Supporting Information

# Synergistic effects of bithiophene ammonium salt for high-performance perovskite solar cells

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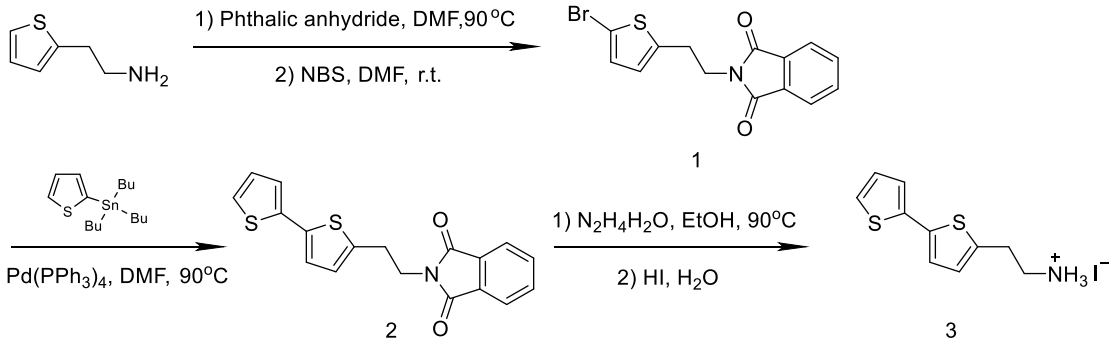
## 1. Experimental Procedures




**Scheme S1** Synthetic routes of the **2TEAI (3)**.

***2-(2-(5-bromothiophen-2-yl)ethyl)isoindoline-1,3-dione (1)***

To a solution of 2-(thiophene-2-yl)ethan-1-amine (20 g, 157 mmol) in DMF (150 mL) was added phthalic anhydride (23.1 g, 157 mmol). After stirring at 165 °C for 4 hs, NBS (28.0 g, 157 mmol) was added at 0 °C. The reaction mixture was kept at 0 °C for 5 hs and diluted with $CH_2Cl_2$, washed with saturated $NaHCO_3$ aqueous solution and water, and then dried over $Na_2SO_4$. After removing the solvent by evaporation, the crude product was purified by silica gel chromatography using petroleum ether/$CH_2Cl_2$ (1/2, V/V) as the eluent to give the desired product **1** as a white solid (31.2 g, 65.0% yield). $^1$H NMR (400 MHz, $CDCl_3$, rt): 7.85 (dd, J = 5.4, 3.0 Hz, 2H), 7.72 (dd, J = 5.5, 3.0 Hz, 2H), 6.85 (d, J = 3.7 Hz, 1H), 6.63 (d, J = 3.7, 1.0 Hz, 1H), 3.93 (m 2H), 3.19 - 3.12 (m, 2H).

***2-([2,2'-bithiophen]-5-yl)ethan-1-aminium iodide (3)***

To a solution of compound **1** (10 g, 29.7 mmol) and tributyl(thiophene-2-yl)stannane (14.84 g, 29.7 mmol) in toluene/DMF (4/1, V/V, 200 mL) was added $Pd(PPh_3)_4$ (1.60 g, 1.40 mmol) under a nitrogen atmosphere. After stirring at 120 °C for 8 hs, the reaction mixture was diluted with hexane/ethyl acetate (1/1, V/V), washed with water, and then dried over $Na_2SO_4$. After removing the solvent by evaporation, the crude product was purified by silica gel chromatography using hexane/ethyl acetate (3/1, V/V) as the eluent to give the desired product as a pale yellow solid (8.65g, 85.9% yield), getting the product **2**. To a solution of compound **2**, 100 ml HI solution was added, after stirring for 1 h, yellow solid was obtained. Recrystallizing three times with DMF, product **3** was obtained (5.78 g, 67.2%). $^1$H NMR (400 MHz, DMSO-*d6*) δ 7.80 (s, 3H), 7.50 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.25 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.18 (d, *J* = 3.7 Hz, 1H), 7.08 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.94 (d, *J* = 3.6 Hz, 1H), 3.08 (m, 4H).

