Supporting Information

Interface Engineering of Perovskite Hybrid Solar Cells with solution-processed Perylene-Diimide Heterojunctions toward High Performance

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Experimental Section

Materials and preparation of perovskite

The molecular structure of PDINO is shown in Figure 1b, and its synthesis and characterization was reported elsewhere.[1] PCBM, lead chloride ($PbCl_2$) and anhydrous *N*, *N*-dimethylformamide (DMF) were purchased from Sigma-Aldrich and used without further purification. Methyl ammonium iodide (CH_3NH_3I) and the precursor solution of ammonium lead iodide ($CH_3NH_3PbI_{3-X}Cl_X$) were prepared as previously reported.[2] To prepare the perovskite precursor solution, CH_3NH_3I and $PbCl_2$ powder were mixed in anhydrous DMF with a molar ratio of 3:1. The solutions (25%) were stirred at 60 °C for 3 h inside a glovebox filled with nitrogen gas and filtered with 0.2 μm PEFT filters before device fabrication.

Fabrication of perovskite solar cells

The devices were fabricated in the configuration of indium tin oxide (ITO)/PEDOT:PSS/$CH_3NH_3PbI_{3-X}Cl_X$/PCBM/EELs/Ag. Pre-structured ITO coated glass substrates were subsequently cleaned in acetone and isopropyl alcohol for 10 min each. After drying, the substrates were coated via doctor blading with 40 nm PEDOT:PSS (Heraeus, Clevios P VP.Al 4083). To avoid oxygen and moisture, the substrates were transferred into a N_2-filled glovebox, where the perovskite layers (ca. 150 nm) were spin-coated from a homogeneous 25 wt% $CH_3NH_3PbI_{3-X}Cl_X$ precursor solution at 2k rpm for 45 s. After that, the samples were gradient annealed from room temperature to 110 °C using 40 min, and then further annealed at 110 °C for 40min. Afterward, the PCBM (20 mg mL^{-1} in chlorobenzene) and PDINO (1 mg mL^{-1} in methanol) were then sequentially deposited by spin coating at 1k rpm for 30 s and 1k rpm for 45s, respectively. In addition, the ZnO (nanoparticle suspensions, provided by NanoGrade, Lot#5039) was deposited on top of PCBM by spin coating at 2k rpm for 45 s. Finally, 100 nm Ag was deposited sequentially under 6×10^{-6} Torr by thermal evaporation through a shadow mask to form an active area of 10.4 mm^2. The configuration for the various cathodes is illustrated in Figure 1a. The current-voltage characteristics of the solar cells were measured under AM 1.5G irradiation on an OrielSol1A Solar simulator (100 mW cm^{-2}). The light source was calibrated by using a silicon reference cell. Most of device performances mentioned in this paper are corrected to the EQE of the particular device. The EQE was measured with a Cary 500 Scan UV–Vis–NIR Spectrophotometer under mono-chromatic illumination, which was calibrated with a mono-crystalline silicon diode. The thickness of the PDINO layer was determined by a Profilometer (Ambios Tech. XP-2) in combination with extrapolation from an absorbance-thickness curve that assumed a linear dependence on film thickness of the PDINO absorption feature at 480 nm. The other layers were determined by a tencor profilometer. The tapping-mode AFM images were obtained by using a Veeco Model D3100. The cross-section was prepared using a focused ion beam (FIB, FEI Helios NanoLab 660) and subsequently imaged with the electron beam of the same instrument.

