Supporting information for

Thoils as interfacial modifiers to enhance the performance and stability of perovskite solar cells

Jing Cao,[a] Jun Yin,[a,b] Shangfu Yuan,[a] Yun Zhao,[a] Jing Li,[b] and Nanfeng Zheng[a]*

[a] State Key Laboratory for Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.
E-mail: nfzheng@xmu.edu.cn; Fax: +86-592-2183047.

[b] Pen-Tung Sah Institute of Micro-Nano Science and Technology, Xiamen University, Xiamen 361005, China.

Experimental Section

Materials synthesis

All chemicals and reagents were used as received from chemical companies without any further purification. The CH_3NH_3I was synthesized and purified according to the literature method.[1] To a stirred solution of methylamine in methanol (40 wt.%, 24 mL) was slowly added aqueous hydroiodic acid (57 wt.%, 25 mL) at 0 °C. After 2 h, the precipitate was collected by evaporation at 50 ℃ for 1 h. The as-obtained product was washed with diethyl ether three times and then finally dried at 60 °C in a vacuum oven for 24 h to afford the desired pure CH_3NH_3I as white crystals.

Solar Cell Fabrication

Fluorine-doped Tin Oxide (FTO) glass substrates with dimension of 2.0 cm × 2.0 cm were patterned by etching with zinc powder and 2 M hydrochloric acid. The substrates were then sequentially washed in ultrasonic baths of acetone, distilled water and ethanol. A compact TiO_2 blocking layer was spin-coated onto the cleaned FTO glass using 0.15 M Titanium tetraisopropanolate in 1-butanol solution at 2000 rpm for 30 s. The substrate was heated at 120 °C for 15 min, and then annealed at 550 °C for 30 min. After cooling to the room temperature, the film was immersed into the 20 mM $TiCl_4$ solution at 70 °C for 30 min. After dried, a ~200 nm thick mesoporous TiO_2 film was deposited on the pre-treated FTO substrate by spin-coating of the TiO_2 paste (Dyesol DSL 18NR-T) with ethanol (1:3, mass ratio), which was followed by the heating at 550 °C for 30 min. The porous substrate was dipped in 2 mM solution of HOOC-R-SH in ethanol for 30 min for introducing anchor motifs on the titania film, the mesoporous TiO_2 substrate was washed thoroughly by ethanol three times to remove physically absorbed HOOC-R-SH ligands. For the perovskite layer, the as-prepared

substrate was infiltrated with a hot solution of PbI_2 in *N*, *N*-dimethylformamide (462 mg/1 mL) by spin-coating at 5000 rpm. for 30 s, and then dried at 120 °C for 5 min. After cooling to room temperature, the film was dipped into the solution of CH_3NH_3I in 2-propanol (10 mg/mL) for 30 min, which was spun at 3000 rpm for 20 s and then heated at 100 °C for 5 min. After the deposition of the perovskite layer, the substrate was dipped into a 100 mg/mL solution of HS-R′ in CH_2Cl_2 for 30 s, followed by baking at 100 ℃ for 5 min. After that, the hole transport layer solution were coating via solution process at 4000 rpm for 30 s, where Spiro-OMeTAD/ chlorobenzene (90 mg/1 mL) solution was employed with the additives containing 17.5 μL Li-TFSI)/acetonitrile (520 mg/1 mL) and 28.8 μl TBP. Finally, a 80 nm thick Au counter electrode was deposited by thermal evaporation under reduced pressure of 2×10^{-7} Torr. The active area was 0.12 cm^2.

Device Characterization

Current-voltage characteristics were recorded from a solar simulator equipped with a Keithley 2400 source meter and 300 W collimated Xenon lamp (Newport) calibrated with the light intensity to 100 mW cm^{-2} at AM 1.5 G solar light condition by the certified silicon solar cell. Incident photon-to-electron conversion efficiency (IPCE) was measured on a computer-controlled IPCE system (Newport) containing a Xenon lamp, a monochromator and a Keithley multimeter. The system was calibrated with the certified silicon solar cell and the IPCE data were collected at DC mode. XRD patterns were analyzed by an X-ray diffractometer (Rigaku, RINT-2500) with a CuKa radiation source. The surface morphology of were recorded via a SEM-4800 field-emission scanning electron microscope (SEM). The UV-vis spectra were measured with the perovskite infiltrated mesoscopic TiO_2 films supported by FTO glass using a cary-5000 UV-vis spectrophotometer. The Time-resolved photoluminescence (PL) spectra were measured using an Edinburgh Instruments FLS920 spectrometer.