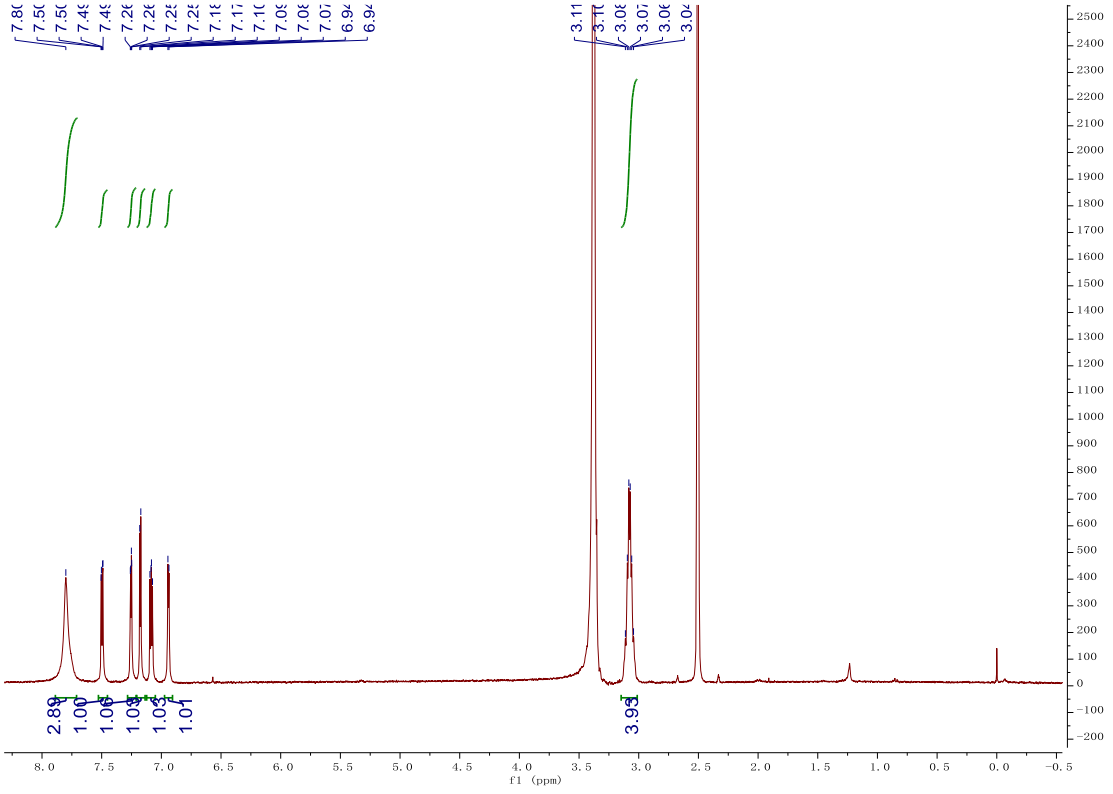


**Fig. S1** $^{1}$H NMR spectrum of **2TEAI** (**3**) in DMSO-*d6*.

## 2. Results and Discussion

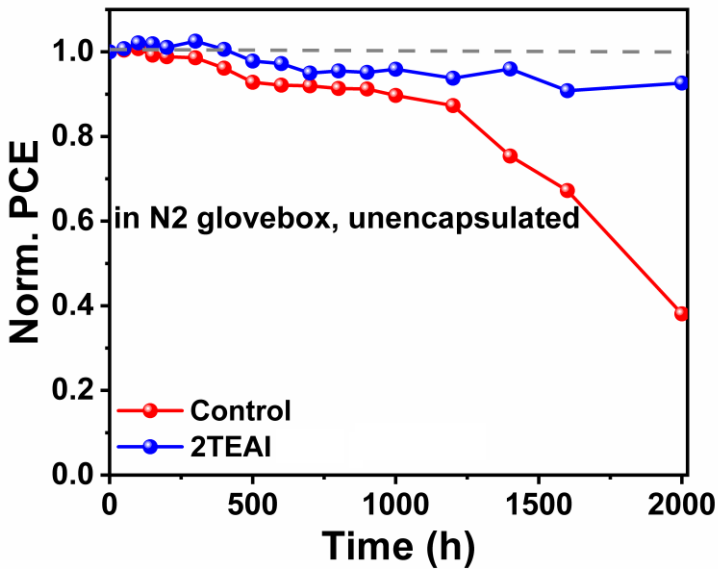



**Fig. S2** Long-term stability of the devices with and without **2TEAI** modification, which

were stored in an $N_2$ glovebox without encapsulation.