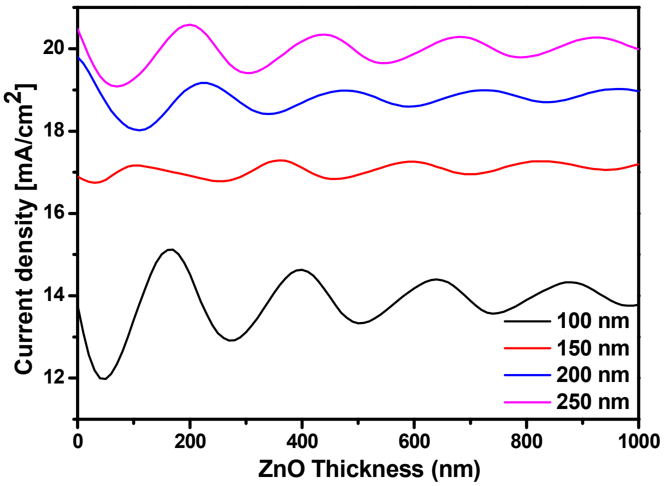

Figure S1. The optical calculated short circuit current of devices with various perovskite layer thicknesses as a function of the ZnO layer thickness.

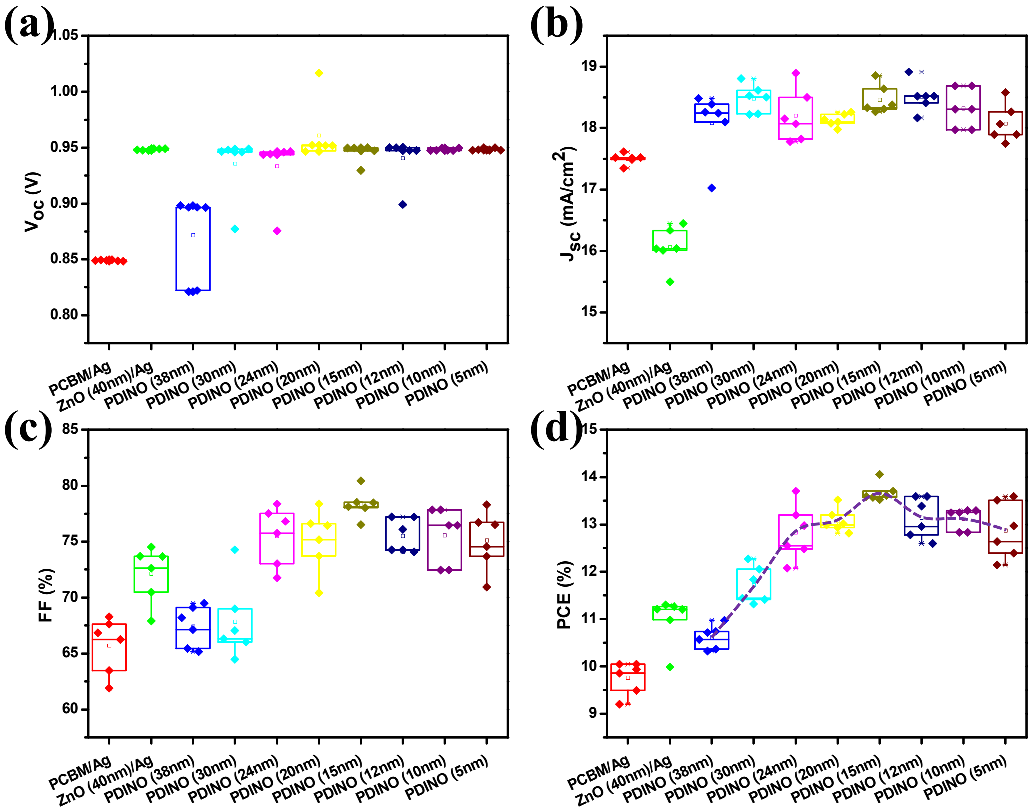

Figure S2. The ranges of (a) J_{sc}, (b) V_{oc}, (c) FF and (d) PCE of conventional pero-HSCs with ZnO layer and various thick PDINO layers from six cells. The open square inside the box denotes the mean value.

Table S1. The photovoltaic parameters of conventional pero-HSCs with ZnO layer and various thick PDINO layers.

