Electronic Supplementary Information for

Improving the Performance and Stability of Perovskite Solar Cells via Surface Passivation of Phthalimide N-alkylammonium Iodides

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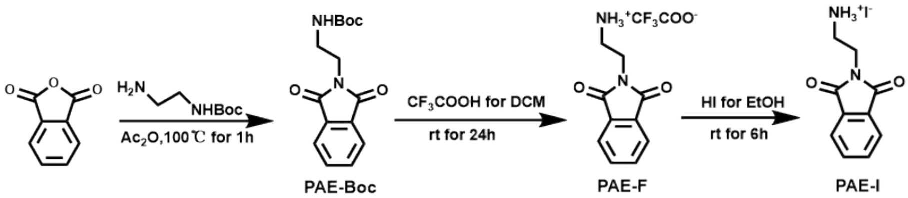
1. Experiments

1.1. Materials and measurements

Hydroiodic acid (HI) (55-57 wt.% in water, stabilized with 1.5 wt.% hypophosphorous) was purchased from Aladdin. *N*-Boc-Ethylenediamine (97%) was purchased from Bidepharm. Phthalic anhydride (PA) (99%) was purchased from Innochem. The SnO_2 colloid precursor was purchased from Alfa Aesar (Tin (IV) oxide, 15% in H_2O colloidal dispersion). Lead iodide (PbI_2, 99%), formamidinium iodide (FAI), methyl ammonium chloride (MACl), bis(trifluoromethane)-sulfonimide lithium salt (Li-TFSI), and 4-*tert*-butylpyridine (4-TBP) were purchased from Xi'an Polymer Light Technology Crop., N, N-dimethylformamide (DMF, anhydrous, 99.8%), dimethylsulfoxide (DMSO, anhydrous, 99.8%), Chlorobenzene (CB, anhydrous, 99.8%) and isopropanol (IPA, anhydrous, 99.5%) were obtained from Acros. 2,2',7,7'-Tetrakis[*N*,*N*-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD) was purchased from Shenzhen Feiming Science and Technology Co., Ltd..

1.2. Material Synthesis



Scheme S1. Synthetic route to the PAE-I.

Synthesis of Boc-protected PAE-Boc (1): A 100 mL rb flask was charged with phthalic anhydride (4.069 g, 27.5 mmol) and *N*-Boc-ethylenediamine (17 g, 106.1 mmol) in 26 mL of acetic acid. The reaction was kept stirring at 100 °C for 1 h. After completion of the reaction (monitored by TLC), the mixture was concentrated under reduced pressure to give a residue which was purified by column chromatography using DCM/ethyl acetate 1:10 mixture as eluent to afford PAE-Boc as a white solid. Yield: 5.59 g (19.25 mmol, 72%).

Deprotection of PAE-F salt (2): Free PAE-I amine was obtained by stirring the protected PAE-Boc (200 mg, 0.69 mmol) and trifluoroacetic acid (7.86 g, 68.9 mmol) in 20 mL DCM solution. During the process of reaction, more and more powder deposits were precipitated out. The powders were filtered, washed with ethyl acetate. And the white filter residue was put in a 65 °C high vacuum overnight. Yield: 194 mg (0.64 mmol, 92%).

Salt-formation of PAE-I salt (3): The dry solid (578 mg, 1.89 mmol) was redissolved in 15 mL methanol and 6.70 g of 57% HI solution was added in a nitrogen atmosphere and protected from light. After stirring the mixture for 6 hours, solid amine iodine precipitated as a yellowish solid. The solids were filtered and washed with ether. The resulting yellow filter residue is placed in a 65 °C high-vacuum overnight. Yield:

560 mg (1.76 mmol, 94%)

1.3. Preparation of Perovskite Precursor Solution

For FAPbI3 perovskite precursor solution, the powder of PbI_2 (1.5M) was dissolved in a mixed solvent of DMF: DMSO with a volume ratio 9:1, and the mixed powders of FAI: MACl (90 mg: 9 mg) were dissolved in 1 mL IPA. When preparing the target devices, different concentrations of PAE-I were pre-dissolved in IPA solution. The solution was stirred at 60 °C for 2h. The whole process was carried out in the N_2 glove box.

1.4. Device Fabrication

The ITO/glass substrates were cleaned in an ultrasonic cleaner with detergent, deionized water, acetone, and isopropanol for 15 min each as well as dried in an oven at a temperature of 75 °C. For depositing the electron transport layers, the ITO substrates were further treated by a UV-O_3 for 12 min. The diluted SnO_2 colloid precursor (3 wt%, diluted by water) was spin-coated at 3000 rpm for 30 s onto the ITO substrates, and then annealed at 120 °C for 10 min and at 150 °C for 20 min. Before device fabrication, all the SnO_2/ITO substrates were treated by UV-O_3 for 12 min. For fabricating the perovskite films. PbI_2 (25 μL) solvent was spin-coated onto SnO_2 at 1500 rpm for 30 s, and annealed at 70 °C for 1 min, then cooled to room temperature, a solution of FAI/MACl (75 μL) was dynamic spin-coated onto the PbI_2 at spin rate of 1800 rpm for 30 s, and annealed at 90 °C for 1 min, and the perovskite precursor film was taken out from the nitrogen glove box to ambient air for thermal annealing at 150 °C for 15min in humidity conditions (30-40 % humidity). For the target devices, different concentrations of PAE-I/IPA solution were dropped on the $FAPbI_3$ precursor films then spin-coated at 5000 rpm for 30 s and further annealed at 100℃ for 10 min. Next, the hole transport layers precursor was spin-coated at 4000 rpm for 30 s, which contains 72.3 mg of Spiro-OMeTAD, 17.5 μL of Li-TFSI stock solution (52 mg of Li-TFSI in 100 μL of acetonitrile) and 28.8 μL of TBP. Finally, an 80 nm thick gold electrode was thermally evaporated on the film under a vacuum of ∼10−4 Pa.