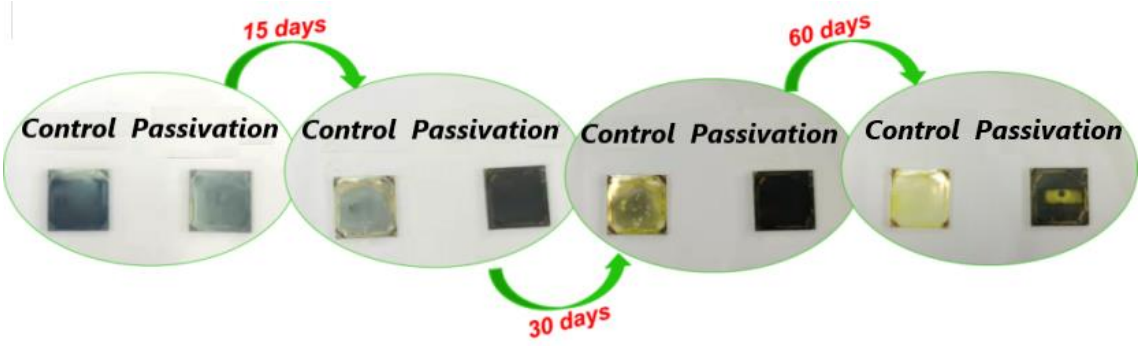



**Fig. S3** The degradation behavior of the control device and **2TEAI** modified device in the ambient air environment.

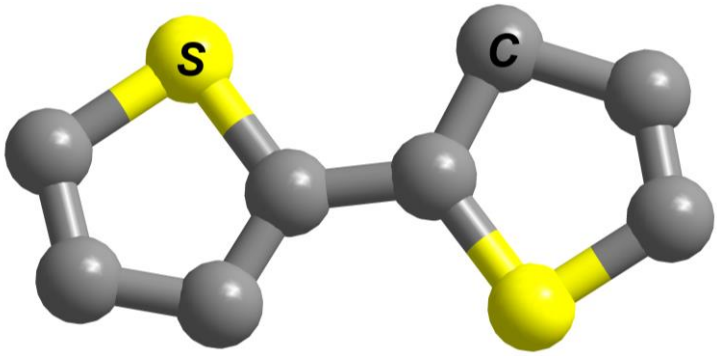



**Fig. S4** The molecular structure of **2T**, the H-bond had been omitted for clarity.

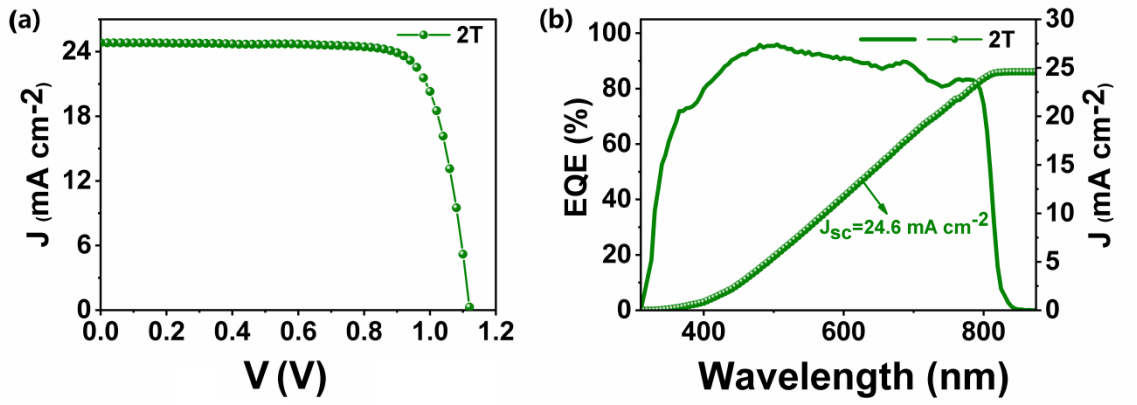



**Fig. S5** Device performance. (a) *J-V* characteristics and (b) EQE spectra of the **2T**-modified PVSCs.