Cathode	Thickness of interface layer	V_{oc} [V]	J_{sc} [mAcm^{-2}]	FF [%]	PCE^{a} [%]	PCE^{b} [%]
Ag		0.85	17.5	67.6	10.0	9.8
ZnO/Ag	40 nm	0.95	16.0	74.5	11.3	11.0
PDINO/Ag	38 nm	0.90	18.2	67.1	11.0	10.6
PDINO/Ag	30 nm	0.95	18.8	69.0	12.3	11.7
PDINO/Ag	24 nm	0.94	18.9	76.8	13.6	12.8
PDINO/Ag	20 nm	0.95	18.2	78.4	13.6	13.1
PDINO/Ag	15 nm	0.95	18.8	78.5	14.0	13.7
PDINO/Ag	12 nm	0.95	18.3	77.2	13.4	12.7
PDINO/Ag	10 nm	0.95	18.3	76.4	13.3	13.1
PDINO/Ag	5 nm	0.95	18.2	78.3	13.5	12.9

[a] The highest PCEs of conventional pero-HSCs with ZnO layer and various thick PDINO layers measured under illumination of an AM 1.5G solar simulator (100 mW/cm^2); [b] The average PCEs of pero-HSCs corresponding to (a).

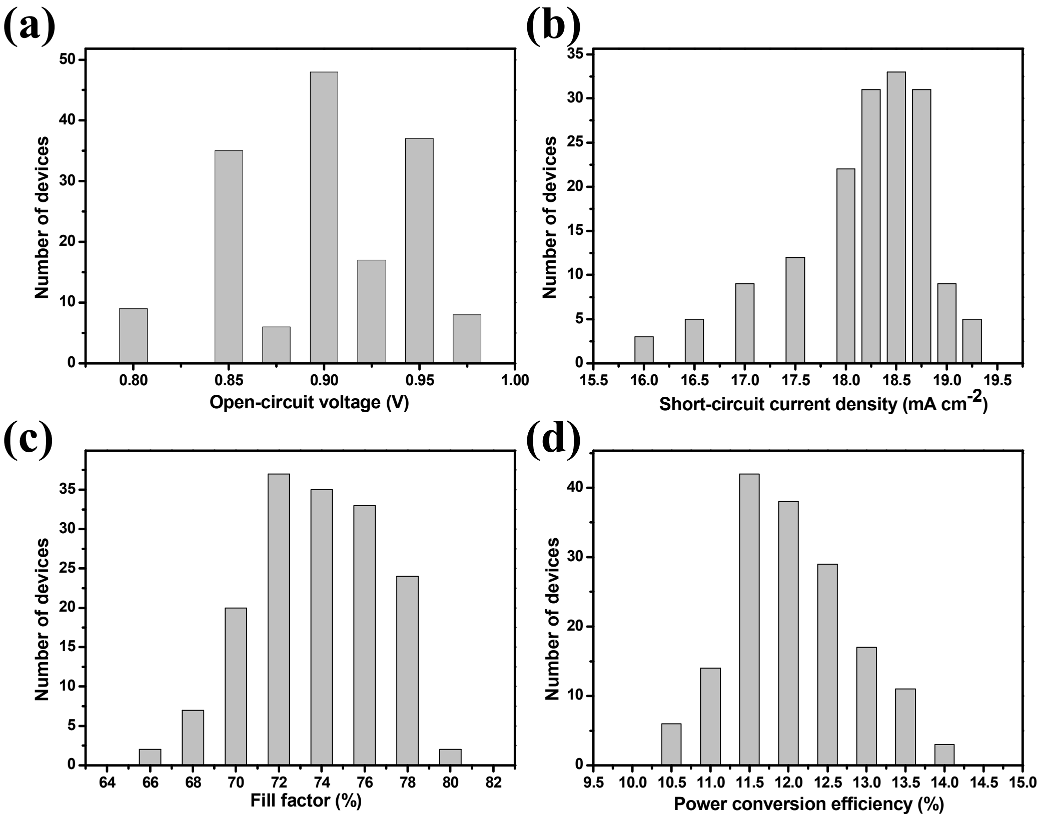

Figure S3. Histograms of device parameters measured for 160 separate ITO/PEDOT:PSS/$CH_3NH_3PbI_{3-X}Cl_X$/PCBM/PDINO/Ag devices. a-d, V_{oc} (a), J_{sc} (b), fill factor (c) and PCE (d).

