

## Supporting Information

Highly Efficient Fullerene/Perovskite Planar Heterojunction Solar Cells via Cathode Modification with an Amino-Functionalized Polymer Interlayer

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### Experimental section

#### Synthetic procedures for PN4N

Synthesis of 1,2-bis(2-(4-bromophenoxy)ethoxy)ethane (M1):

4-bromobenzaldehyde(3.79g, 20.5 mmol) and N1,N1'-(ethane-1,2-diyl)diethane-1,2-diamine (1.456g, 10 mmol) were loaded on a 50 mL flask and stirred for 45 min. The 4-bromobenzaldehyde should be completely transformed (indicated by TLC) and then the reactant was cooled to 0°C with an ice bath, 1.15g of sodium borohydride (30 mmol) in 16 mL of methanol was added into the reactant dropwisely in 10 min. The reactant was finally left to stir at ambient temperature for 6 hours. The reactant was poured into 20 ml of chloroform and the organic phase was separated. The aqueous layer was extracted with chloroform for several times. All the organic phases were collected and the solvent was removed. The crude product was redissolved with several milliliter ethanol. The hydrochloride salts of the product would be precipitated by adding several milliliter hydrochloride (3M), the salt was then recrystallized with deionized water for two times. The final pure M1 was obtained by alkalizing its hydrochloride salts with several milliliter of sodium hydroxide (1M). 2.4g of M1 (4.97 mmol, 49.7%) was obtained as pale yellow oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ(ppm): 7.42-7.38(d,4H), 7.18-7.14(d,4H), 3.67(s,4H), 2.68-2.66(m, 12H). <sup>13</sup>C(75MHz, CDCl<sub>3</sub>), δ(ppm): 139.45, 131.40, 129.80, 120.63, 53.22, 49.34, 48.79. MS (APCI, +MS): m/z =485.3.

M2 was synthesized according to the reported procedure.<sup>41</sup>

Polymer PN4N were prepared via Suzuki coupling reaction from monomer M1 and M2 with the existence of palladium catalyst. 241 mg (0.5 mmol) M1 and 246 mg (0.5 mmol) M2 were added into a mixture of 4 mL of toluene and 2 mL of 2M Na<sub>2</sub>CO<sub>3</sub> aqueous solution in the protection of argon flow. And then 5 mg of Pd(PPh<sub>3</sub>)<sub>4</sub> was added, followed by heating up to 95°C for 48 h. Thus the reaction was finished and the product was precipitated in mixture of hexane and acetic ether(3:1), the crude product was then redissolved in THF/CHCl<sub>3</sub> and extracted with de-ionized water for several times. The organic layer was finally solution was filtered with a 0.45 μm PTFE filter, concentrated and reprecipitated in a mixture of hexane and acetic ether (3:1). The resulting polymers were collected and dried under vacuum for 24h, yielding 230 mg product, (yield =62%). Mw=31k.

#### Materials:

Methylammonium iodide (CH<sub>3</sub>NH<sub>3</sub>I) was synthesized according to the reported procedure.<sup>8</sup> To prepare the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>x</sub>Cl<sub>3-x</sub>, CH<sub>3</sub>NH<sub>3</sub>I and PbI<sub>2</sub>, PbCl<sub>2</sub> (Alfa Aesar) were mixed in DMF to form a solution at 60°C overnight while being stirred in a glovebox with moisture and oxygen levels <1ppm. [6,6]-Phenyl-C61-butyric acid methyl easter (PC61BM, Nano-C®) was dissolved in chlorobenzene (CB, Sigma-Aldrich).