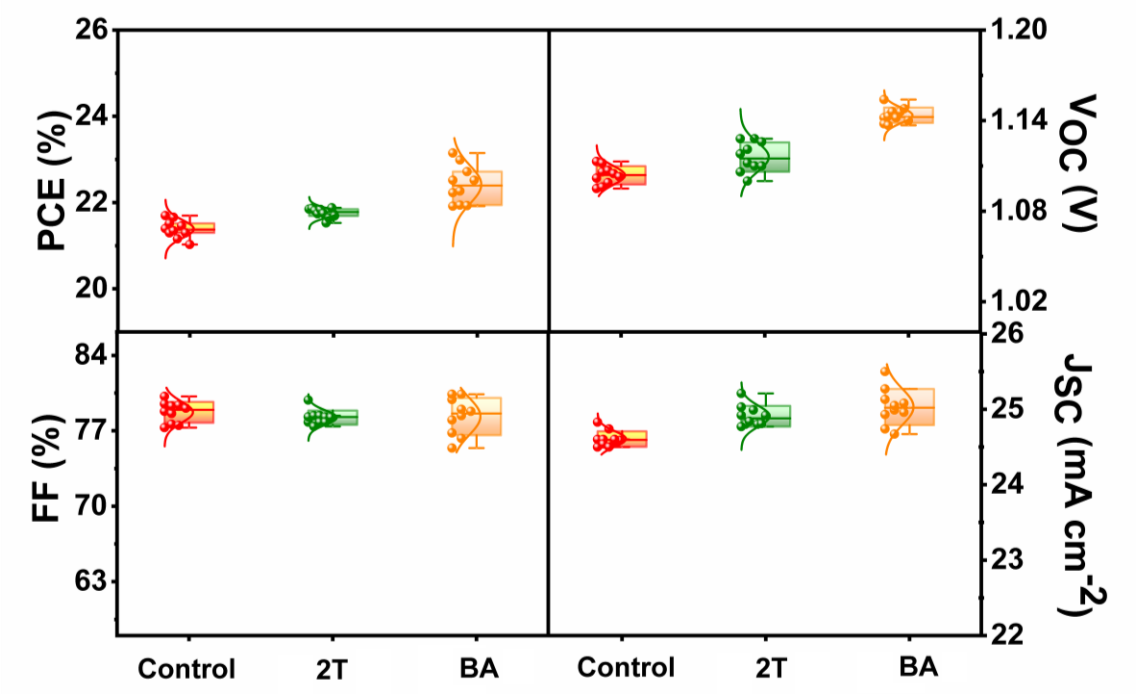



**Fig. S6** PCE, *Voc*, *FF*, and *Jsc* distribution statistics for 30 devices (10 control devices, 10 **2T**-modified devices, and 10 **BAI**-modified devices).

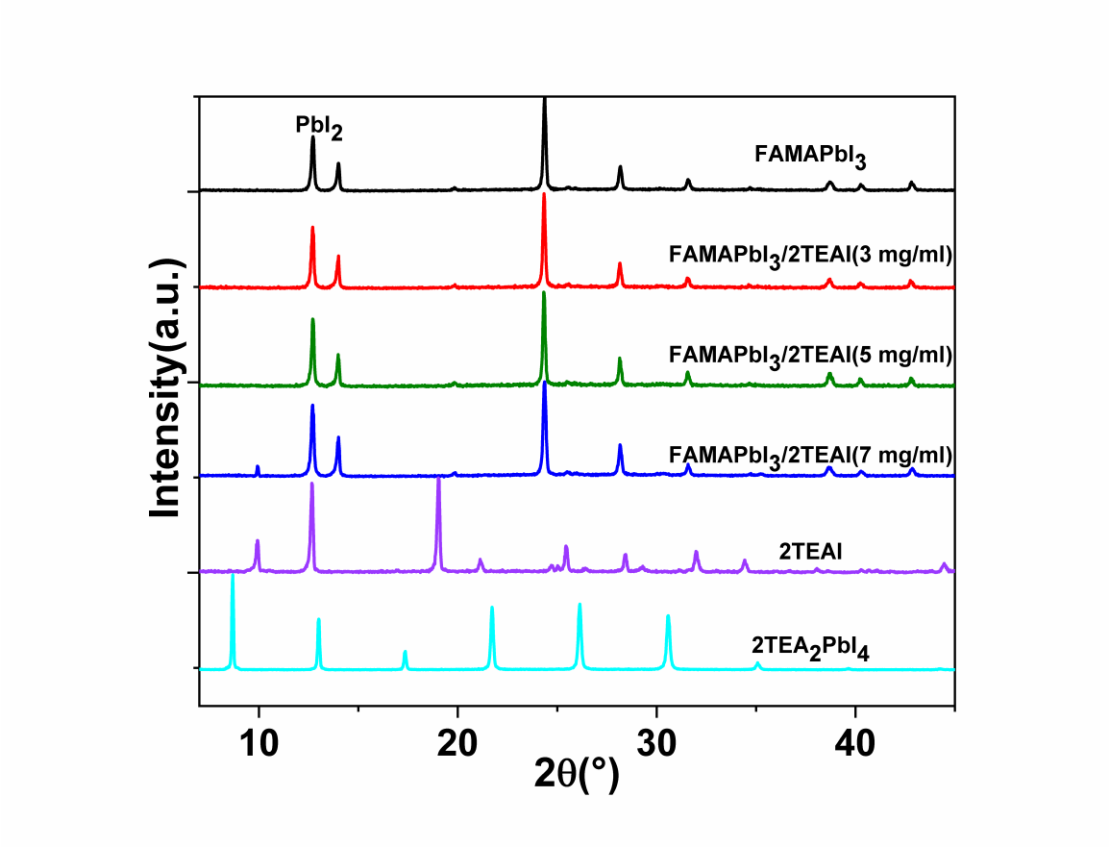



**Fig. S7** XRD patterns of perovskite films before and after **2TEAI** treatment. The diffraction patterns of the **$(2TEAI)_2PbI_4$** film are also shown.