Reference

1. J.-H. Im, C.-R. Lee, J.-W. Lee, S.-W. Park and N.-G. Park, *Nanoscale*, 2011, **3**, 4088-4093.

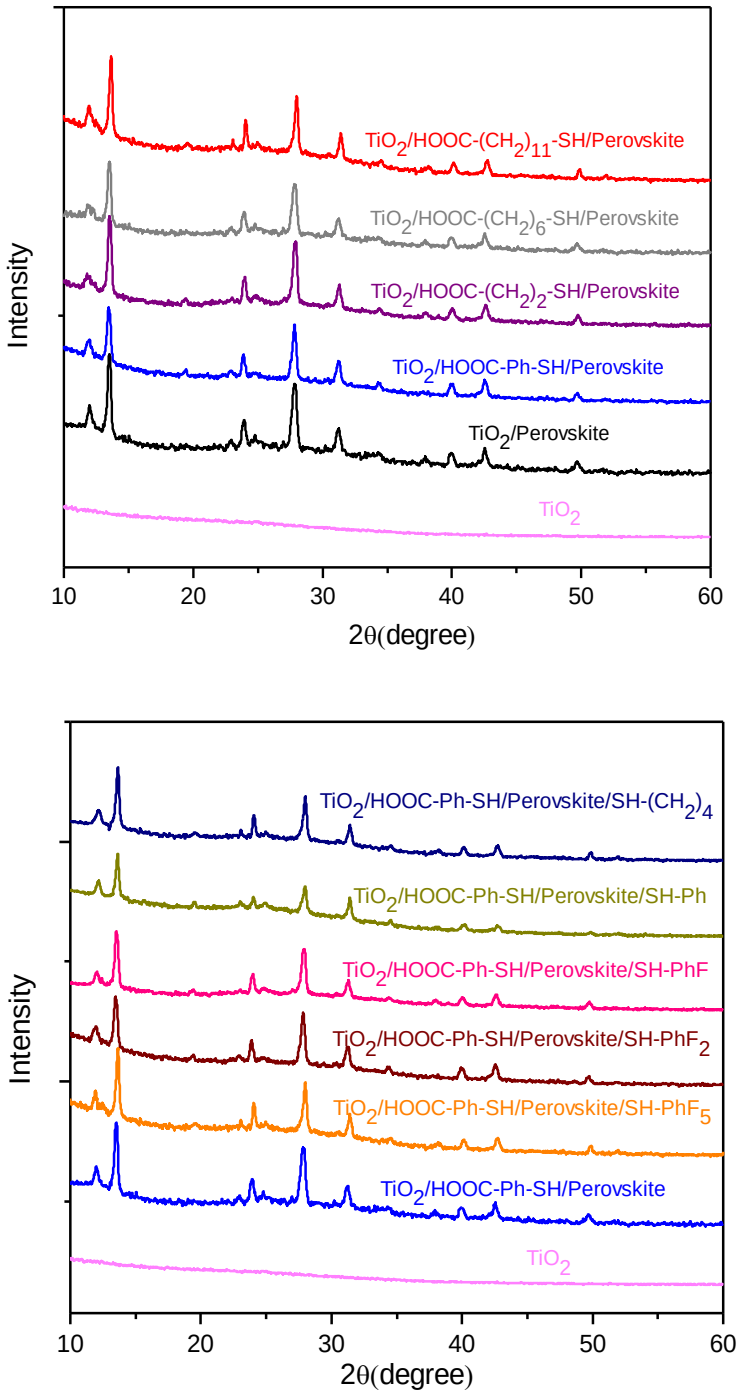


Fig. S1 The XRD spectra of the films.