1.5. Characterization

^{1}H NMR and ^{13}C NMR spectra for the ammonium salt were recorded on a Nuclear Magnetic Resonance Spectrometer (AVANCE III). All *J–V*, *I–V* curves and steady-state power output of the devices were recorded using a Keithley 2400 Source Meter under simulated AM 1.5G illumination (100 mW cm^{-2}) with an Oriel Sol3A simulator (Newport), and the light intensity had been accurately calibrated with a National Renewable Energy Laboratory (NREL)-certified silicon reference cell. The external quantum efficiency (EQE) was measured using an EQE measurement system (Newport). The absorption spectra were obtained by using a UV-Vis spectrophotometer (Perkin-Elmer, Lambda 365). By using a UV/V/NIR Fluorescence Spectrometer (Edinburgh Instruments, FLS980), the PL spectra were obtained for perovskite films with an excitation wavelength of 460 nm, and the TRPL spectra were measured by Laser excitation at 375 nm. X-ray diffraction (XRD) patterns for perovskite films were performed on a Rigaku Mini Flex diffractometer at room temperature. The images of scanning electron microscopy were obtained by on the Field Emission Scanning Electron Microscope (SU-8010). The root-mean-square (RMS) roughness of perovskite film was investigated by Scanning Probe Microscope (Bruker, Dimension Icon).

2. Other Related Figures

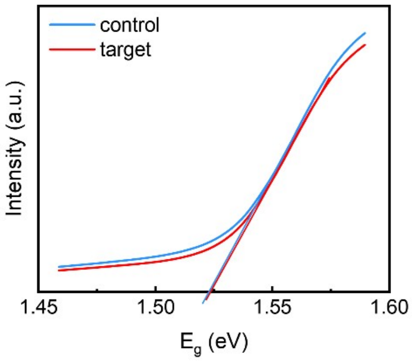


Fig. S1. Tauc plots of control and target perovskite films.

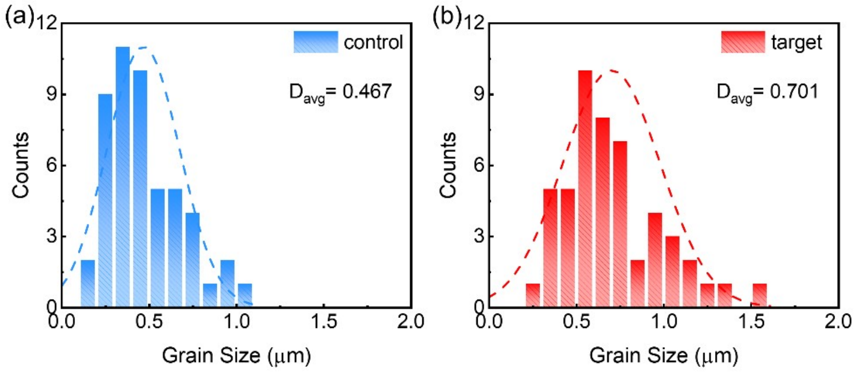


Fig. S2. The statistical distribution histograms of perovskite grain sizes without (a) and with (b) PAE-I passivation obtained from the top-view SEM images.

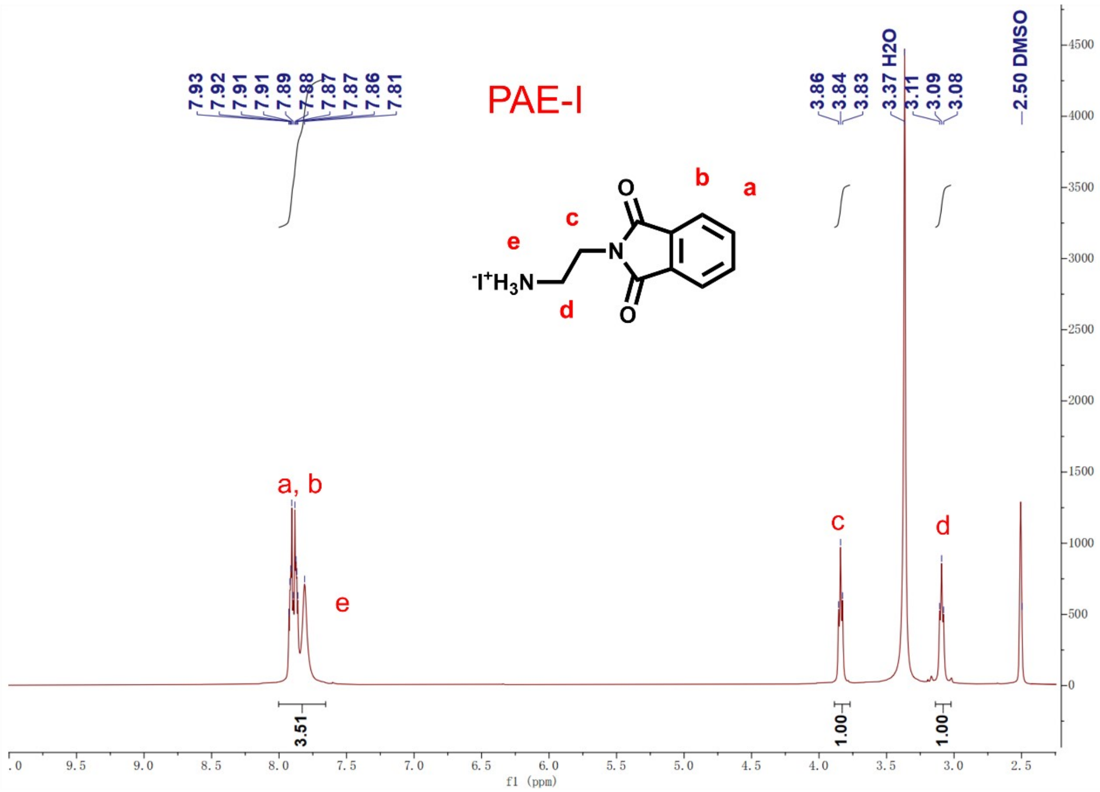


Fig. S3. ^1H NMR spectra of PAE-I (0.05M) in DMSO-d_6.

