Electronic Supplementary Material (ESI) for Nanoscale Horizons.

# Supporting Information

## Enhanced moisture stability of metal halide perovskite solar cells based on sulfur-oleylamine surface modification

*Yu Hou,‡ Zi Ren Zhou,‡ Tian Yu Wen, Hong Wei Qiao, Ze Qing Lin, Bing Ge and Hua Gui Yang**

Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, 130 Meilong Road, 200237 Shanghai, China.
*E-mail: hgyang@ecust.edu.cn

## Experimental section

### Materials.

Methylamine solution (33 wt% in absolute ethanol), hydroiodic acid (HI, 57 wt% in aqueous solution), dimethyl sulfoxide (DMSO, 99.9%), Lead iodide ($PbI_2$, 99.999%) and Oleylamine (Oam, 70%) were purchased from Sigma-Aldrich. N,N-dimethylformamide (DMF, 99%) was purchased from Alfa Aesar. Cyclohexane ($C_6H_{12}$, 99.5%) and Sublimed Sulfur (S, 99.5%) was purchased from Shanghai Lingfeng Chemical Reagent. 1-Octadecene ($C_{18}H_{36}$, 90%) was purchased from Aladdin. 2,2',7,7'-tetrakis-[(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene] (Spiro-OMeTAD) was purchased from Nichem chemicals and tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt (III) tris(bis(trifluoromethylsulfonyl)imide) (FK209) was purchased from 1-Material Inc. FTO (8 Ω per square) was purchased from Nippon Sheet Glass.

### Synthesis of S-Oam solution.

For preparation of 0.125 M S-Oam solution, 40 mg Sublimed Sulfur (powder) was added into 10 mL Oleylamine and stirred at 1000 rpm under dark. The reaction was proceeded at 40 °C overnight to generate a clear, dark red S-Oam solution. All solutions were filtered by 0.45 μm needle filters (PTFE) before using.

### Synthesis of perovskite precursors.

Methylammonium iodide (MAI) was synthesized by a solution reaction of Methylamine solution, HI and Ethanol.[1] Firstly, 10 mL HI was injected into a 250 mL round-bottomed flask containing 100 mL Ethanol swiftly at 0 °C in Argon atmosphere. Then Methylamine solution was injected into the stirred solution dropwise, the reaction was thought to be completed 2 h later. The pure white precipitate was obtained by rotation evaporation at 55 °C for 1 h, then washed with diethyl ether three times, and finally dried at vacuum oven overnight. Next, 60 mg MAI was dissolved in 1 mL 2-propanol to form MAI precursor. $PbI_2$ precursor (1.3 M) was prepared by dissolving 599.3 mg $PbI_2$ in DMSO (3:7 mole ratio) DMF.

### Surface modification

1-Octadecene and S-Oam solution were preheated to 40 °C before sulfurization treatment. Then 0 µL, 25 µL, 50 µL, 100 µL and 150 µL S-Oam solutions were added into 3 mL 1-Octadecene, respectively. The annealed perovskite films were dipped in variable S-Oam solution in 1-Octadecene at 40 °C for 3min and then rinsed with cyclohexane. Finally, the sulfurized perovskite films were dried under argon flow.

### Device fabrication.

A planar heterostructure (FTO/compact-$TiO_2$/$MAPbI_3$/Spiro-OMeTAD/Ag) was adopted for Solar Cell fabrication. Firstly, the fluorine-doped Tin oxide (FTO) glass (Nippon Sheet Glass, 8 Ω/square) substrates were washed by ultrasonication with soap, acetone, ethanol and deionized water sequencially for 15 min and then treated with ultraviolet ozone cleaner for 15 min. A 30 nm-thick compact-$TiO_2$ (c-$TiO_2$) layer was prepared by spinning coating 0.15 M solution of titanium diisopropoxide bis(acetylacetonate) in ethanol on FTO substrates at 3000 rpm for 30 s and then annealing at 500 °C for 30 min. Next, two-step method was adopted to fabricate perovskite film according to the literature.[2] $PbI_2$ film was first prepared by spinning coating $PbI_2$ precursor on c-$TiO_2$ at 3000 rpm for 30 s, then MAI precursor was loaded on $PbI_2$ film for 5 s, followed by spinning coating at 5000 rpm for 30 s and annealed at 100 °C for 10 min. Afterwards, the perovskite film were proceeded with sulfurization treatment. Then Spiro-OMeTAD, doped with bis(trifluoromethanesufonyl)imide lithium salt (Li-TFSI), FK 209 and 4-tert-butylpyridine (tBP), was spin coated on the perovskite films at 4000 rpm for 30 s. Finally, 100 nm-thick Ag was thermally evaporated onto the hole transport layer as back contact.

