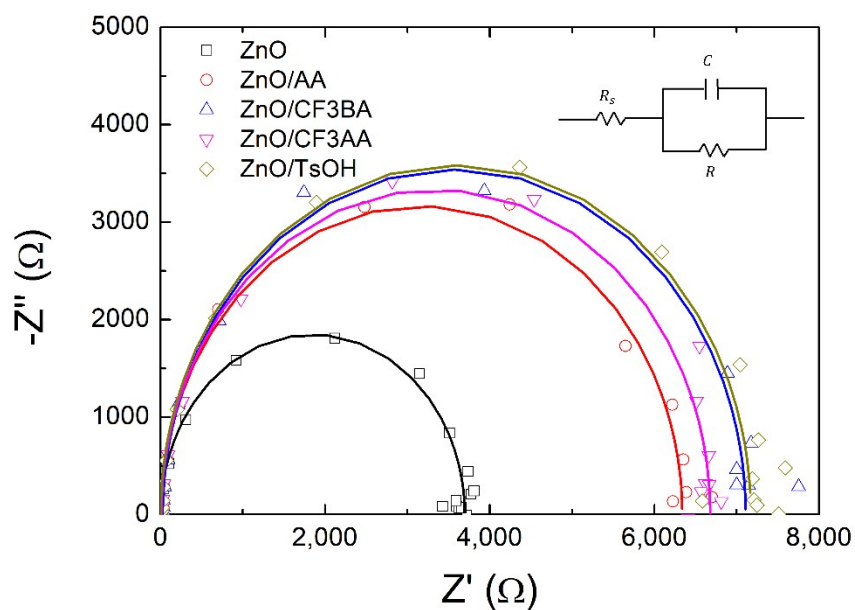
**Figure S2.** This static water contact angle of ZnO and ZnO/PFN-diverse acid.



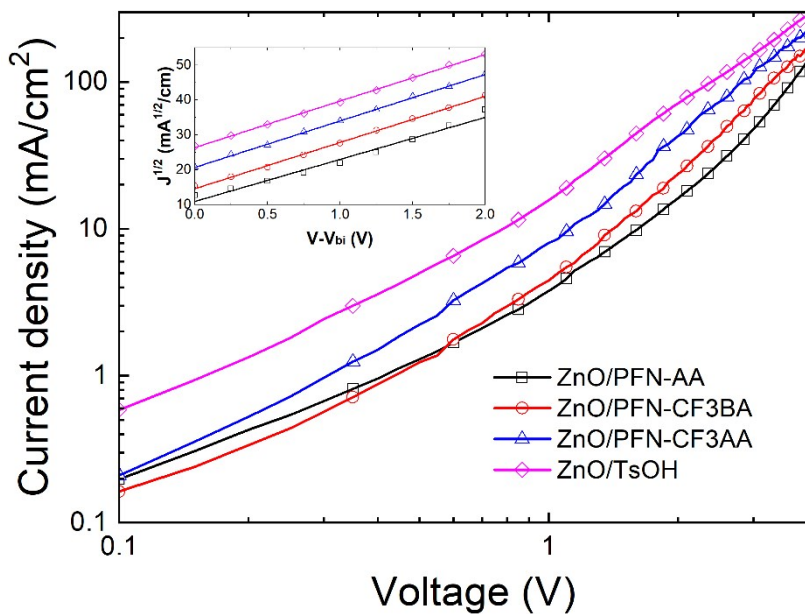
**Figure S3.** AFM images of (a) pristine ZnO, (b) ZnO/PFN with 1.0 eq of CF<sub>3</sub>AA, and (c) ZnO/PFN with 6.0 eq of CF<sub>3</sub>AA.



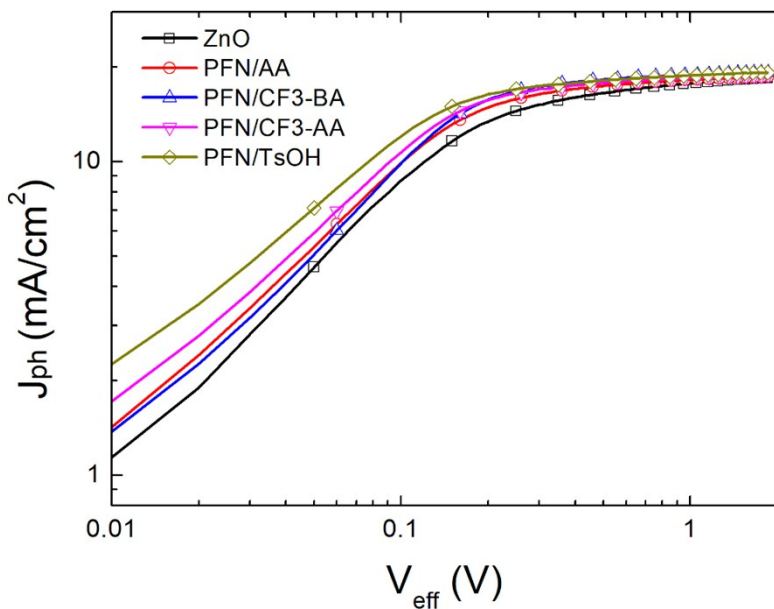
**Figure S4.** Incident photon-to-current efficiency (IPCE) spectra of the PSCs.



**Figure S5.** EIS spectra at 0 V under 1.0 sun condition, inset shows the equivalent circuit for analysis of EIS spectra ( $R_s$ : Ohmic resistance including the electrodes and bulk resistance,  $R$ : resistance associated with the interface charge transport,  $C$ : capacitance).



**Figure S6.** Current density–voltage curves of electron-only device with a configuration of ITO/ZnO (25 nm)/PFN with 1.0 eq. of AA, CF3BA, CF3AA, and TsOH /PC<sub>71</sub>BM (60 nm)/Al (100 nm). (inset: with fitted line,  $V$ : applied voltage,  $V_{bi}$ : built-in voltage).



**Figure S7.** Photo-generated current density ( $J_{ph}$ ) vs. effective voltage ( $V_{eff}$ ) plots of the PSCs.