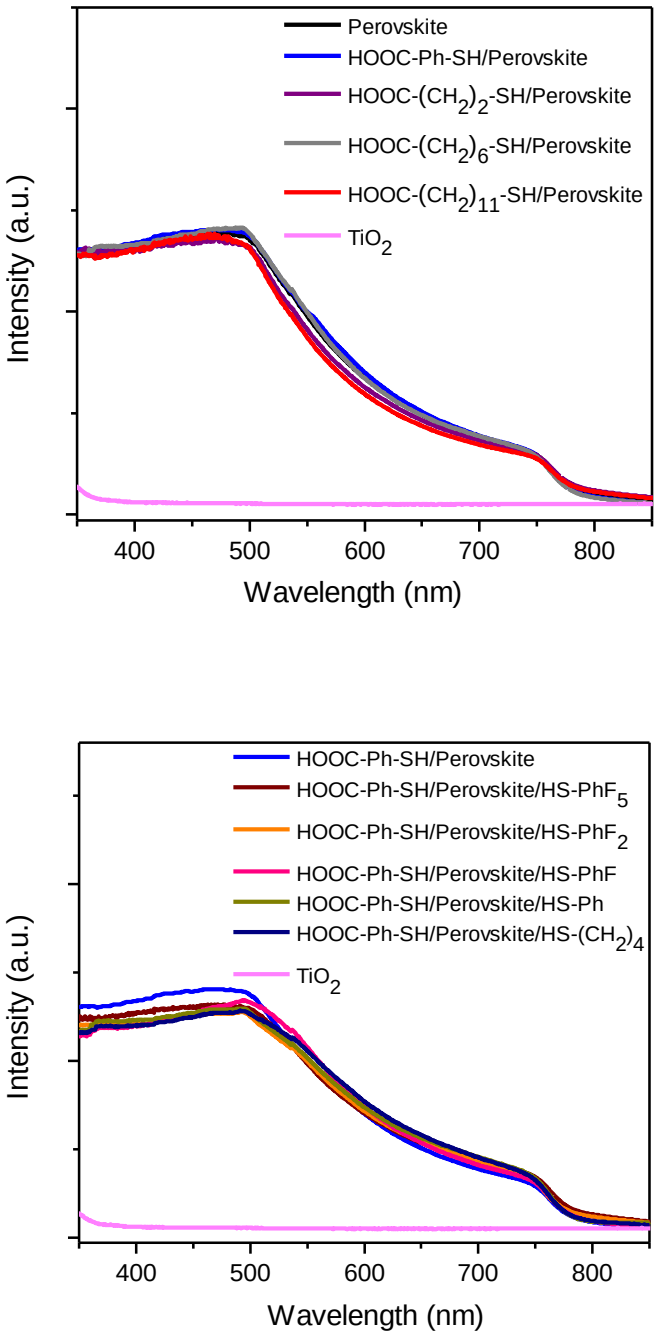
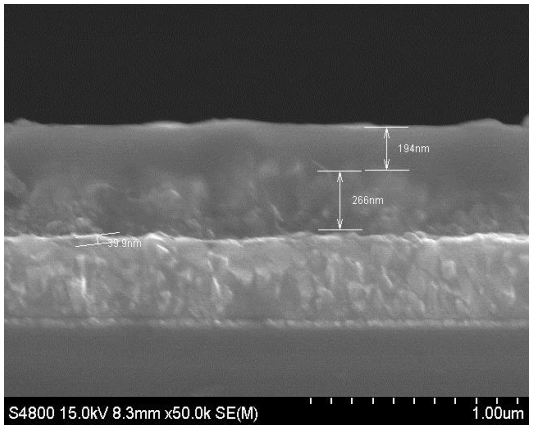
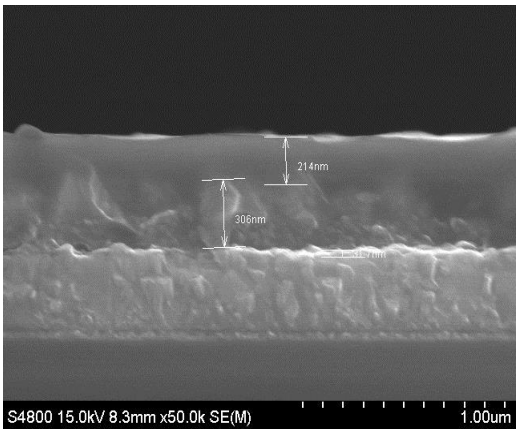


Fig. S2 The UV-vis spectra of the films.



TiO_2/Perovskite/Spiro-OMeTAD



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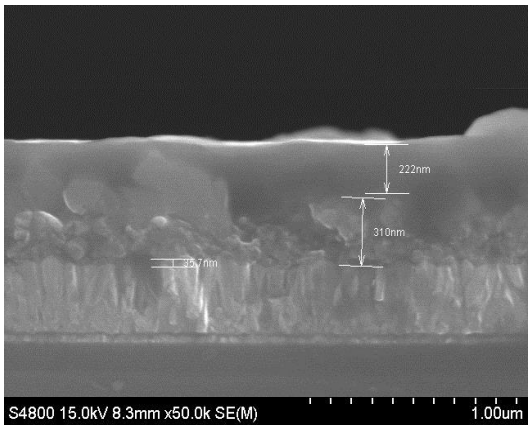
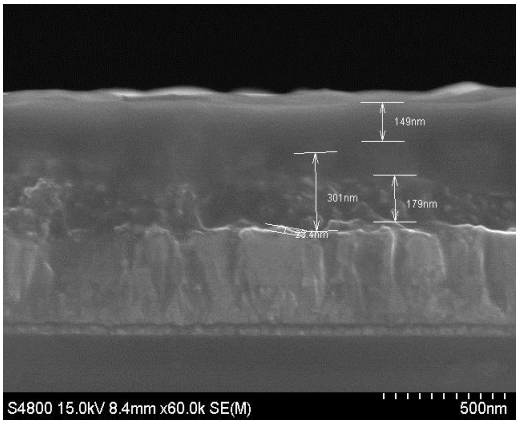