## Characterization

### Film characterization.

The morphology and roughness of perovskite films were characterized by field emission scanning electron microscopy (FESEM, HITACHI S4800) and atomic force microscopy (AFM, Veeco/DI). The crystallographic information of perovskite films was investigated by powder X-ray diffraction (PXRD, Bruker Advance D8 X-ray diffractometer, Cu Kα radiation, 40 kV). X-ray photoelectron spectroscopy (XPS, PHI5300, Mg anode, 250 W, 14 kV) was used to analyze the elemental composition of perovskite film before and after sulfurization treatment. All spectra were calibrated by using data of inorganic carbon at 284.8 eV as a reference. Nuclear magnetic resonance (NMR, Bruker Avance III 400, 500 MHz) with super conducting Fourier spectrometer was utilized to acquire the $^1$H-HCOSY 2D NMR spectra, which were recorded at a sample temperature of 25 °C. All data were internally corrected by the $CH_3$ reference with a value of 0.88 ppm. The elemental contents of perovskite film was quantitatively measured by Inductively coupled plasma atomic emission spectrometer (ICP-AES, Agilent 725). Water droplets (about 5 μL) were carefully dropped on the coated films by Dataphysics OCA20 contact-angle system, then measurements were processed at ambient atmosphere. Cary 500 UV-Vis-NIR spectrophotometer was applied to measure the optical absorption spectra of the perovskite films. The photoluminescence measurement was carried out at room temperature by means of Fluorolog-3-p spectrophotometer with light excited at 400 nm. PH meter (I.N.E.S.A, PHS-3C) was utilized to measured the pH value of S-Oam and S-Oam / octadecene solution at 40 °C.

**Device characterization.**

The solar cells were illuminated by a solar light simulator (Solar IV-150A, Zolix) and light intensity was calibrated by a standard Newport calibrated KG5-filtered Si reference cell. The J-V curves of devices were measured with Keithley 2400 digital sourcemeter under AM 1.5 G irradiation (100 mW cm$^{-2}$) at a scan rate of 0.15 V s$^{-1}$. Devices were masked with a metal aperture to define the active area of 0.0625 cm$^2$. The steady state photocurrent output of champion device was measured by biasing the device at maximum power point for 120 s.