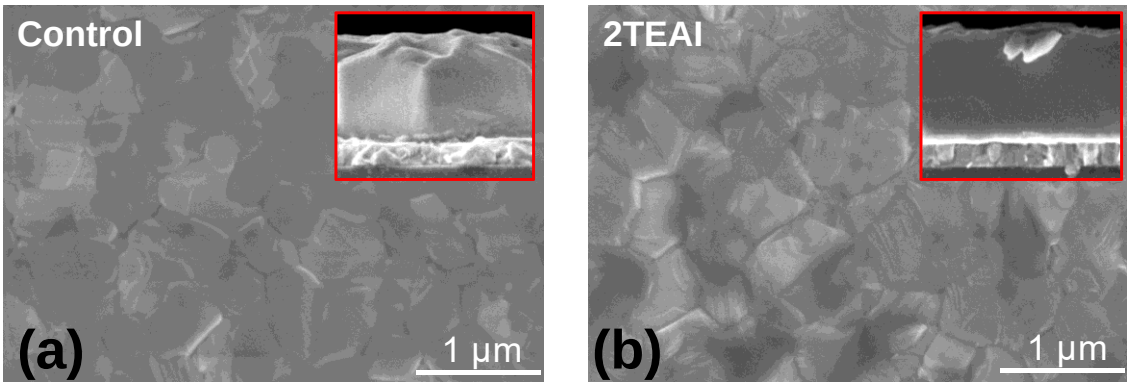



**Fig. S8** Cross-sectional SEM images of perovskite solar cells with and without **2TEAI** modification.

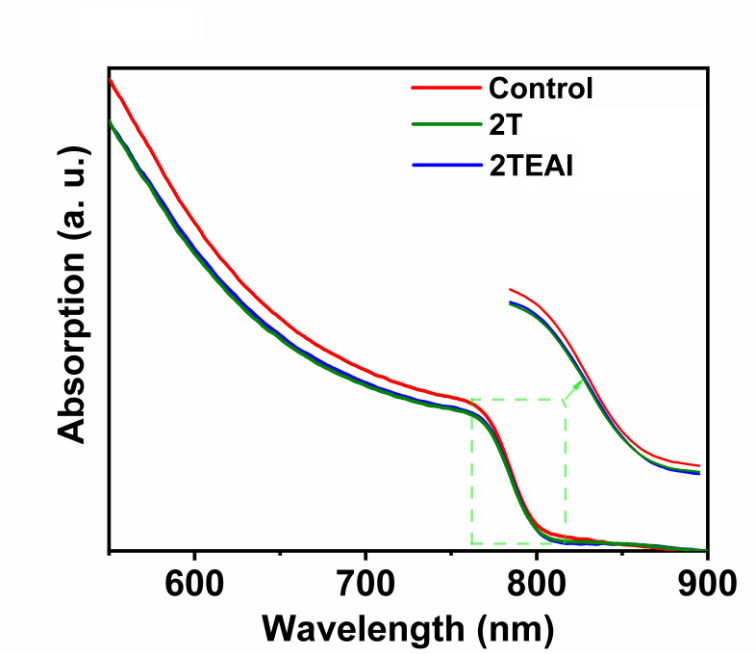



**Fig. S9** UV-vis spectra of the control, **2T**-modified, and **2TEAI**-modified perovskite films.

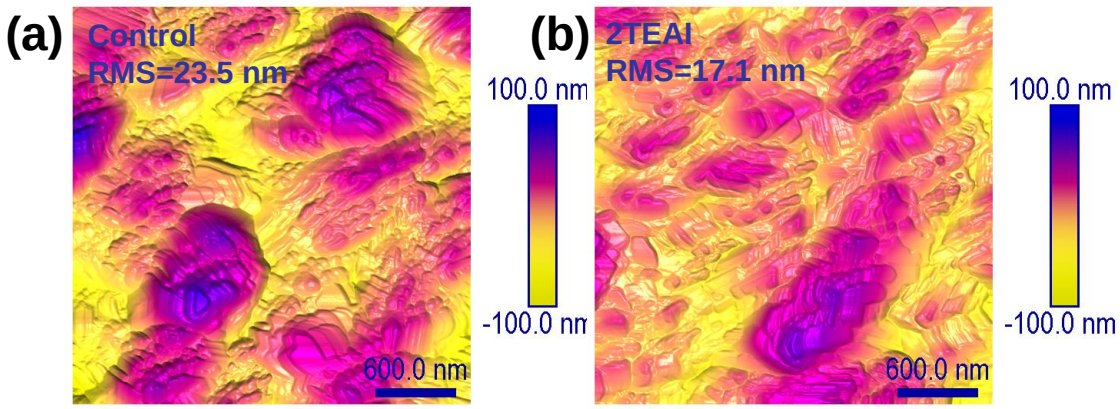



**Fig. S10** AFM images of control and **2TEAI**-modified perovskite films.

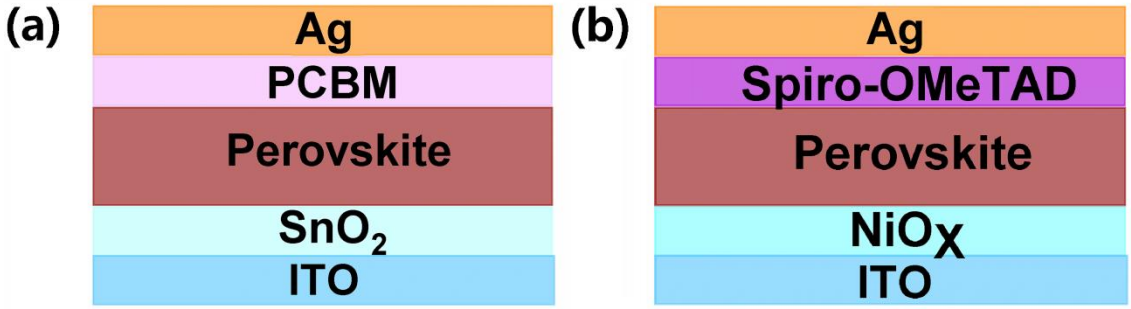