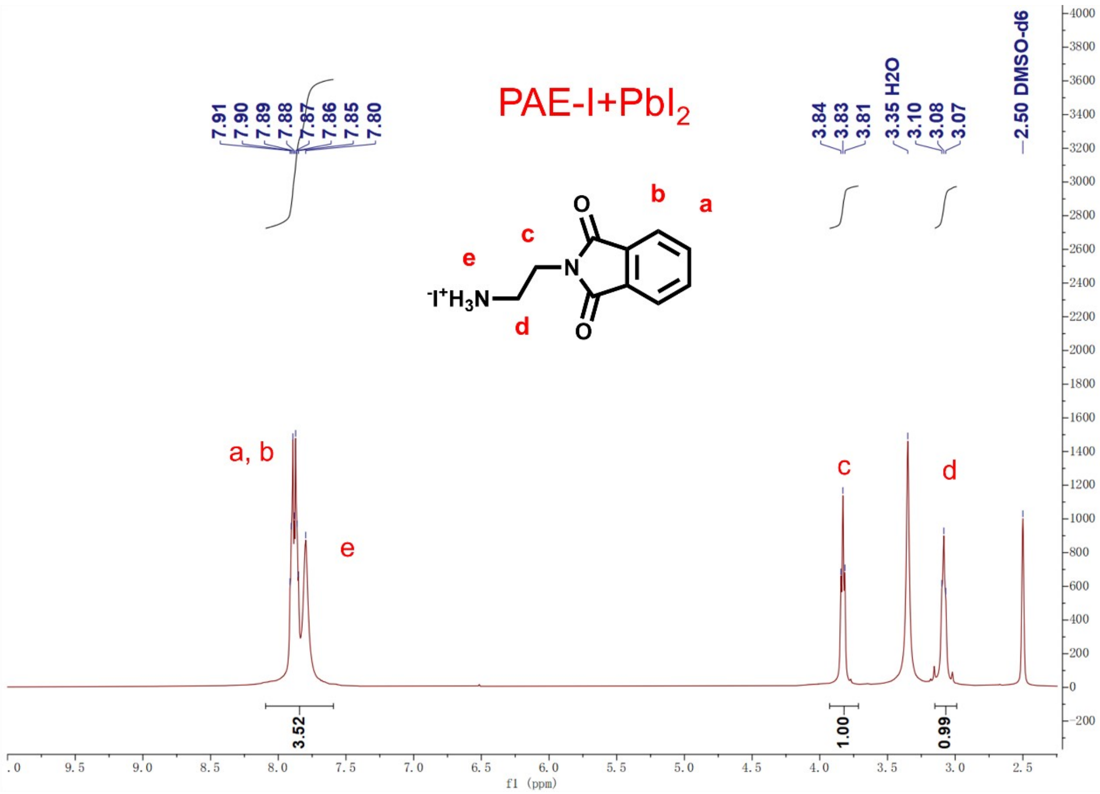


Fig. S4. ^1H NMR spectra of PbI_2 (0.05M) and PAE-I (0.05M) in DMSO-d_6.

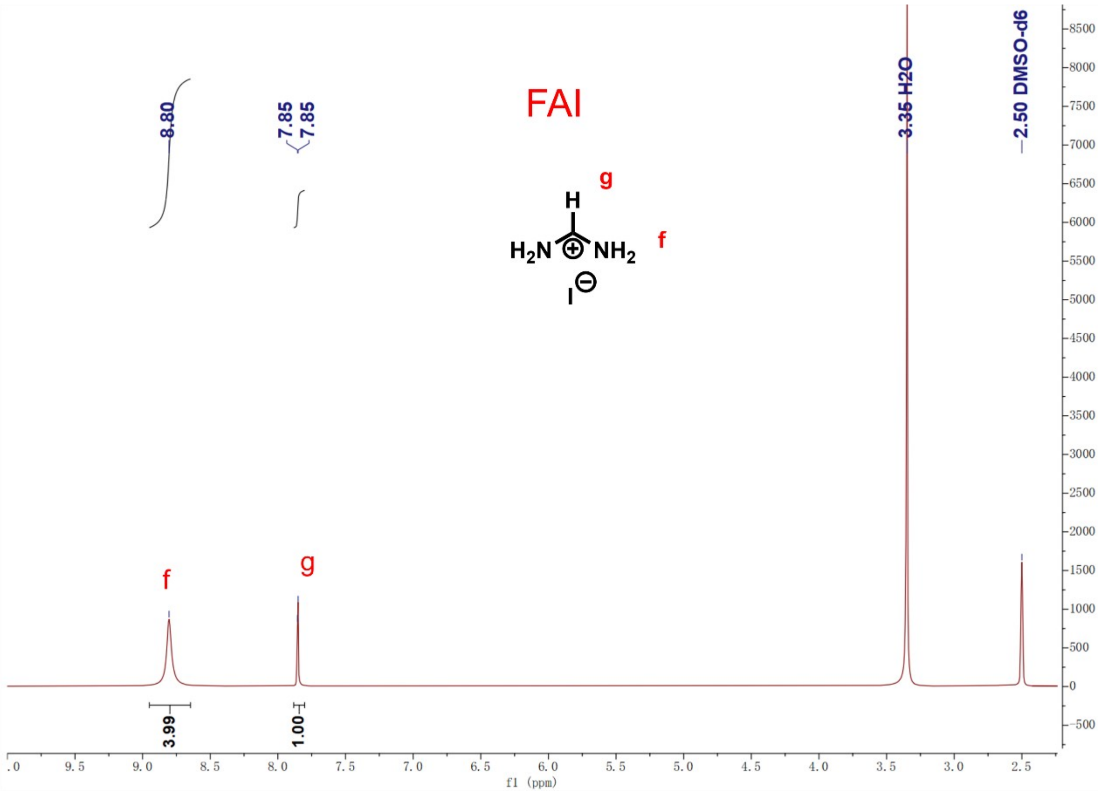


Fig. S5. ^1H NMR spectra of FAI (0.05M) in DMSO-d_6.