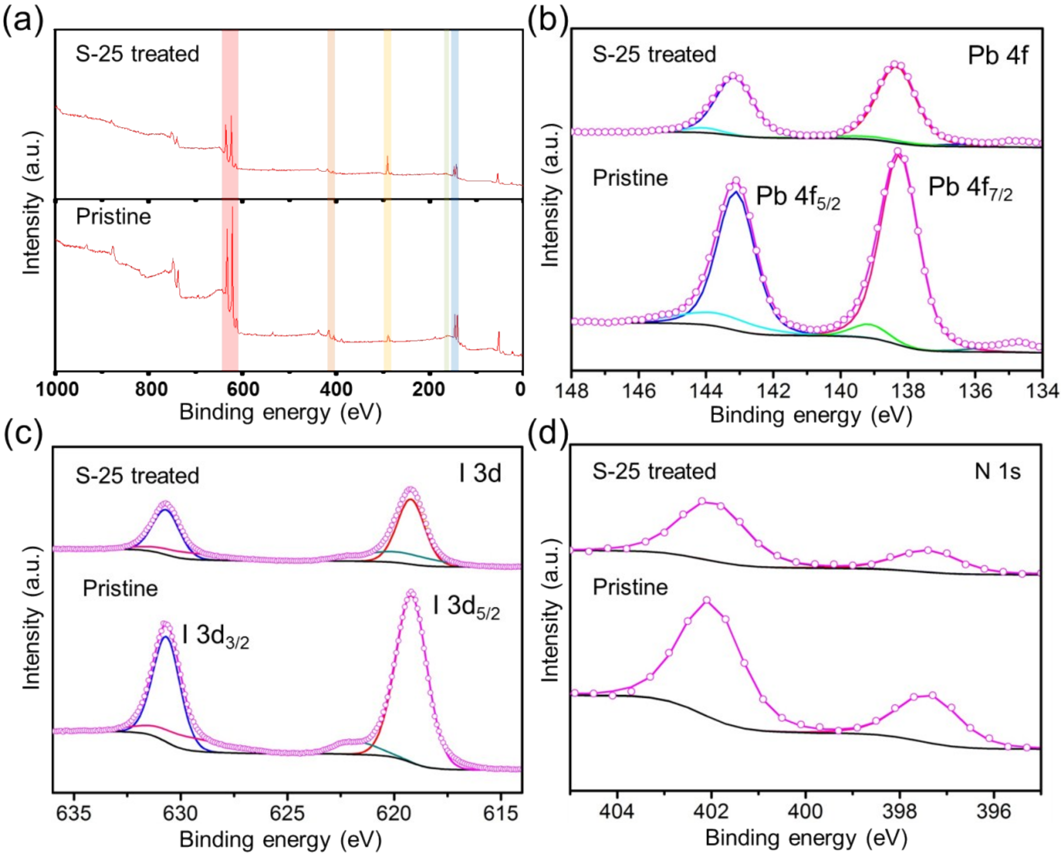

**Figure S1**. High resolution XPS spectra of (a) full spectra, (b) Pb 4f, (c) I 3d and (d) N 1s for pristine and S-25 samples.

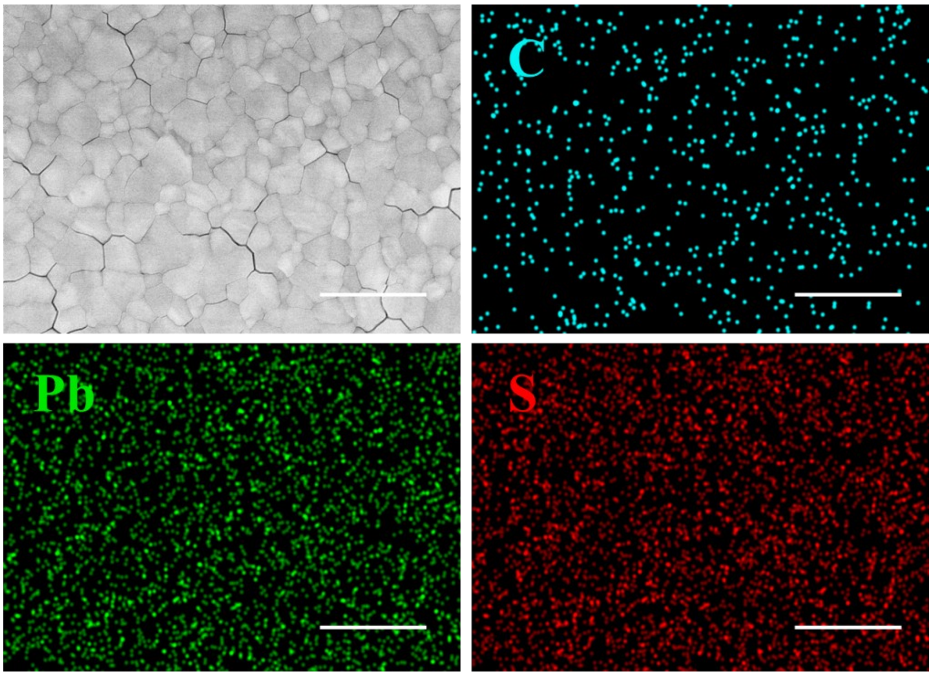

**Figure S2**. Energy-dispersive spectroscopy (EDS) selected area mapping of S-25 sample (blue: carbon, green: lead, red: sulfur). All scale bars are 1 µm.

