# **Supporting Information**

Enhanced Long-Term Stability of Perovskite Solar Cells by Double-

## Layer Hole Transport Materials

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### Methods

Materials:

Lead acetate tri-hydrate (PbAc<sub>2</sub>·3H<sub>2</sub>O, 99.998%) and hypo-phosphorous acid (H<sub>3</sub>PO<sub>2</sub>) solution (50 wt. % in water) were purchased from Aladdin. Methylamine iodide (MAI) was bought from Dyesol. Titanium diisopropoxide bis(acetylacetonate) solution (75 wt. % in isopropanol), dipropyl sulfide (PS, 97%), acetic acid (99.99%) and copper thiocyanate (CuSCN, 99%) were obtained from Sigma-Aldrich. 2,2',7,7'-tetrakis(N,N-p-dimethoxy-phenylamino)-9,9'-spirobifluorene (spiro-OMeTAD, 99.8%) was got from Yingkou OPV Tech New Energy Co. Ltd.. N,N-dimethylformamide (DMF, 99.8%), chlorobenzene (99.8%) and acetonitrile (ACN, 99.9%) were bought from J&K Scientific Ltd.. 4-tert-butylpyridine (4-TBP, 96%) was got from TCI. Lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI, 98%), aniline (99%) and benzonitrile (99%) were purchased from Alfa Aesar. All the chemicals were used as received.

Solution preparation:

To prepare the TiO<sub>2</sub> precursor solution, 0.6 mL of Titanium diisopropoxide bis(acetylacetonate) solution was diluted in 1 mL ethanol and stirred for about 1 h. For the preparation of perovskite precursor, 342 mg PbAc<sub>2</sub>·3H<sub>2</sub>O and 430 mg MAI were dissolved in 1.5 mL DMF, and then 7  $\mu$ L H<sub>3</sub>PO<sub>2</sub> solution was added as antioxidant. The spiro-OMeTAD solution was prepared by mixing 73.4 mg spiro-OMeTAD, 17.6  $\mu$ L Li-TFSI solution (520 mg Li-TFSI in 1 mL ACN) and 28.8  $\mu$ L 4-TBP in 1 mL chlorobenzene. The CuSCN solution was prepared by dissolving 20 mg CuSCN powder in 1 mL PS, and adding different type of chemicals as additive with different amount. The specific additive components and the adding amount were as mentioned in the main text. The CuSCN solution was stirred overnight before usage.

#### Substrate preparation:

FTO-coated glasses, purchased from Pilkington (7  $\Omega$ /square), were etched by laser to remove the FTO. Then substrates were cleaned by ultrasonic cleaner using deionized water, acetone and isopropanol sequentially, followed by a plasma treatment for 3 min. A compact TiO<sub>2</sub> layer was deposited by spray pyrolysis of TiO<sub>2</sub> precursor solution under 450°C and annealed at 500°C for 30 min.

#### Perovskite solar cells fabrication:

Perovskite layer was deposited on the substrates by spin-coating perovskite precursor solution at 1800 r.p.m. for 45 s in a nitrogen-filled glove box, followed by annealing at 110 °C for 10 min. After cooling to room temperature, the spiro-OMeTAD layer was spin-coated onto the perovskite film at 3000 r.p.m. for 45 s. Finally, 60 nm Au electrode was thermally evaporated on top of the spiro-OMeTAD layer to complete the devices. For the devices with CuSCN layer, the CuSCN layer was fabricated by spin-coating method at 1500 r.p.m. for 45 s.

### Device characterization:

The surface and cross-sectional morphology of the device were measured by scanning

electron microscope (Nova Nano SEM 430, FEI) under 5 kV electron beam accelerate voltage. The current density-voltage characteristics were performed using an Agilent B2900 Series precision source/measure unit, and the cells were illuminated by a solar simulator (Solar IV-150A, Zolix) under AM 1.5G irradiation (100 mW/cm<sup>2</sup>) in a nitrogen-filled glove box. Light intensity was calibrated with a Newport calibrated KG5-filtered Si reference cell. The perovskite solar cells' active area is 9 mm<sup>2</sup>.

X-ray photoelectron spectroscopy (XPS) measurement:

The XPS measurements were conducted on a ThermoFisher Scientific ESCALAB 250X system. Al  $K_{\alpha}$  (1486.6 eV) was used as X-ray source and the analyzer was put at 54.7° relative to the source. For the etching study, argon ion beam was used to etch the sample and the ion beam accelerate voltage was 3 kV.