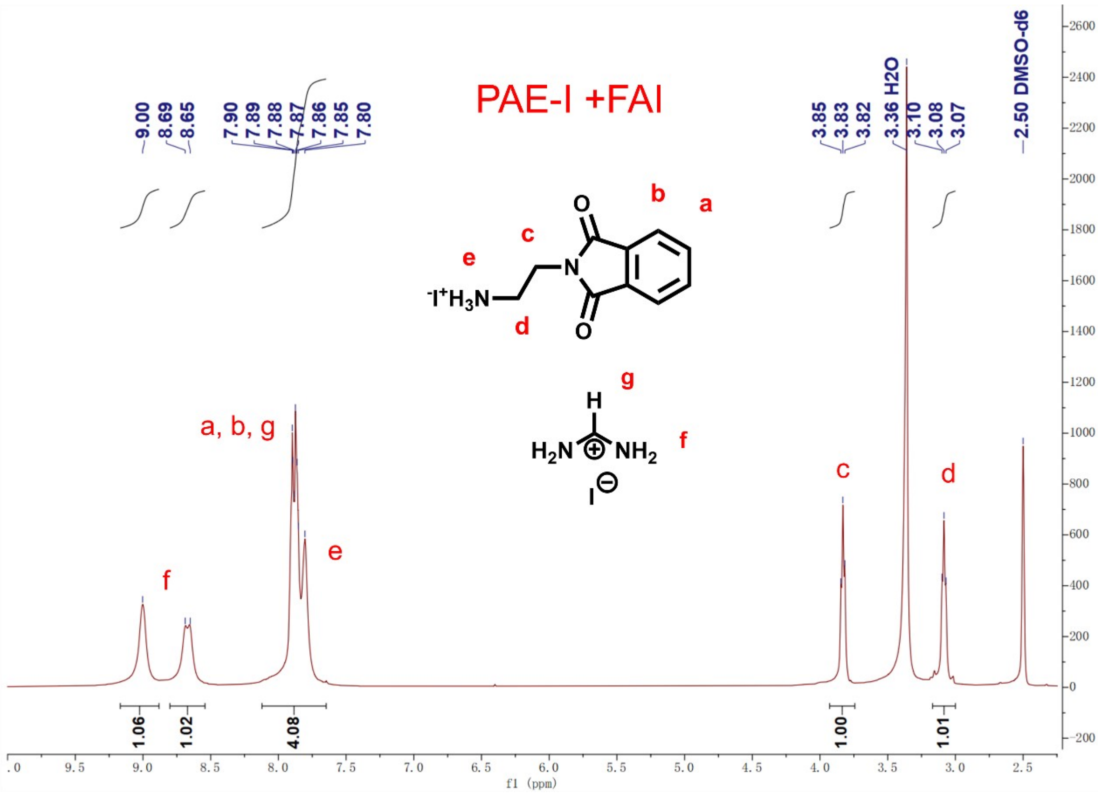


Fig. S6. ^1H NMR spectra of PAE-I (0.05M) and FAI (0.05M) in DMSO-d_6.

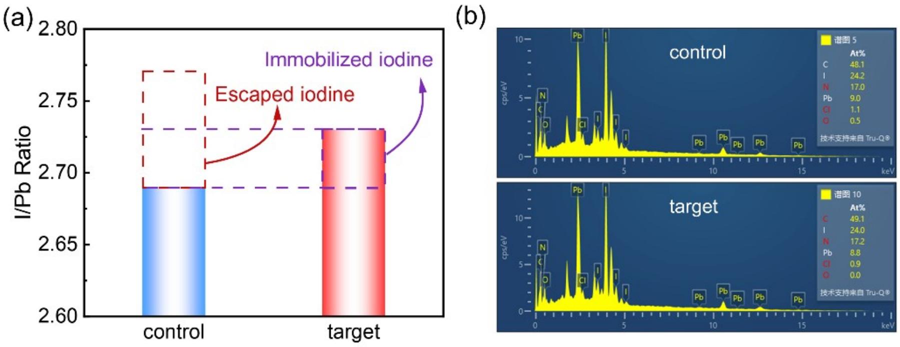


Fig S7. (a) I/Pb ratio gotten by EDS of perovskite films with/without PAE-I; (b) EDS spectra of the perovskite film with and without PAE-I-treated.

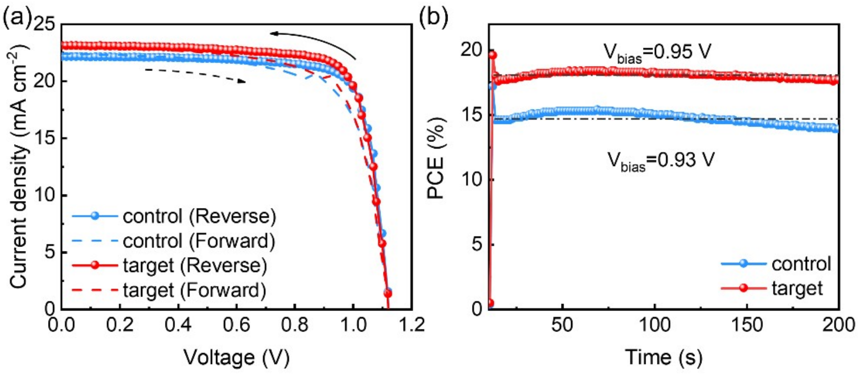


Fig. S8. (a) Reverse and forward *J-V* curves of the PSCs without and with PAE-I-treated; (b) the steady-state device based on target and control at the maximum power point for 200 s.

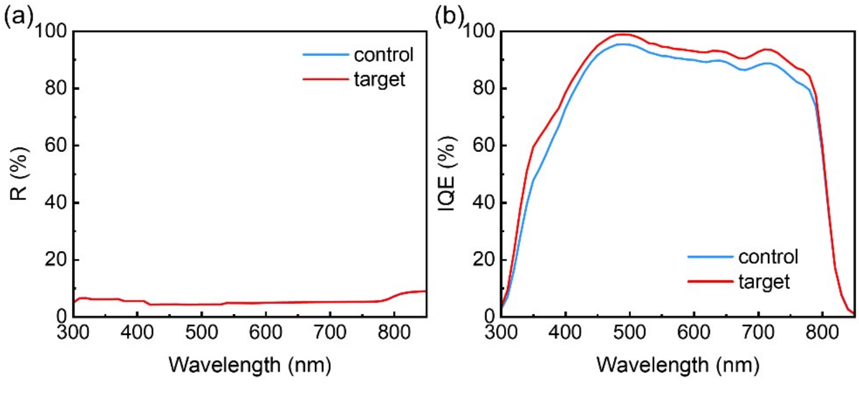


Fig. S9. (a) Reflectance curves of the PSCs without and with PAE-I-treated; (b) IQE curves calculated by the reflectance and EQE curves.