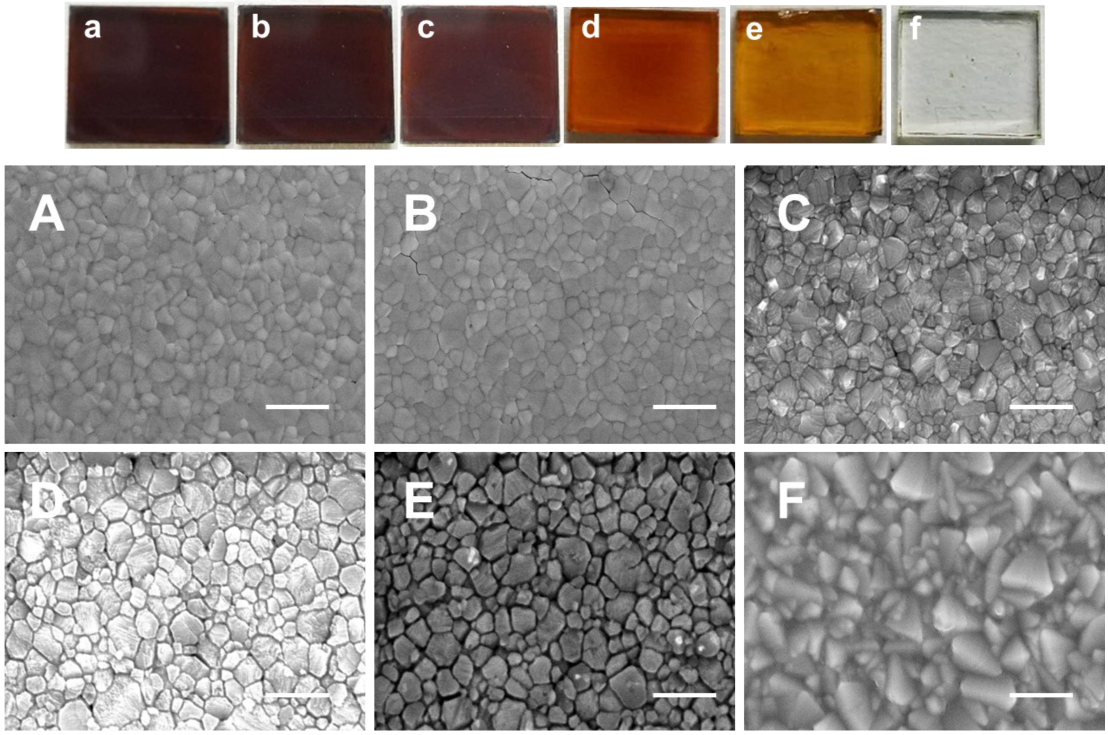

**Figure S3.** Photographs (a-f) of perovskite thin films after treated with different volume of S-Oam solution; Top-view Scanning Electron Microscope (SEM) images (A-F) of S-Oam treated perovskite film (a, A: pristine; b, B: S-0; c, C: S-25; d, D: S-50; e, E: S-100; f, F: S-150). All scale bars: 1 µm.