## Device fabrication and characterization:

The patterned ITO-coated glass was cleaned by sonication in detergent, deionized water, acetone and isopropyl alcohol subsequently and then dried under 80°C in baking oven, followed by an oxygen plasma treatment for 4 min. A 30 nm thick poly(3,4-ethylenedioxythiophene) : poly(styrene sulfonate) (PEDOT:PSS, Clevios™ P VP AI 4083) was spun cast onto the ITO substrate and then dried at 120°C for 20 min. We adopted a modified precursor solution formula employing ternary mixture of CH<sub>3</sub>NH<sub>3</sub>I, PbI<sub>2</sub> and PbCl<sub>2</sub> (molar ratio 4:1:1) at a total concentration of 40wt%. The perovskite precursor solution was then spuncast on the PEDOT:PSS layer resulted in a composite film with nominal thickness of ~ 450 nm. The film was then further annealed at 100°C for 1h to promote crystallization of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>x</sub>Cl<sub>3-x</sub> perovskite. An 80 nm-thick PC<sub>61</sub>BM was then spuncast onto the perovskite layer from chlorobenzene followed by the spuncast of PFN or PN4N from MeOH or IPA with a concentration of 0.2mg/ml at a spin rate of 2000 rpm, respectively. The thickness of the PN4N layer was tuned by varying the concentration from 0.2mg/ml to 1mg/ml. Finally, 100 nm of aluminum was thermally evaporated onto the substrates through a shadow mask at a base pressure of 1×10<sup>-6</sup> mbar to complete the devices. The overlapping area between the cathode and anode defined the device area of 0.16 cm<sup>2</sup>.

Current density-voltage (*J-V*) characteristics for the devices were measured under 100 mW cm<sup>-2</sup> air mass 1.5 global (AM 1.5 G) illumination with a solar simulator (Oriel model 91192). The light intensity was calibrated using a National Renewable Energy Laboratory (NREL) calibrated silicon photodiode with a KG5 filter. UV-vis absorption and photoluminescence spectra were recorded on a HP 8453 spectrophotometer and FLS920 spectrofluorimeter (Edinburgh), respectively. The SEM images were obtained using a Zeiss EVO 18 scanning electron microscopy. The crystal structure of perovskite films was investigated with an X-ray diffractometer (PANalytical X'pert PRO) equipped with a Cu-K $\alpha$  X-ray tube. With a scan angle of 1° and a step size of 0.04° as well as a time step of 3 s, we carried out the acquisition in the range of 10–60° in  $\theta$ -2 $\theta$  mode.

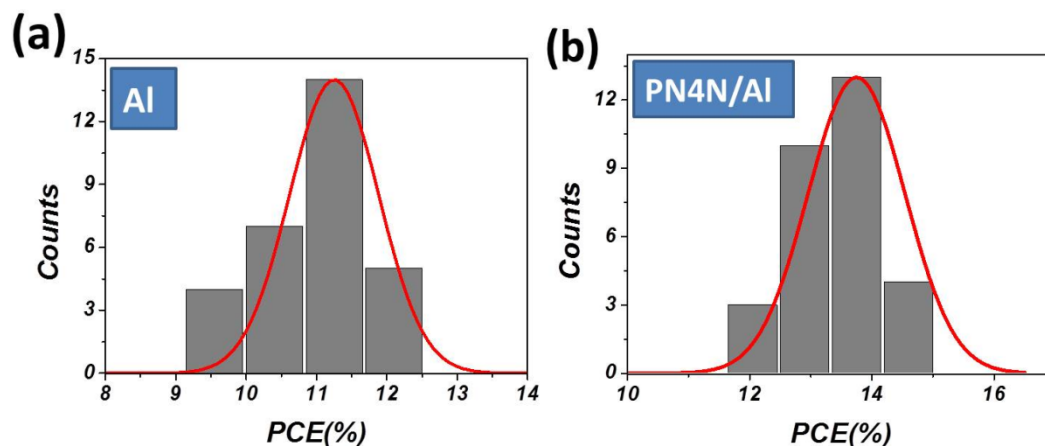


Figure S1. Histogram of the perovskite solar cell efficiencies with (a) Al cathode and (b) PN4N/Al bilayer cathode.