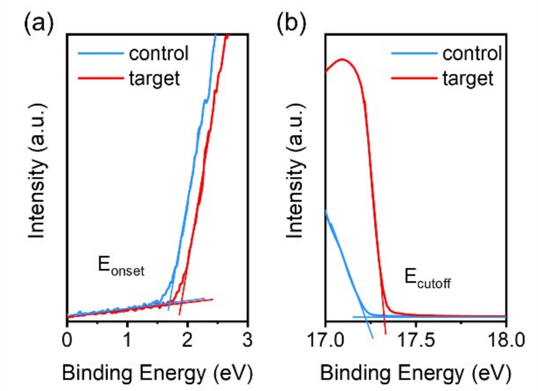


Fig. S10. (a), (b) UPS spectra of secondary electron cutoff and valence band region for the control film and the target.

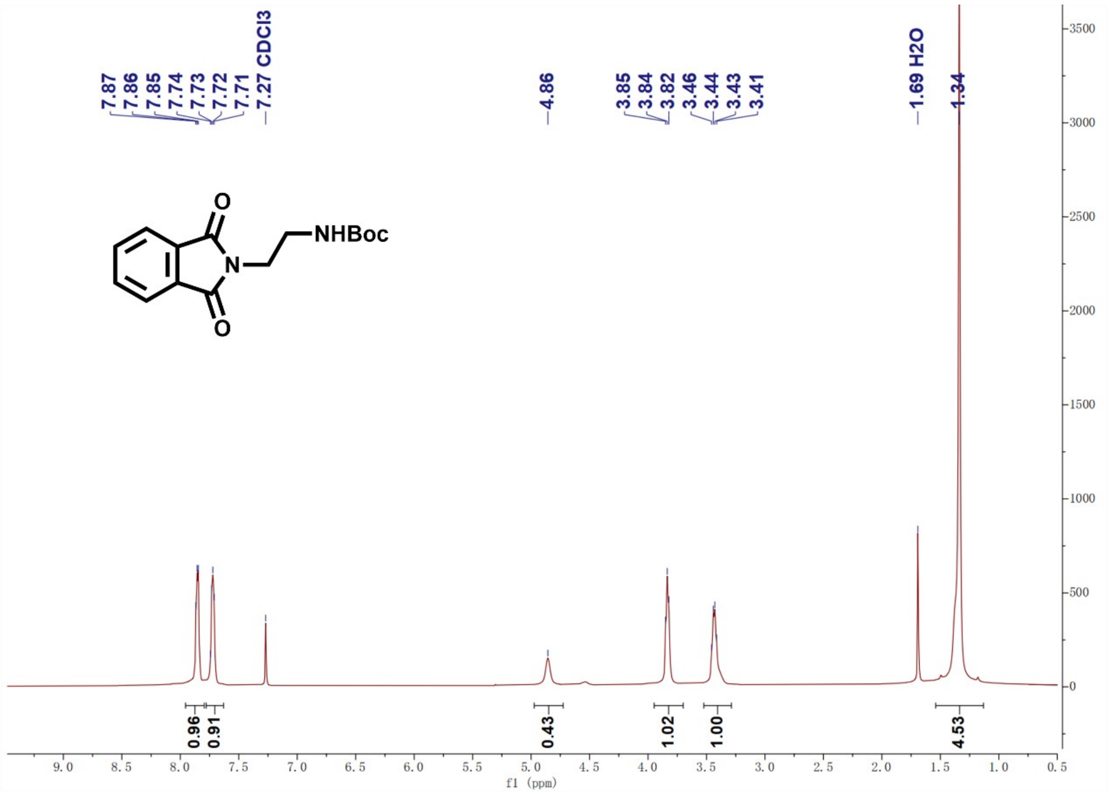


Fig. S11. ^{1}H NMR spectrum of **PAE-Boc** in $CDCl_3$.

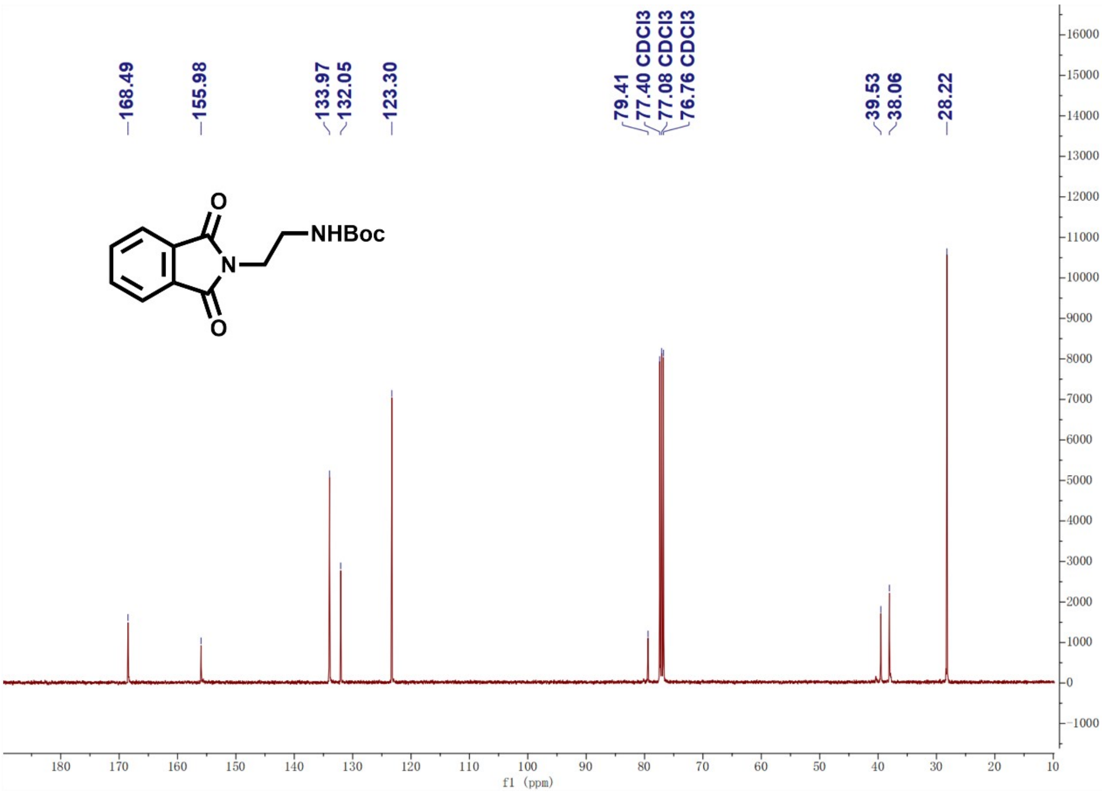


Fig. S12. ^{13}C NMR spectrum of **PAE-Boc** in CDCl$_3$.