TiO_2/HOOC-$(CH_2)_2$-SH/perovskite/Spiro-OMeTAD



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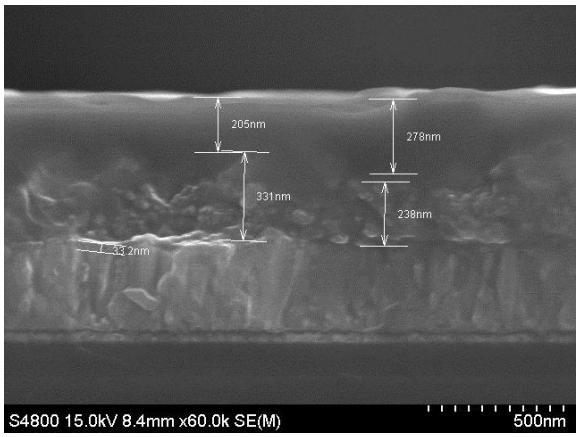
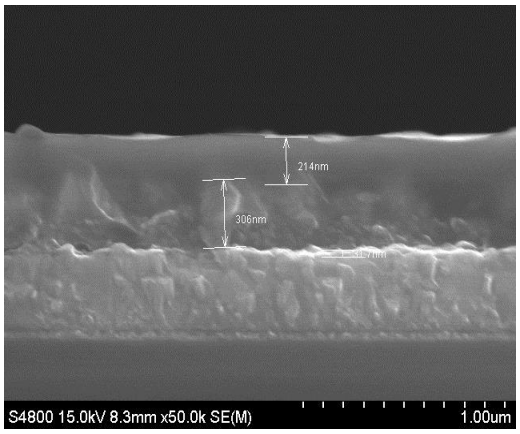
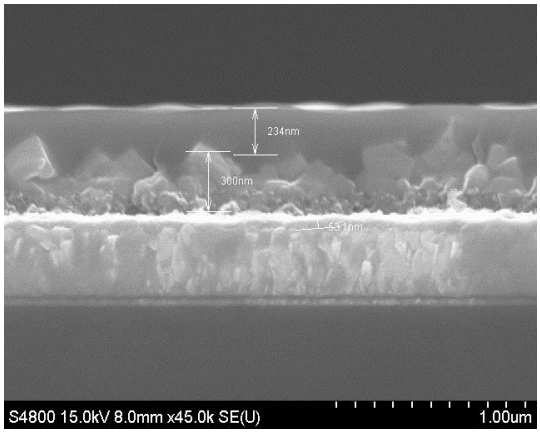


TiO_2/HOOC-$(CH_2)_{11}$-SH/perovskite/Spiro-OMeTAD

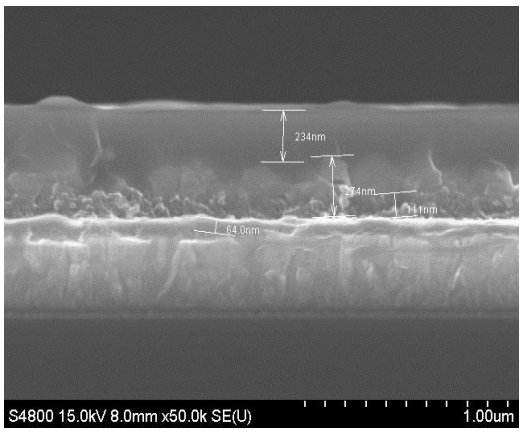
Fig. S3 Cross-sectional SEM images of the photovoltaic devices.



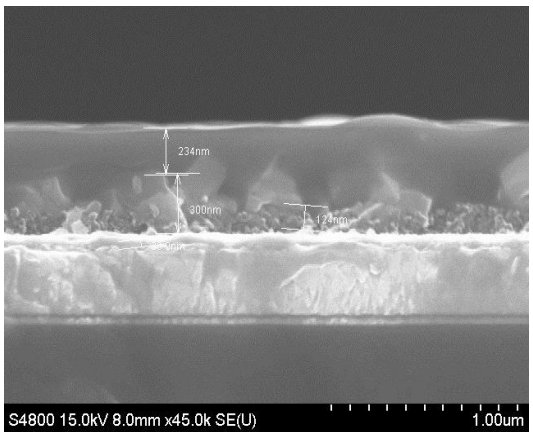
TiO_2/HOOC-Ph-SH/perovskite/Spiro-OMeTAD



