

Improving the intrinsic photostability of MeNH₃PbI₃ layers by passivation with pentaerythritol tetrakis(2-mercaptoacetate)

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Experimental Setup:

Materials:

N, N dimethylformamide (DMF, anhydrous, 99.99%), MAI, PbI₂, Pentaerythritol tetrakis(2-mercaptoacetate) (PETMA) and Toluene were purchased from Sigma-Aldrich and used as received. PCBA, PTA, MAI, PbI₂ powders were used.

Preparation of Precursor Solutions:

To prepare thin films, 0.3M solution of MAPbI₃ combined with and without PETMA additive was used. DMF was used to prepare precursors with and without additives. 5 weight percentage of PETMA additive was used to prepare the MAPbI₃+PETMA film. 0.45µm PTFE filter was used to filter the solution.
¹. Filtered solutions were used for film fabrication and characterisation.

Film Preparation:

Glass substrates were cut into 25 mm * 25 mm size and cleaned. Deionised water, acetone and isopropanol were used to give an ultra-sonication bath for 15 minutes in this particular sequence for cleaning substrates. Upon cleaning, substrates were plasma treated for 5 minutes and then transferred into Argon filled glovebox. Perovskite film on the glass substrate was spun at 3000 rpm and annealed at 100°C for a minute. These perovskite films were further used to conduct thin-film photostability test.

Thin Film Characterisation:

To explicitly understand the impact of the PETMA incorporation onto intrinsic photostability of MAPbI₃, the ageing of thin films was performed under the inert glovebox environment (H₂O <0.1ppm and O₂ < 0.1 ppm). So that degradation due to moisture and air can be minimised. For the ageing experiment, MAPbI₃ thin films with additive were illuminated under the light intensity of 70-80 mW cm⁻² around 50-60 °C up to 1400 h inside the glovebox as per the ISOS-I protocol ². UV-Vis spectra were measured using AvaSpec-2048-2 UV-Vis fibre spectrometer integrated inside the glove box. The instrument has a wavelength accuracy within ±0.5 nm.

X-ray diffraction patterns were measured using a Bruker D8 Advance powder diffractometer (Cu-Kα radiation, 5-60° 2 theta range, 0.0219° increment step). Measurements were carried out in fixed illumination mode with no sample rotation. The time interval of 0.2 seconds, voltage 40kV, filament current 40 mA was used for all the measurements.

SEM measurements were performed using the Helios G4 Plasma FIB Uxe dual-beam scanning electron microscope. A top view imaging was performed in field-free mode using ETD detector and immersion mode using TLD detector, both in secondary electron (SE) mode at 5 kV with I = 50 pA. While 1 kV and 25 pA were used for cross-section visualisation. The sample was mounted to the stage and grounded by carbon conductive tape without the deposition of extra conductive layers. It should be noted here; samples

were prepared on Glass/ITO substrate (instead of the only glass substrate) to obtain the FIB-SEM cross-sectional view.

PL measurements were carried out using Automatic Research GmbH LBIC+PL+EL microscopy setup with Horiba spectrometer. All samples were measured with 532 nm laser wavelength at 0.05s integration time, 0.5 slit-width.

AFM topography and surface potential data were obtained in a two pass amplitude modulation Kelvin probe force microscopy mode using Cypher ES atomic force microscope installed in an Ar-filled glovebox. W₂C coated Si probes with 145 kHz resonance frequency and 3.5 N/m spring constant were used.

FTIR spectra were obtained using Bruker Alpha II with ATR module (diamond crystal).

Device Preparation:

ITO-coated glass substrates (25 mm × 25 mm) were cleaned by sequential ultrasonication in deionized water, acetone, and isopropanol (15 min each), followed by 5 min plasma treatment. A 10% SnO₂ solution, prepared by diluting a 15% commercial dispersion with deionized water in a 2:1 ratio, was ultrasonicated, filtered (0.45 µm PES), and spin-coated at 4000 rpm. Substrates were annealed at 170 °C for 15 min in air, then transferred to an Ar-filled glovebox for further heating at 150 °C for 10 min. All subsequent layers were processed in the glovebox. PCBA (0.6 mg/ml in toluene) was spun at 3000 rpm and annealed for 5 minutes at 100°C. The perovskite layer was deposited via one-step spin coating at 4000 rpm with toluene dripping at 20 s, followed by annealing at 100 °C for 10 min. PTA (6 mg/mL in toluene) was applied at 3000 rpm. Then, polystyrene (PS) (0.4 mg/ml in ethyl acetate) was spun at 2000 rpm. Finally, MoO₃ (10 nm) and Ag (100 nm) electrodes were thermally evaporated. These devices were used to evaluate photovoltaic performance

Device Characterisation:

Current–voltage (J–V) measurements were conducted under AM 1.5G illumination (100 mW cm⁻²) using a Newport VeraSol AAA-class solar simulator, operated within a nitrogen-filled glovebox. The light intensity was calibrated prior to each measurement using a certified silicon photodiode with known spectral response. J–V curves for all devices were recorded using Advantest R6240A source measurement units, with a metal mask defining an active area of 0.041 cm².