**Fig. S1** (**a**) Top-view scanning electron microscope (SEM) image of CuSCN layer. (**b**) Cross-sectional SEM image of a perovskite solar cell with CuSCN HTM layer.



Fig. S2 Time-resolved photoluminescence (PL) measurements of perovskite on glass(a), perovskite/Spiro on glass (b), and perovskite/CuSCN on glass (b).

We conducted time-resolved photoluminescence (PL) measurements on three different samples. First sample was bare perovskite on glass and the PL result was shown in Fig. S2a. Because of the insulation nature of glass, perovskite cannot inject electrons or holes into it. So the result of this sample indicates the intrinsic lifetime of carriers in perovskite. The lifetime was 166.2 ns extracted from PL curve by single exponential fitting. The other two samples also contain perovskite on glass, and one of them has a spiro-OMeTAD layer on perovskite and the other has CuSCN layer on perovskite. The result of PL measurement of these samples was shown Fig. S2b. Because these samples also have insulating glass substrate, the electrons cannot conduct to it. Thus the shorter carrier lifetime only derived from hole injection into hole transport materials. As exhibited in the figure, by single exponential fitting, these two samples shown remarkably short lifetime within 10 ns. This means that both spiro-OMeTAD and CuSCN have excellent hole extraction ability. But compared with 7.12 ns lifetime of spiro-OMeTAD sample, CuSCN sample has a longer lifetime of 9.33 ns, indicating that CuSCN has inferior hole-collection ability than spiro-OMeTAD.



**Fig. S3** XPS spectra of target elements at interface after argon ion etching. (a-b) XPS spectra of Pb 4f peaks at interface between perovskite layer and spiro-OMeTAD layer of "fresh-spiro" device (a) and "worked-spiro" device (b). (c) XPS spectra of S 2p peaks at interface between spiro-OMeTAD layer and CuSCN layer of "worked-double" device.



**Fig. S4** Curve fitting results of XPS spectra of "worked-spiro" sample target elements at interface after argon ion etching. (a) Curve fitting result of XPS spectra of Pb 4f peaks at interface between perovskite layer and spiro-OMeTAD layer. (b) Curve fitting result of XPS spectra of I 3d peaks at interface between perovskite layer and spiro-OMeTAD layer.

#### Note S1.

We perform quantitative analysis to the XPS spectra of Pb, I and N elements of "worked–spiro" sample after etching. The curve fitting results of Pb and I were shown in Fig. S3a and Fig. S3b. And the curve fitting result of N was already shown in Fig. 4c in main article. The computing process of quantitative analysis was simply described below and the result was also shown.

It should be stressed that these spectra were obtained simultaneously after a period of time of Argon ion etching, so the spectra can be used to conduct quantitative analysis. Firstly, we subtracted background signal of the spectra, and the baseline in the Fig. S3a, Fig. S3b and Fig. 4c stand for the background. Then we used Gaussian equation to fit each peak. Finally, we performed integral calculation to the peaks to obtain their areas. The result of integral areas is 1177.1 for Pb 4f 5/2 peak, 1210.0 for Pb 4f 7/2 peak, 4135.7 for I 3d 3/2 peak, 5382.6 for I 3d 5/2 peak and 1024.1 for N 1s peak located at 401.7 eV. We find the atomic sensitivity factors of different elements for X-ray source at 54.7°, which is 8.329 for Pb 4f peaks, 6.206 for I 3d 5/2 peak and 0.477 for N 1s peak. So after taking atomic sensitivity factors into consideration, the relative amount of Pb: I: N = (1177.1+1210.0)/8.329: 5382.6/6.206: 1024.1/0.477 =

286.6: 867.3: 2146.9. The relative amount between Pb and I approximately equals 1:3, means that the I signal we observed derived almost totally from perovskite areas come out on surface. But the amount of N in MA nearly an order larger than Pb! It is obvious that if all the N in MA signal originate from perovskite areas, the N and Pb should have same amount. So the calculation results prove that the signal of N in MA not only from perovskite areas, but mainly from other surface areas covered by spiro-OMeTAD, which means that MA ions have penetrated into spiro-OMeTAD layer already.

#### Note S2.

The calculation result in **Note S1.** showed that the relative amount between Pb and I approximately equals 1:3, which means that the I signal we observed derived almost totally from perovskite. Considering that the most of surface area was still covered by Spiro-OMeTAD after Argon ion etching, so this result indicate that after the device worked for a long time under light illumination, almost no I<sup>-</sup> ion migrate to spiro-OMeTAD layer.