TiO_2/HOOC-Ph-SH/perovskite/HS-PhF_5/Spiro-OMeTAD



TiO_2/HOOC-Ph-SH/perovskite/HS-PhF_2/Spiro-OMeTAD



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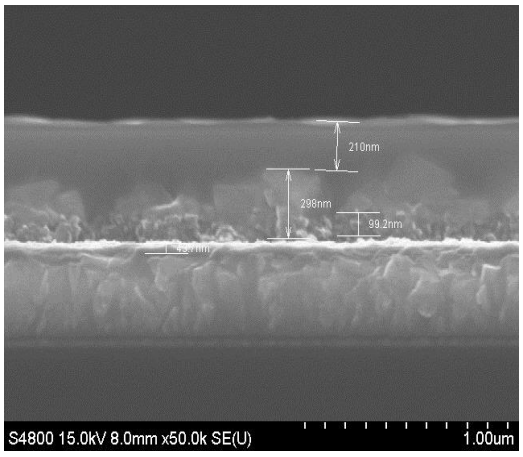
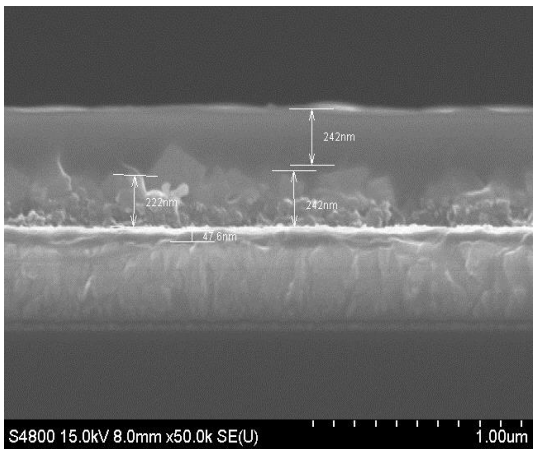


TiO_2/HOOC-Ph-SH/perovskite/HS-Ph/Spiro-OMeTAD



TiO_2/HOOC-Ph-SH/perovskite/HS-$(CH_2)_4$/Spiro-OMeTAD

Fig. S4 Cross-sectional SEM images of the photovoltaic devices.