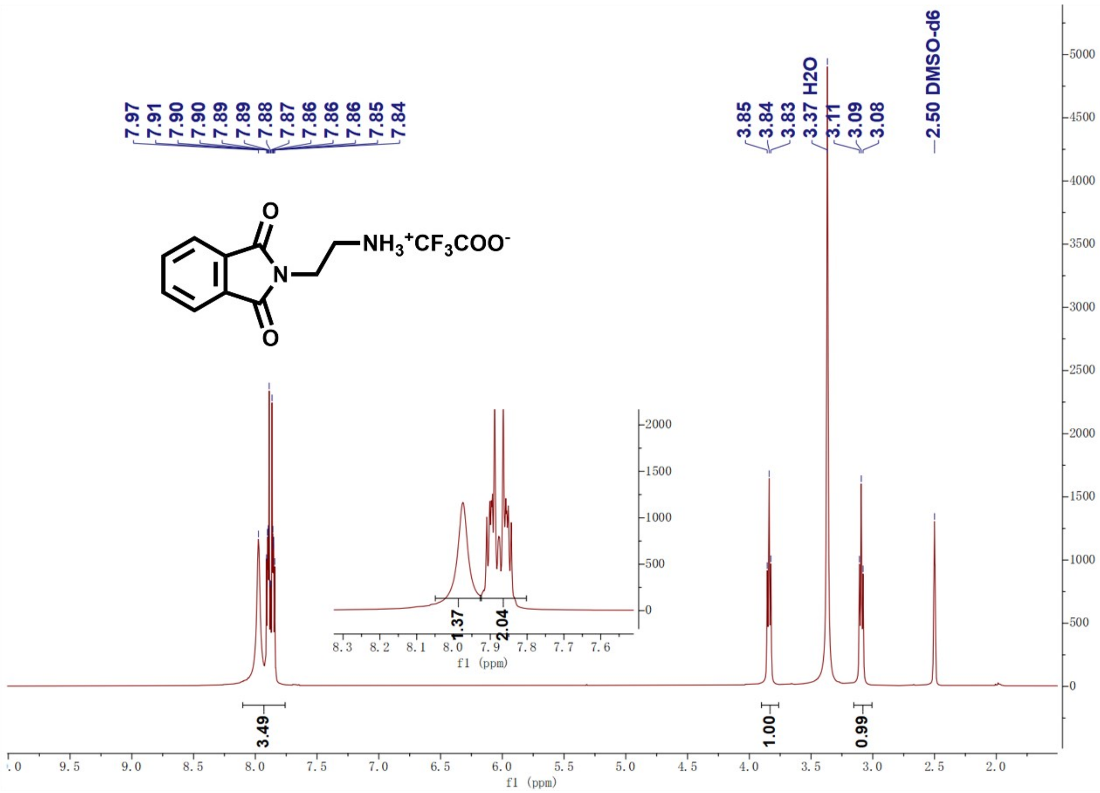


Fig. S13. ^{1}H NMR spectrum of **PAE-F** in DMSO-*d*$_6$.

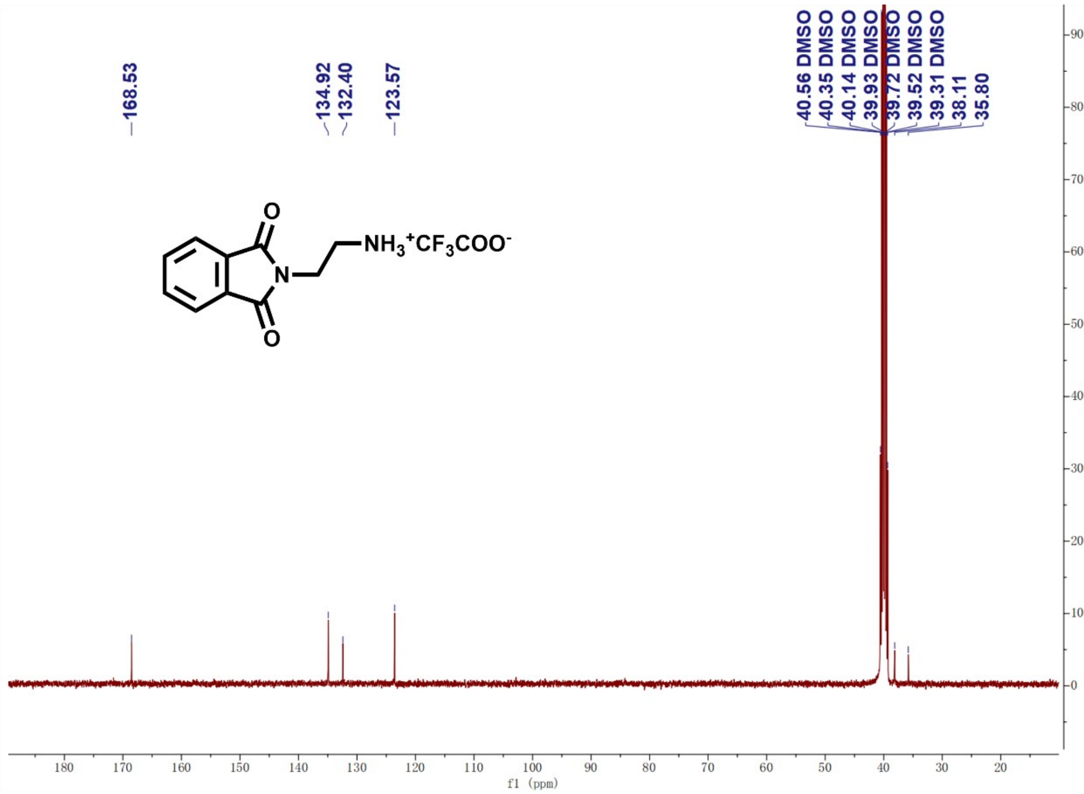


Fig. S14. ^{13}C NMR spectrum of **PAE-F** in DMSO-d_6.