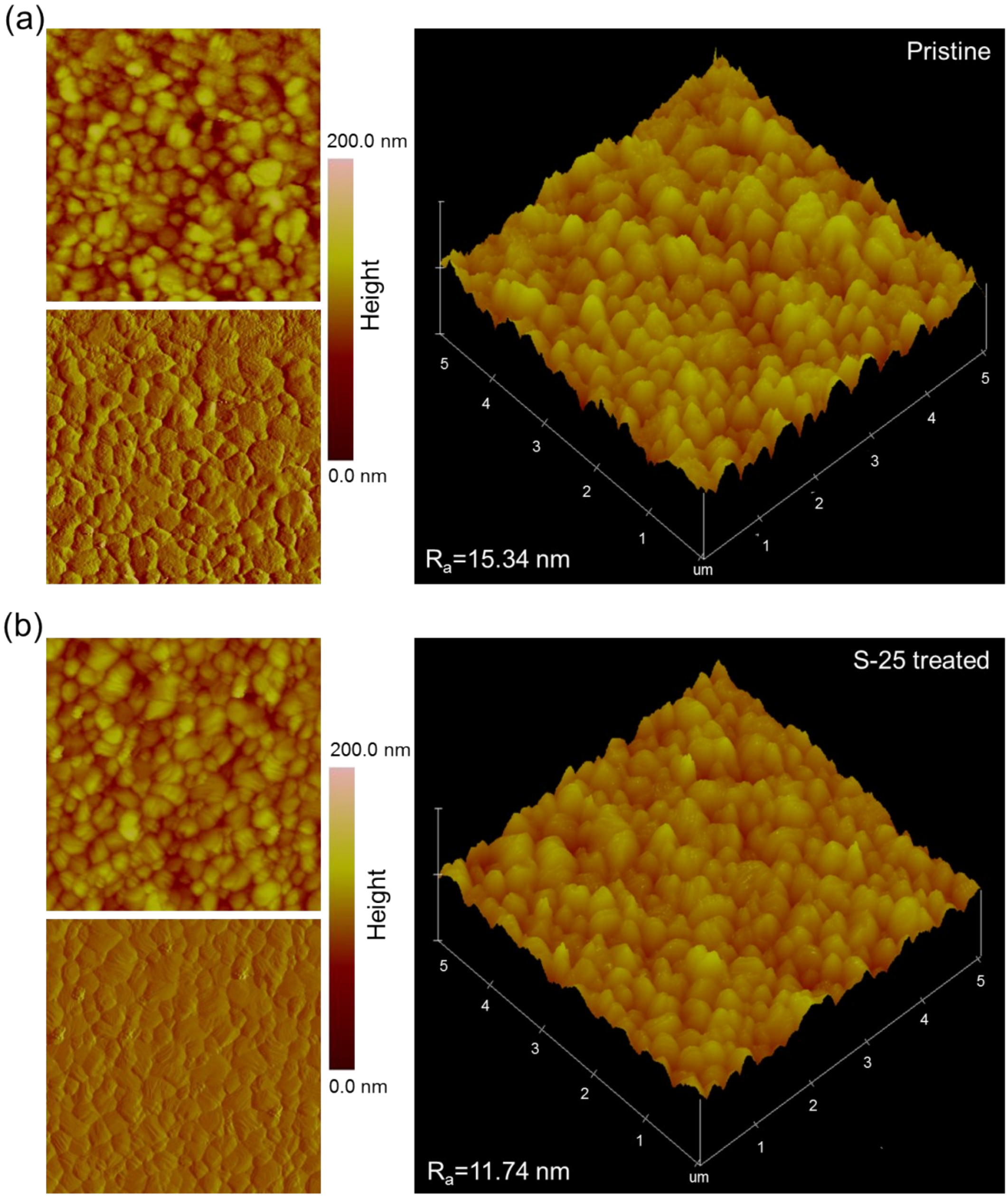

**Figure S4**. AFM height and roughness images of perovskite film with an area of 5 µm × 5 µm size. $R_a$ represents mean roughness of the film. (a) Pristine sample. (b) S-25 treated sample.