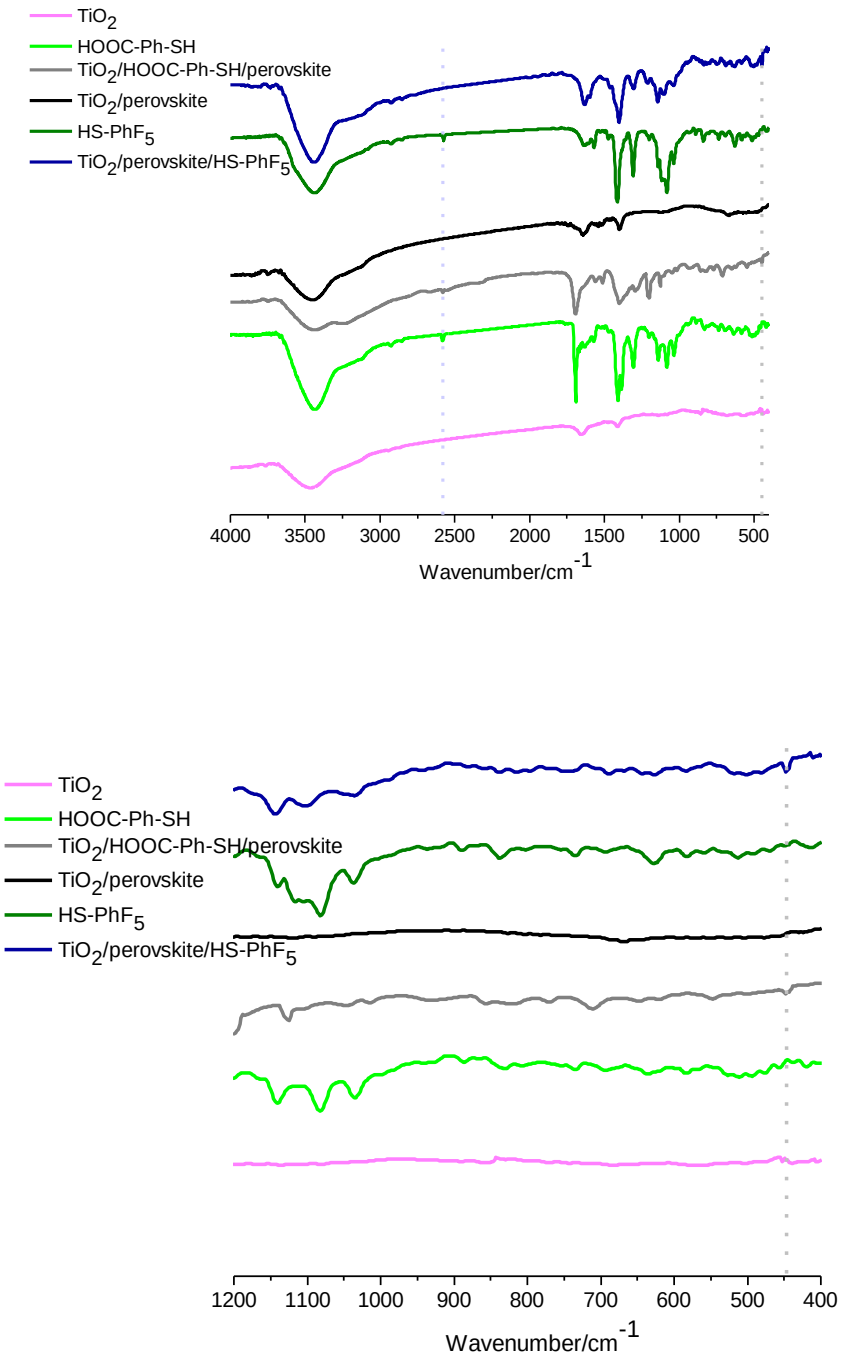


Fig. S5 The FTIR spectra of the films with different components and modifications.

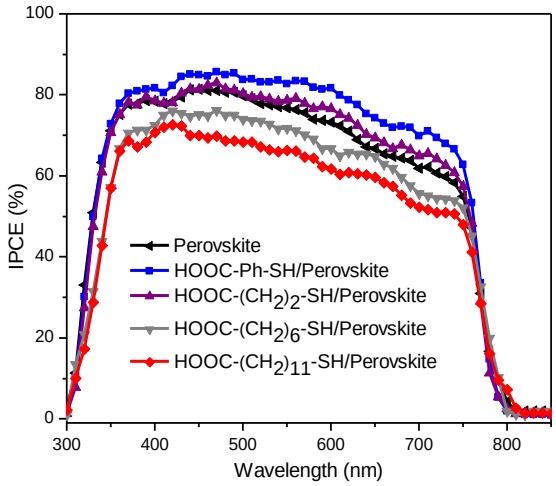


Fig. S6 The IPCE spectra of the devices.

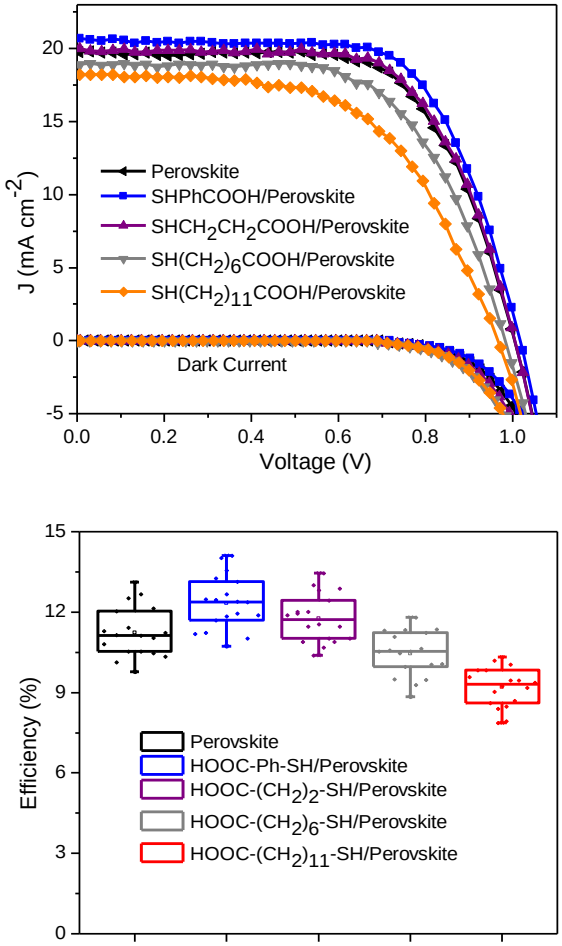


Fig. S7 The best I-V characteristics (top), comparison of the performance distributions of 18 individual devices (bottom) of perovskite and HOOC-R-SH/perovskite solar cells.