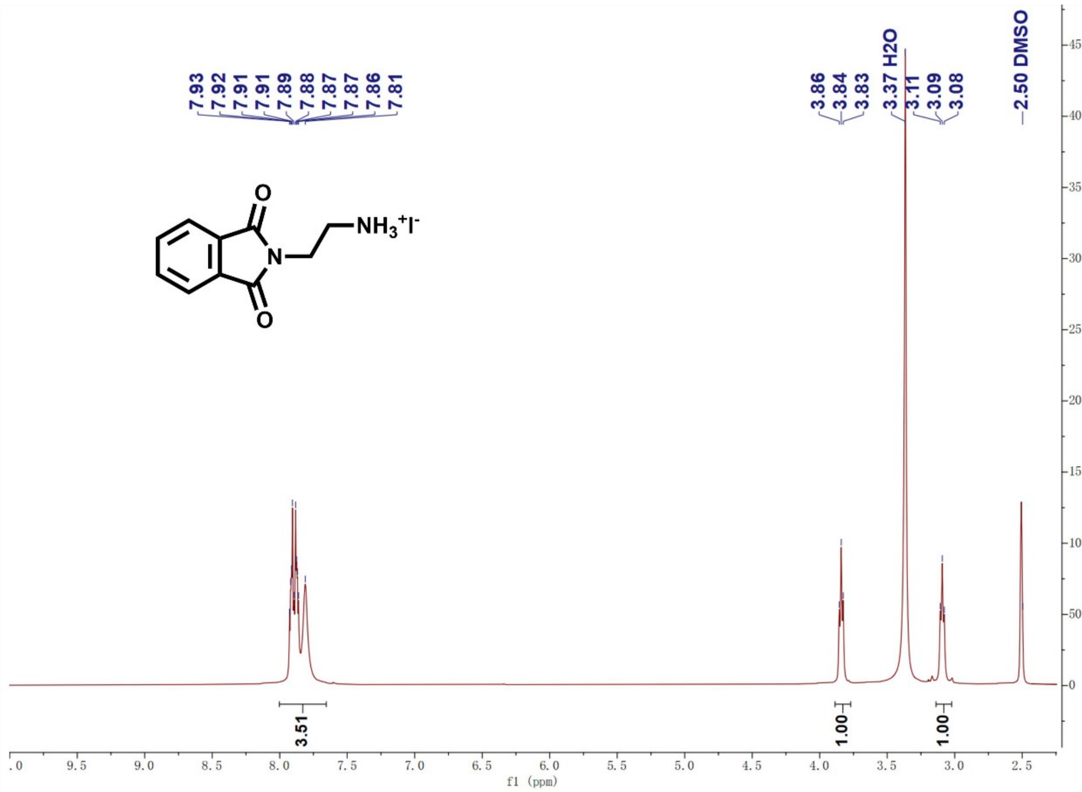


Fig. S15. ^{1}H NMR spectrum of **PAE-I** in DMSO-d_6.

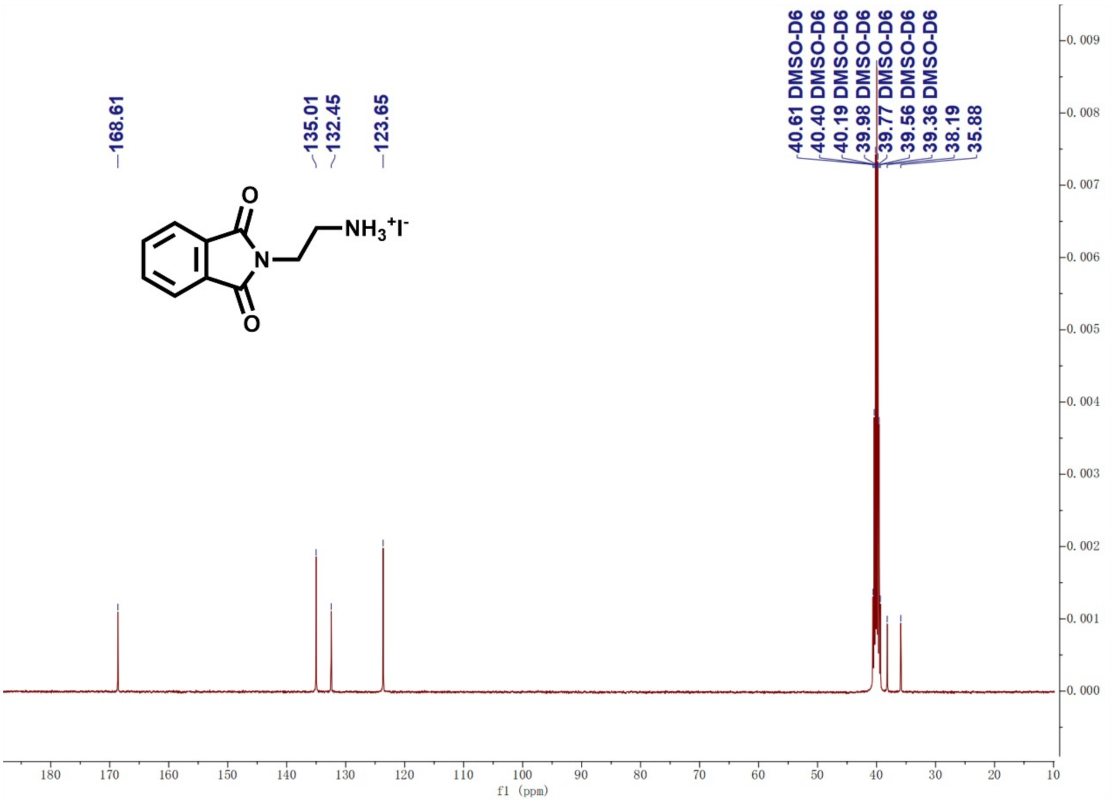


Fig. S16. ^{13}C NMR spectrum of **PAE-I** in DMSO-d_6.