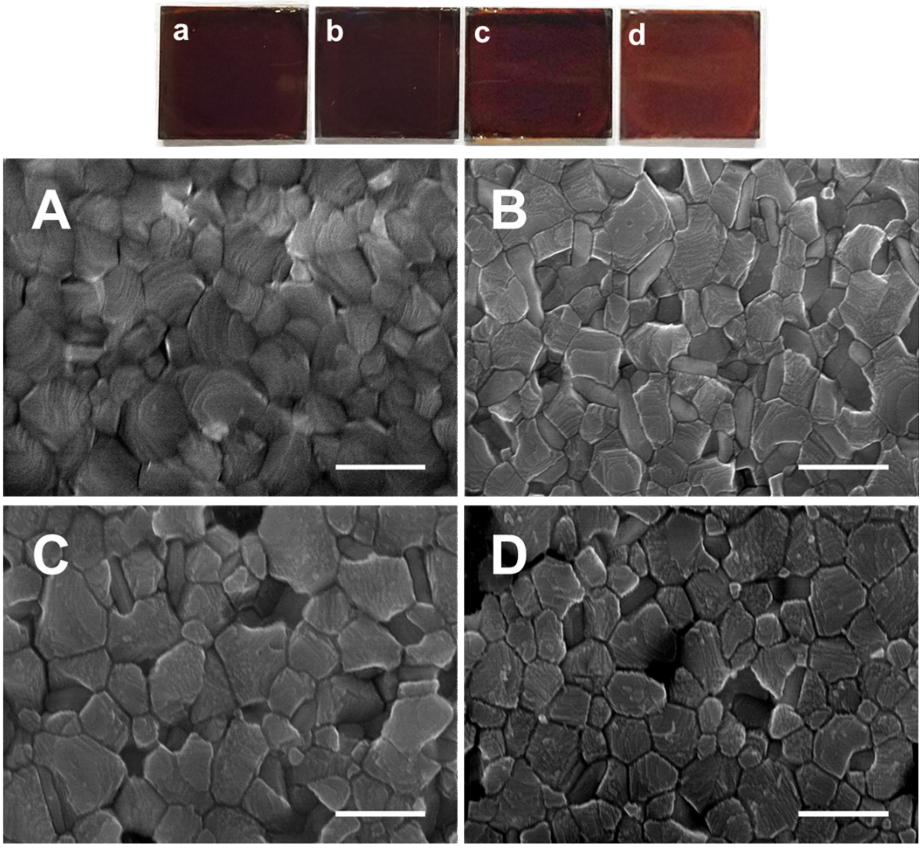

**Figure S5.** Photographs (a-d) of perovskite thin films after treated with different volume of Oam solution; Top-view Scanning Electron Microscope (SEM) images (A-D) of Oam treated perovskite film (a, A: O-25; b, B: O-50; c, C: O-100; d, D: O-150). All scale bars: 500 nm.