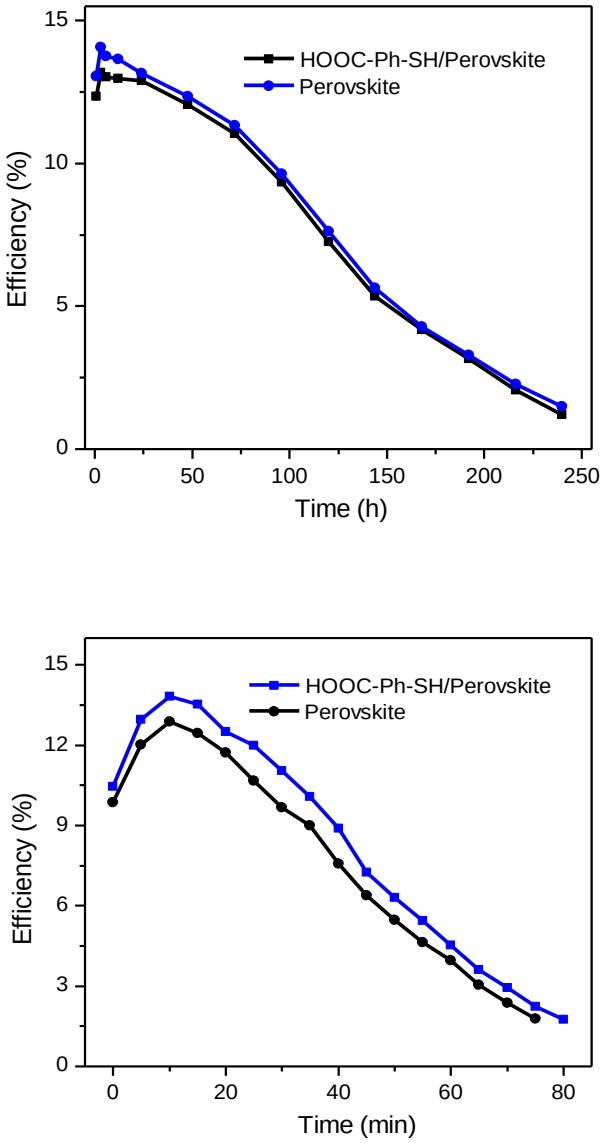


Fig. S8 The efficiency variation of the devices stored in air at room temperature with the humidity of 45% (top) and under illumination at AM 1.5 G (bottom).

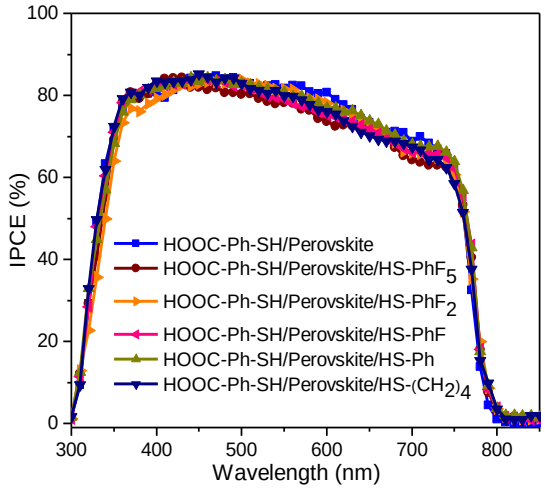


Fig. S9 The IPCE spectra of the devices.

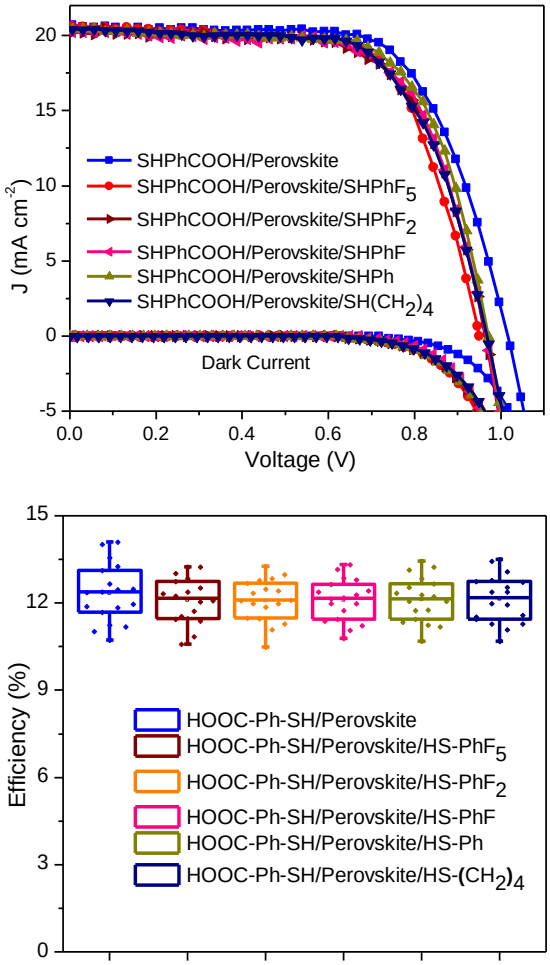


Fig. S10 The best I-V characteristics (top), comparison of the performance distributions of 18 individual devices (bottom) of HOOC-Ph-SH/perovskite and HOOC-Ph-SH/ perovskite/HS-R′.