**Fig. S11** The device architecture used for SCLC measurements. (a) the electron-only device; (b) hole-only device.

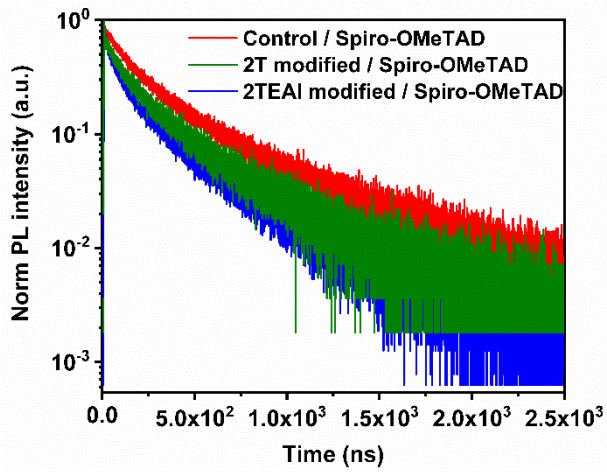



**Fig. S12** Time-resolved PL at the perovskite films with and without **2TEAI/2T** modification.

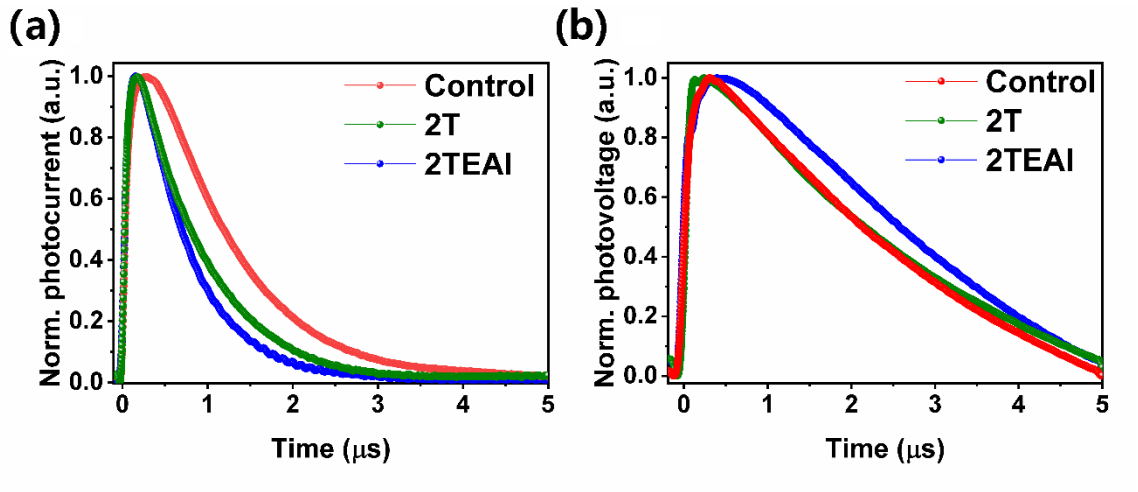



**Fig. S13** (a) TPC decay kinetics of PVSCs with and without **2TEAI/2T** modification. (b) TPV decay kinetics of PVSCs with and without **2TEAI/2T** modification.