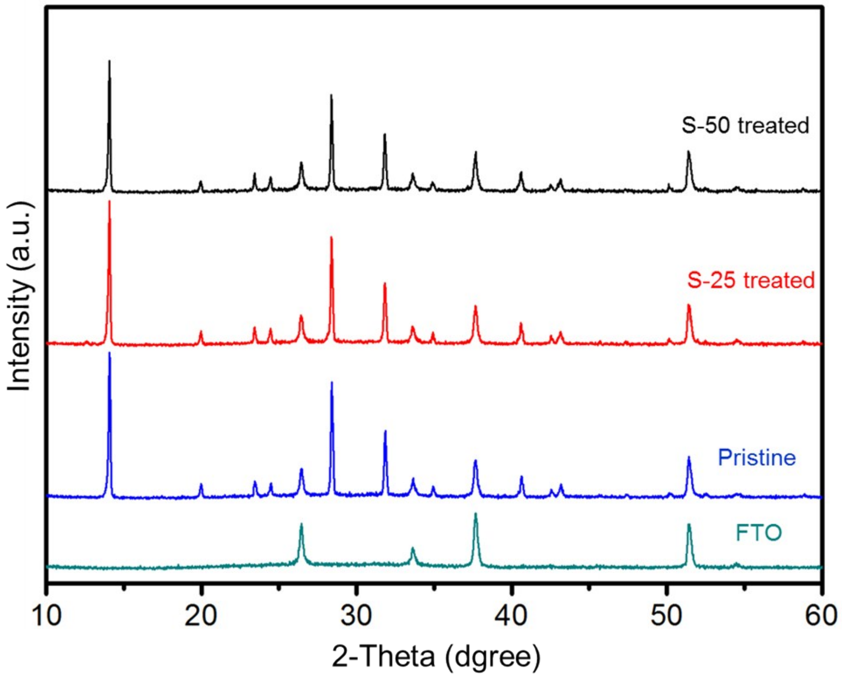

**Figure S6.** XRD pattern of pristine, S-25 treated, S-50 treated perovskite films and FTO substrate.

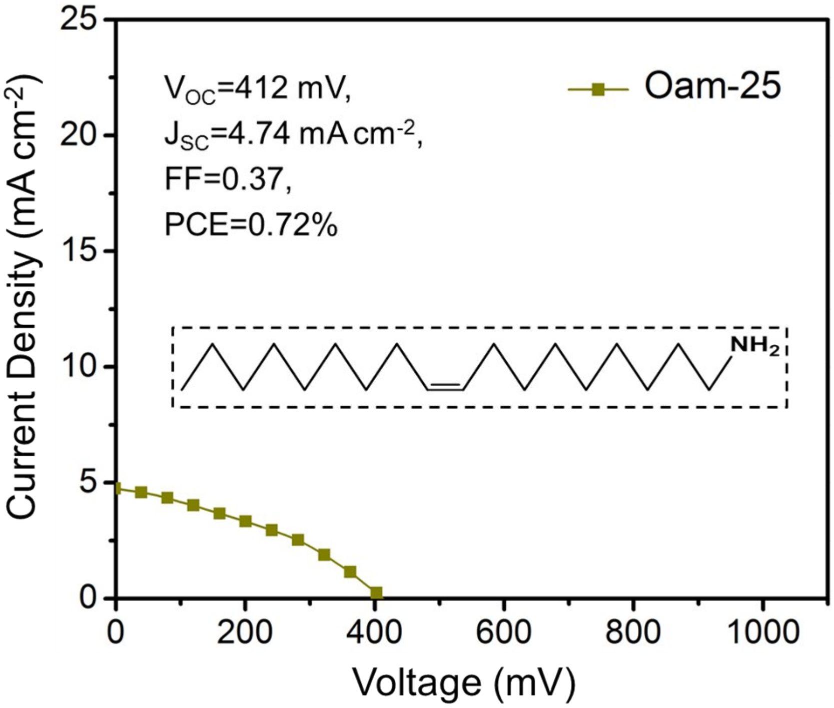

**Figure S7.** J-V curve of Oam-25 treated device. Assembled by hydrogen bond crosslinking, the sharply declined PCE can be ascribed to the insulating properties of long carbon chains in oleylamine molecules. The molecular structure of oleylamine is presented in dashed rectangle.

**Table S1.** The results of ICP-AES elemental analysis for pristine and S-25 treated perovskite films.

| Sample | Pb [wt %] | S [wt %] |
|---|---|---|
| Pristine | 37 | 0 |
| S-25 | 39 | 0.14 |

**Table S2.** Photovoltaic parameters of pristine, sulfurized and oleylamine-treated devices in reverse scan with a sweeping rate of 0.15 V $s^{-1}$, measurements were carried under AM 1.5 G irradiation.

| Device | $J_{SC}$ (mA $cm^{-2}$) | $V_{OC}$ (V) | FF | $\eta_0$ (%) | $\eta_{AVG}$% |
|---|---|---|---|---|---|
| Pristine | 21.87 | 1.03 | 0.68 | 15.35 | 14.54 |
| S-0 | 21.59 | 1.03 | 0.68 | 15.20 | 14.16 |
| S-25 | 21.87 | 1.04 | 0.69 | 15.71 | 14.71 |
| S-50 | 20.25 | 0.99 | 0.61 | 12.33 | 10.61 |
| S-100 | 14.72 | 0.81 | 0.45 | 5.40 | 3.55 |
| S-150 | 3.66 | 0.49 | 0.22 | 0.40 | 0.10 |
| Oam-25 | 4.74 | 0.41 | 0.37 | 0.72 | 0.49 |

# References

[1] Y. C. Zheng, S. Yang, X. Chen, Y. Chen, Y. Hou and H. G. Yang, *Chem. Mater.*, 2015, **27**, 5116-5121.

[2] M. Saliba, T. Matsui, J. Y. Seo, K. Domanski, J. P. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt and M. Grätzel, *Energy Environ. Sci.,* 2016, **9**, 1989-1997.