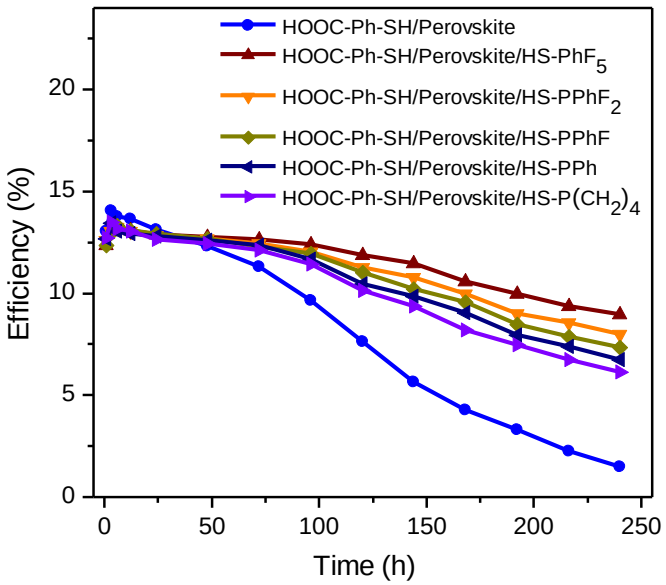


Fig. S11 The efficiency variation of the devices stored in air at room temperature with a humidity of about 45%.

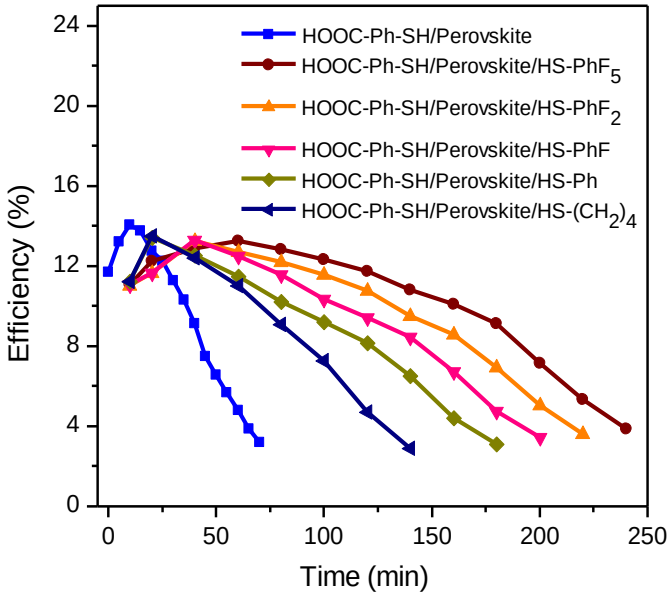


Fig. S12 The variation of the device efficiency under illumination at AM 1.5 G.

Table S1. Summary of photovoltaic parameters of cells with different modifications.

Dye	J_{sc}/mA·cm^{-2}	V_{oc}/V	*FF*/%	η/%	*Rs*/Ω·cm^{-2}	*Rsh*/Ω·cm^{-2}
Perovskite	19.81	1.00	66.43	13.18	8.95	1021.10
HOOC-Ph-SH/Perovskite	20.66	1.02	66.54	14.11	8.49	923.10
HOOC-$(CH_2)_2$-SH/Perovskite	20.08	1.01	66.38	13.45	8.64	1060.90
HOOC-$(CH_2)_6$-SH/Perovskite	19.04	0.98	63.18	11.80	9.77	1833.17
HOOC-$(CH_2)_{11}$-SH/Perovskite	18.28	0.97	57.71	10.32	11.59	734.01
HOOC-Ph-SH/Perovskite/HS-PhF_5	20.66	0.97	65.79	13.21	10.08	639.26
HOOC-Ph-SH/Perovskite/HS-PhF_2	20.58	0.97	65.85	13.22	9.18	733.38
HOOC-Ph-SH/Perovskite/HS-PhF	20.56	0.97	65.97	13.28	8.89	723.46
HOOC-Ph-SH/Perovskite/HS-Ph	20.56	0.97	66.07	13.30	9.54	493.05
HOOC-Ph-SH/Perovskite/HS-$(CH_2)_4$	20.58	0.97	66.11	13.32	9.39	996.53