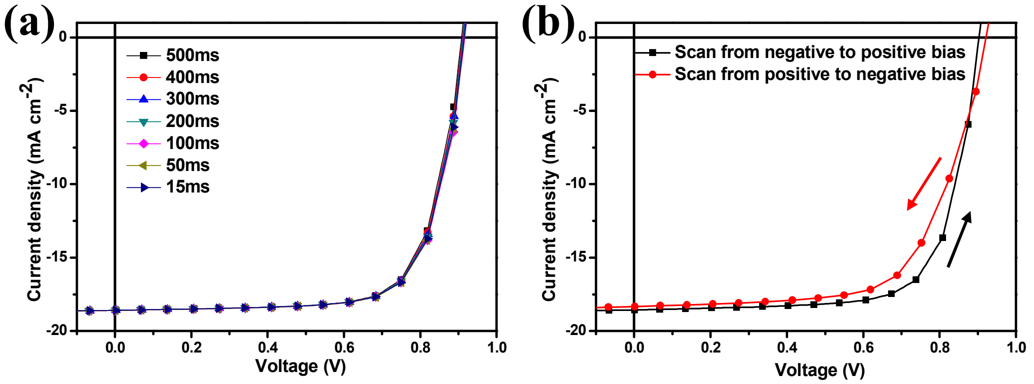

Figure S4. (a) J-V curves measured with different delay time between each measuring point. (b) *J-V* curves measured at different sweep directions with 10 mV voltage steps and 500 ms delay times under AM 1.5 G illumination. (The device structure: ITO/PEDOT:PSS/$CH_3NH_3PbI_{3-X}Cl_X$/PCBM/PDINO/Ag).

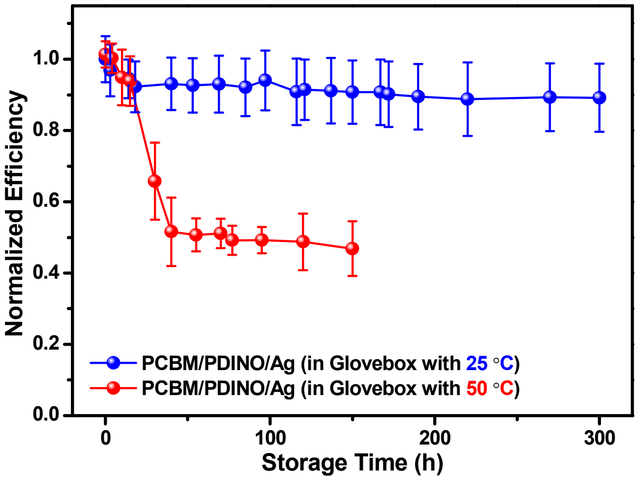

Figure S5. Normalized cell efficiency plotted as a function of storage time for PDINO based perovskite solar cells stored in nitrogen environment with 25 °C and 50 °C, respectively. Measurements were made on six devices of each type without any encapsulation, and the error bars represents plus or minus one standard deviation from the mean.

Here we investigated the performance stability of PCBM/PDINO/Ag based devices stored in the nitrogen environment (in glovebox) without and with 50 °C. Despite the high stability of PCBM/PDINO/Ag based devices at room temperature, the PCE decreased dramatically for the related device stored in a 50 °C hot plate, reaching around 50% of its initial PCE after 150 h. This could be attributed to the morphology variation of perovskite layer and contact problems between the related layers.

Reference

[1] Z. G. Zhang, B. Y. Qi, Z. W. Jin, D. Chi, Z. Qi, Y. F. Li, J. Z. Wang, *Energy Environ. Sci.* **2014**, *7*, 1966.

[2] P. W. Liang, C. Y. Liao, C. C. Chueh, F. Zuo, S. T. Williams, X. K. Xin, J. J. Lin, A. K.-Y. Jen, *Adv. Mater*. **2014**, *26*, 3748.