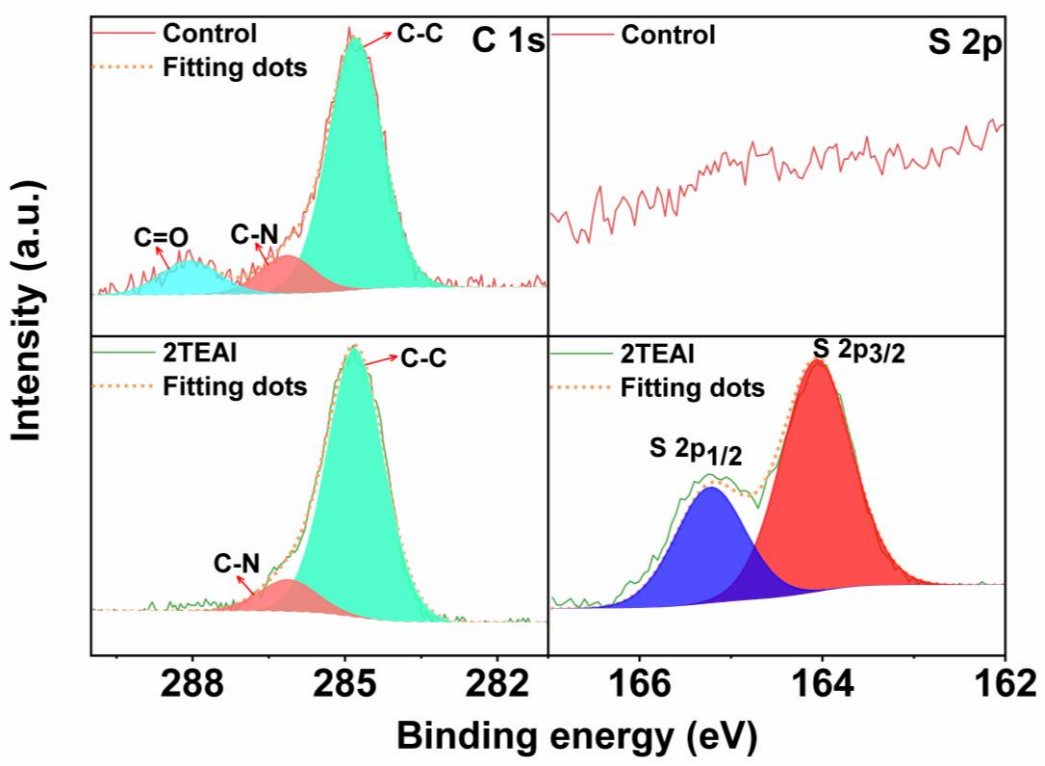



**Fig. S14** The high-resolution XPS spectra of the C 1s and S 2p of perovskite films without and with **2TEAI** modification.

