## Supporting Information

## A Water-Soluble Metallophthalocyanine Derivative as Cathode Interlayer for Highly Efficient Polymer Solar Cells

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Space charge limited current (SCLC) measurements of electron-only devices In order to obtain the electron mobility in the polymer solar cells, we carried out SCLC measurements of electron-only devices, which Device are V(ITO/Al/PTB7:PC<sub>71</sub>BM/Al), **Device** VI (ITO/Al/PTB7:P<sub>71</sub>CBM/0.6% acetic acid/Al), Device **VII**(ITO/Al/PTB7:PC<sub>71</sub>BM/PFN/Al) and Device VIII(ITO/Al/PTB7:PC<sub>71</sub>BM/VOPc(OPyCH<sub>3</sub>I)<sub>8</sub>/Al). The electron mobility can be measured in the SCLC regime as described by

$$J=9\varepsilon_0\varepsilon_r\mu V^2/8L^3,$$
 (1)

where  $\varepsilon_0$  is the permittivity of free space (8.8542×10<sup>-12</sup> F/m),  $\varepsilon_r$  is the dielectric constant of the active layer,  $\mu_e$  is the electron mobility, V is the voltage drop across the device, L is the active layer thickness. The above equation holds if the mobility is field independent.  $\varepsilon_r$  is assumed to be 3.9 and L is 120nm in our analysis. Figure S1 presents our J<sup>0.5</sup>-V analysis for the four electron-only devices (**Devices V-VIII**), where V<sub>r</sub> (the voltage drop due to contact resistance and series resistance across the electrodes) and V<sub>bi</sub> (the built-in voltage due to the difference in work function of the two electrodes at both sides of active layer) are subtracted from experimental applied voltage. The contact resistance and series resistance related with V<sub>r</sub> was measured in the reference devices without active layer. For **Devices V** and **VI**, the reference device is ITO/Al/Al and the obtained resistance is 15  $\Omega$ . For **Device VII**, the reference device is ITO/Al/PFN/Al and the resistance is 14.4  $\Omega$ . For **Device VIII**, the reference device is ITO/Al/VOPc(OPyCH<sub>3</sub>I)<sub>8</sub>/Al and the resistance is 40.3  $\Omega$ . The V<sub>bi</sub> was deduced from the best fit of the J<sup>0.5</sup> versus V<sub>appl</sub> plot at voltages above 1.1 V to Eq. (1) as summarized in **Table S1**. A straight line going through the origin of  $J^{0.5}$ -V curves for the four devices signifies that the mobility is field independent at field up to 2×10<sup>5</sup> V/cm. The field independent mobilities calculated from Eq. (1) are 2.7×10<sup>-5</sup> cm<sup>2</sup>/V s for **Device V**, 3.6×10<sup>-5</sup> cm<sup>2</sup>/V s for **Device VI**, 4.6×10<sup>-4</sup> cm<sup>2</sup>/V s for **Device VII** and 7.1×10<sup>-4</sup> cm<sup>2</sup>/V s for **Device VIII**presented in **Table S1**.For comparison, we also fabricated other four electro only devices (**Devices V<sub>R</sub>**, **VI<sub>R</sub>**, **VII<sub>R</sub>**, **VIII<sub>R</sub>**) with the active layer of 170 nm, parameters of which are as well shown in **Table S1**.



Figure S1.  $J^{0.5}$  vs.  $V_{appl}$ - $V_{bi}$ - $V_r$  plots for the electron-only devices with VOPc(OPyCH\_3I)\_8 (black line), PFN (red line) as a cathode interlayer, and with (magenta line) and without (blue line) 0.6% acetic acid treatment at the surface of active layer.

Electron-only	Resistance related with Vr	$V_{bi}$	mobility
device	$(\Omega)$	(V)	$(cm^2/V s)$
V (120 nm)	15	0.32	2.7×10 <sup>-5</sup>
VI (120 nm)	15	0.25	3.6×10 <sup>-5</sup>
VII (120 nm)	14.4	0.51	4.6×10 <sup>-4</sup>
VIII (120 nm)	40.3	0.48	7.1×10-4
V <sub>R</sub> (170 nm)	15	0.32	1.3×10 <sup>-5</sup>
VI <sub>R</sub> (170 nm)	15	0.25	2.4×10 <sup>-5</sup>
VII <sub>R</sub> (170 nm)	14.4	0.51	1.7×10 <sup>-4</sup>
VIII <sub>R</sub> (170 nm)	40.3	0.48	3.3×10 <sup>-4</sup>

 Table S1. Mobility and related parameters for the electron-only devices.



**Figure S2**.  $J^{0.5}$  vs.  $V_{appl}-V_{bi}-V_r$  plots for the hole-only devices with VOPc(OPyCH<sub>3</sub>I)<sub>8</sub> (black squares and line), PFN (red circles and line) and 0.6% acetic acid treatments (magenta up triangles and line) at the surface of active layer, and without any treatment at the at the surface of active layer (blue down triangles and line).