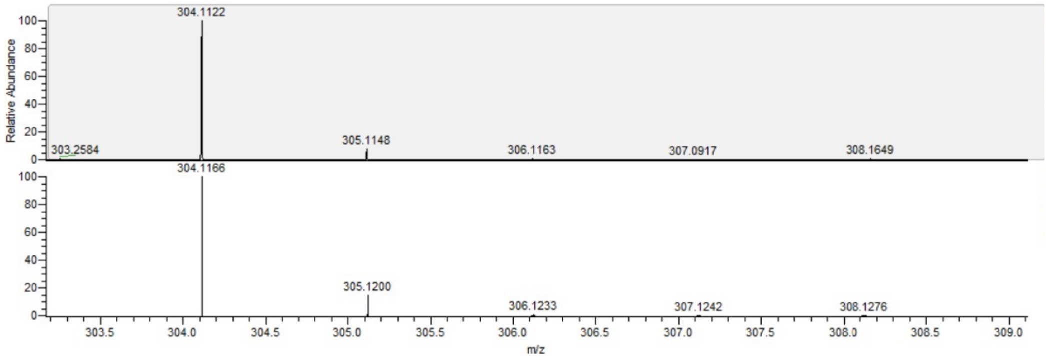


Fig. S17. ESI-HR-MS spectrum of **PAE-I**.

3. Other Related Tables

Table S1. The list of Crystal Data and Structure Refinement Details of PAE-I.

Identification code	PAE-I
Empirical formula	$C_{10}H_{11}O_2N_2I$
Formula weight	286.38
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.8409(3)
b/Å	11.5206(4)
c/Å	12.2248(5)
α/°	90
β/°	91.795(4)
γ/°	90
Volume/Å^3	1103.75(7)
Z	4
ρcalcg/cm^3	1.723
μ/mm^{-1}	11.778
F(000)	563
Radiation	Ga Kα (λ=1.3405)
2ϑ range for data collection/°	4.586 to 60.110
Index ranges	-9≤h≤10 -12≤k≤14 -15≤l≤15
Reflections collected	2449
Independent reflections	12311 [R_{int} =0.0579, R_{sigma} = 0.0406]
Data/restraints/parameters	2449/0/138

Goodness-of-fit on F^2	1.100
Final R indexes [I>=2σ (I)]	R_1=0.0412, wR_2=0.1231
Final R indexes [all data]	R_1= 0.0454, wR_2=0.1260
Largest diff. peak/hole / e Å^{-3}	1.316/-0.858

Table S2. The grain size data calculated employing the Scherrer equation.

	2θ (°)	FWHM	Crystallites Sizes D (nm)	Average Crystallites Sizes D (nm)
control	13.08	0.16	48.68	40.58
	14.38	0.15	52.28	
	24.71	0.18	44.62	
	28.54	0.19	41.63	
	31.95	0.22	37.91	
	38.97	0.24	34.89	
	40.64	0.21	39.22	
	43.17	0.25	34.37	
	50.21	0.24	36.39	
	52.63	0.30	28.77	
	20.21	0.17	47.58	
target	13.08	0.18	44.12	41.77
	14.39	0.14	55.95	
	20.21	0.15	52.53	
	24.73	0.18	45.56	
	28.56	0.20	39.96	
	31.97	0.19	44.08	
	39.00	0.27	31.07	
	40.67	0.20	42.47	
	43.21	0.20	41.30	
	50.24	0.25	34.56	
	52.65	0.31	27.86	

Table S3. The fitted values of τ_1, τ_2, A_1, A_2 and the calculated τ_{ave} of the perovskite film without and with PAE-I passivation.

	τ_{ave} (ns)	τ_1 (ns)	A_1	τ_2 (ns)	A_2
control	1142.15	162.64	0.40	1250.57	0.47
target	1406.07	74.19	0.45	1479.38	0.41

Table S4. Photovoltaic parameters of devices with different concentrations of PAE-I treatment. And the optimal concentration is 0.3 mg/mL. More than 20 devices were fabricated to determine the optimal concentration, and a set of repeatable data were listed as the representative parameters.

	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)	Average PCE (%)
control	1.05	23.76	79.25	19.76	18.78 ± 0.47
0.1 mg/mL	1.08	23.70	77.98	19.95	18.96 ± 0.73
0.3 mg/mL	1.09	24.75	78.62	21.30	20.44 ± 0.36
0.5 mg/mL	1.11	23.24	77.80	20.07	18.83 ± 0.86
0.8 mg/mL	1.09	23.85	76.45	19.94	19.08 ± 0.63

Table S5. Average photovoltaic parameters of devices with different concentrations of PAE-I treatment.

	Average V_{OC} (V)	Average J_{SC} (mA cm^{-2})	Average FF (%)	Average PCE (%)
0.3 mg/mL	1.07	23.81	80.61	20.44 ± 0.36
0.5 mg/mL	1.07	23.08	76.43	18.83 ± 0.86
0.8 mg/mL	1.06	22.79	79.05	19.08 ± 0.63

Table S6. Photovoltaic parameters of the PSCs without and with 0.3 mg/mL PAE-I-treated scan in different directions.

	Scan direction	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)	HI[a)]
control	Reverse scan	1.10	22.17	80.32	19.66	8.1%
	Forward scan	1.10	22.40	73.46	18.01	
target	Reverse scan	1.11	23.13	79.01	20.24	6.6%
	Forward scan	1.11	22.99	74.24	18.91	

[a)] The hysteresis index (HI) is calculated by the formula of $(\mathrm{PCE}_{\mathrm{reverse}}\text{-}\mathrm{PCE}_{\mathrm{forward}})/\mathrm{PCE}_{\mathrm{reverse}}$.

Table S7. EIS fitting parameters for the PSCs without and with PAE-I treating.

	R_s (Ω)	R_{tr} (Ω)	C_{tr} (F)	R_{rec} (Ω)	C_{rec} (F)
control	3.2	69.5	5.0×10^{-9}	361.1	7.4×10^{-9}
target	21.2	98.2	4.9×10^{-9}	741.0	7.9×10^{-9}