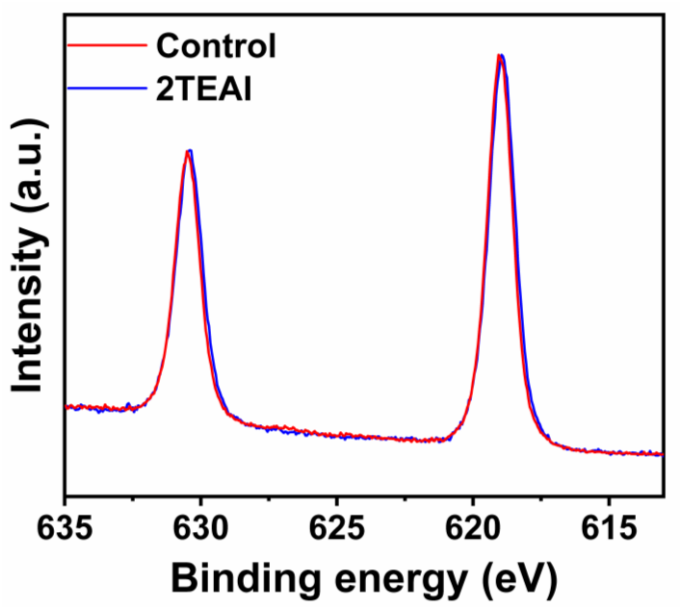



**Fig. S15** The high-resolution XPS spectra of the I 3d of perovskite films without and with **2TEAI** modification.

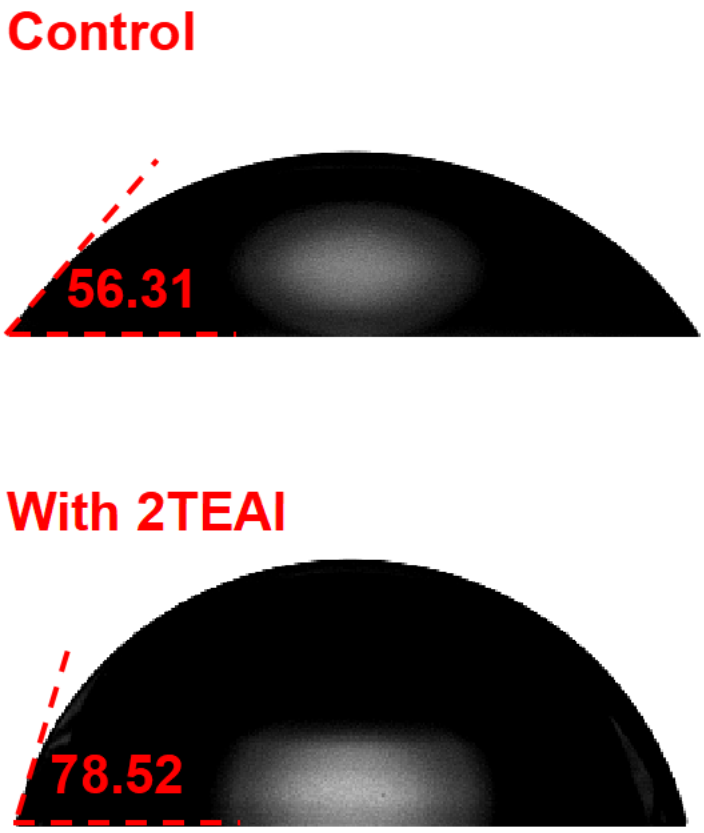



**Fig. S16** The contact angles between the perovskite precursor solutions (for the control and with **2TEAI**, respectively) and the substrates.

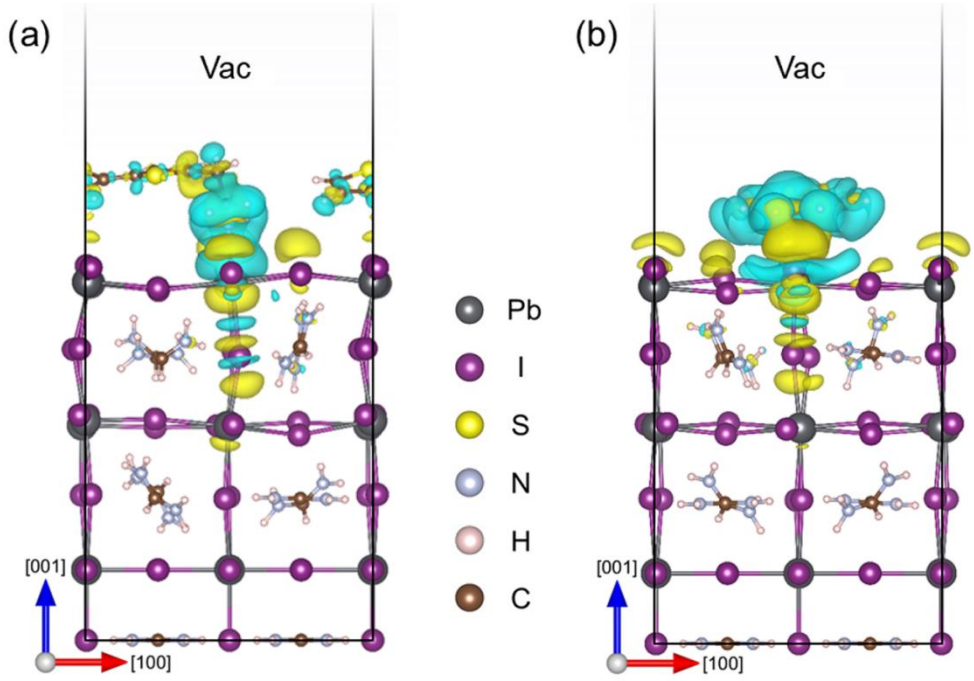



**Fig. S17** The iso-surface plots of differential charge distribution of the $FAPbI_3$ film surface with (a) **2TEAI** molecule adsorption and (b) **2T** molecule adsorption. These pictures are produced by VESTA. [1]

## References

1 K. Momma, F. Izumi, *J. Appl. Crystallogr.,* 2008, **41**, 653.