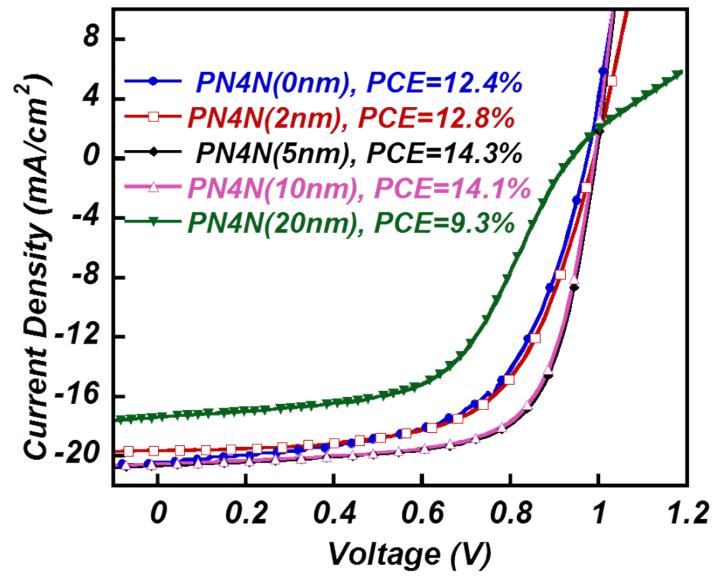


Figure S2. Photocurrents and efficiencies for perovskite solar cells with PN4N interlayer of different thicknesses.

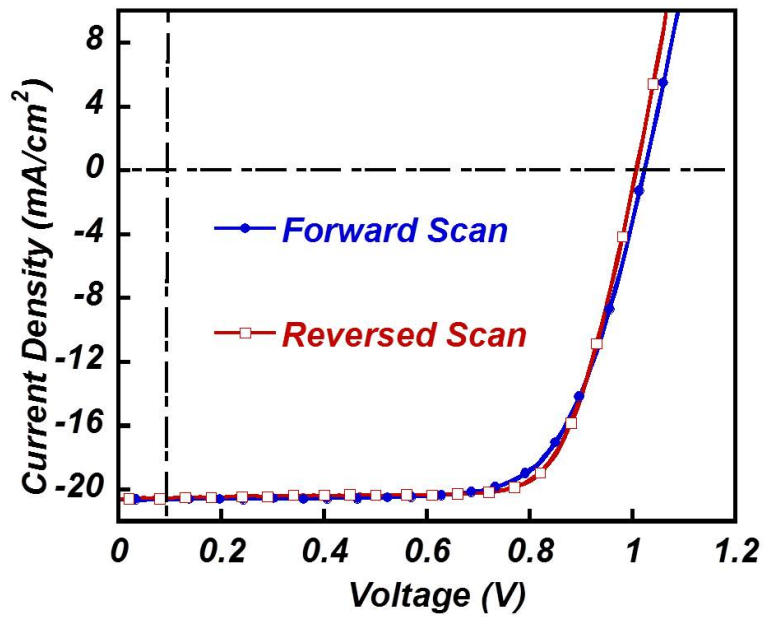


Figure S3. Photocurrents of a high performance perovskite device measured with different sweep directions.

