Enhanced long-term stability of perovskite solar cells by 3-

Hydroxypyridine dipping

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Perovskite solar cell fabrication. FTO-coated glasses, purchased from Pilkington (7 Ω/square), were washed by ultrasonic cleaner using deionized water, acetone and isopropanol sequentially. A compact TiO₂ layer was deposited by spray pyrolysis of ethyl alcohol solution of titanium isopropoxide. Lead acetate trihydrate (PbAc₂•3H₂O) (99.5%, CAS No. 6080-56-4) and hypophosphorous acid (HPA) solution (50 wt % in water, CAS No. 6303-21-5) were purchased from Aladdin. Methylammonium iodide (MAI) was purchased from Dyesol. All of them were used as received. PbAc₂•3H₂O and MAI were dissolved in N,N-Dimethylformamide (DMF) at a ratio of 1:3, and the concentration of the precursor solution is 35 wt %. Then HPA solution was added with a ratio of 7 μL/mL. Perovskites were deposited on the substrates by spin-coating at 1800 r.p.m for 45 s in a nitrogen-filled glovebox. After spin-coating, the substrates were annealed at 100 °C for 10 min. After that, Spiro-OMeTAD layer was spin-coated from a chlorobenzene solution containing additives of lithium bis (tri-fluoromethanesulfonyl) imide and 4-TBP at 3000 r.p.m for 45 s. Finally, 80 nm Au electrodes were thermally evaporated upon the substrates to complete the devices.

3-Hydroxypyridine (3-HP) solution preparation. 300 mg of 3-Hydroxypyridine was dissolved in 28.5 mL chlorobenzene solution with 1.5 mL isopropyl as an additive. Then the mixture was agitated overnight.

Perovskite film Characterization.

X-ray diffraction. XRD spectra were obtained using an X-ray diffractometer (PANalytical X'Pert³ Powder).
X-ray photoelectron spectroscopy. XPS measurements were conducted on a ThermoFisher Scientific ESCALAB
250X system.

Scanning electron microscopy. A field emission SEM (FEI NOVA Nano SEM 430) were used for collecting SEM images.

Time-resolved photoluminescence. PL experiments were performed by exciting the perovskite samples deposited on glass using a FLS980-S2S2-stm spectrometer.

J-V and stability test. J-V curves and steady-state tests were measured using an Aglient B2901 source meter and a solar simulator with an Air Mass 1.5 Global (AM 1.5G) of an irradiation intensity of 100 mW/cm2. All these measurements were carried out in a nitrogen glove box.



Fig. S1 Steady-state efficiency test as a function of time of PSCs with different immersion time of 3-HP.



Fig. S2 SEM images of perovskite films before (a) and after (b) 3-HP dipping. Scale bar, 2 µm.



Fig. S3 J-V (a) and stability (b) test of perovskite solar cells fabricated from $PbCl_2$ instead of $PbAc_2 \cdot H_2O$.



Fig. S4 A comparison of NMR spectra among three samples: deuterated DMF solutions with MAPbI₃, mixture of MAPbI₃+3-HP and 3-HP, respectively.

To prove this interaction between 3-HP molecule and the MAPbI₃ perovskite, we did liquid state ¹H NMR measurements and the spectra were compared in Fig. S4: deuterated DMF solution with MAPbI₃ (Sample 1), with MAPbI₃ + 3-HP (Sample 2) and with 3-HP (Sample 3). Different peaks correspond to different ¹H as we marked. The area ratio of "-NH₃": "-CH₃" and "-OH":"2":"6":"4+5" are 1:1 and 1:1:1:2, respectively. All of these agree well with the experimental or calculated results reported before.^{1,2} The peak of "-NH₃" has broadened, and changes of chemical shifts for signals of 3-HP were observed. Meanwhile, the peak of "-OH" disappeared in the mixture of MAPbI₃ and 3-HP. We speculate that this signal may be covered by other signal such as "-NH₃" or "-CH₃" due to their much stronger intensity. The results indicate that the interaction between 3-HP and MAPbI₃ perovskite is obvious and strong, especially between the hydroxy group and MAPbI₃, though further study needs to be done to analysis the exact form of this interaction between the two components.

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