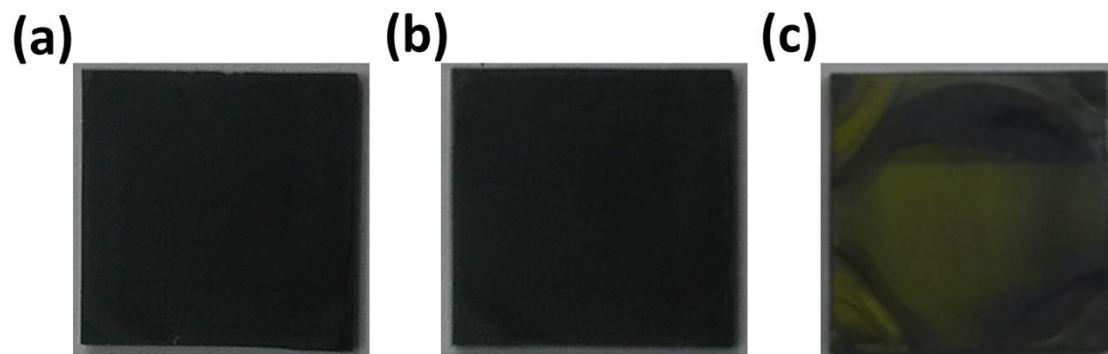


Figure S4. Photographs of (a) perovskite/PC<sub>61</sub>BM film; (b) perovskite/PC<sub>61</sub>BM film after spin coating PFN immediately after casting the solution and (c) perovskite/PC<sub>61</sub>BM film after allowing the PFN solution to stay on the surface for 60s before spincoating.

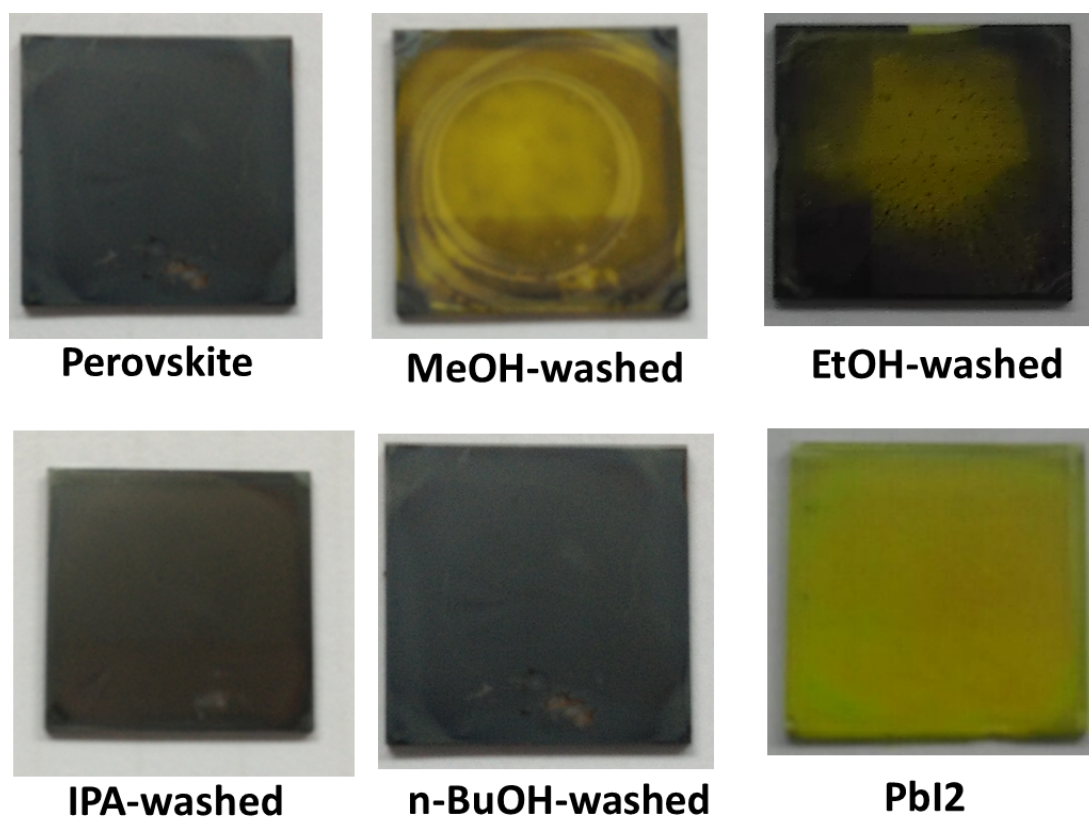


Figure S5. Photographs of pristine perovskite film and perovskite films after washed by spincoating of different alcoholic solvents. A PbI<sub>2</sub> film is shown for comparison.