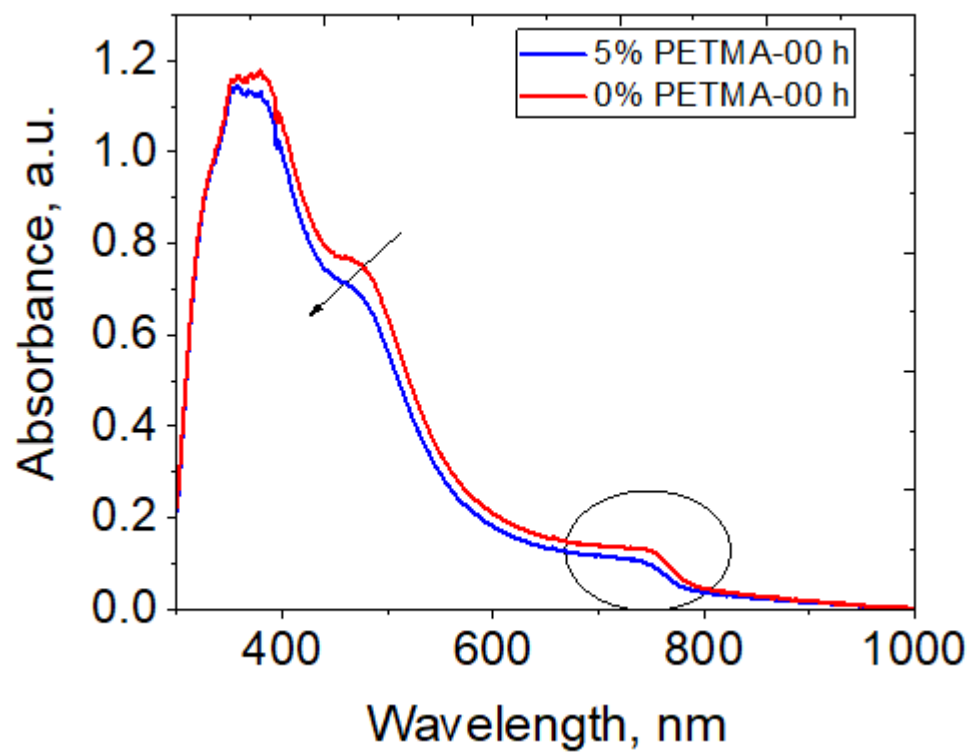


Figure S1 Impact of PETMA incorporation on UV-Vis spectra of MAPbI₃ film (fresh).

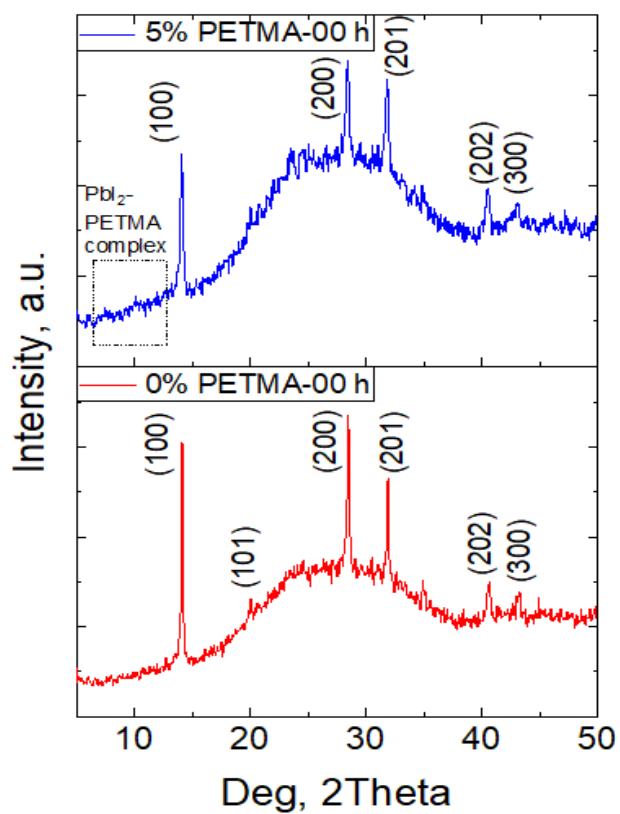


Figure S2 XRD patterns showing complex formation with PbI_2 in MAPbI_3 film upon PETMA incorporation.

The fresh MAPbI_3 +PETMA film displays additional peaks at 7.5° and 10.1° , which may be due to complex formation between PbI_2 and PETMA³.

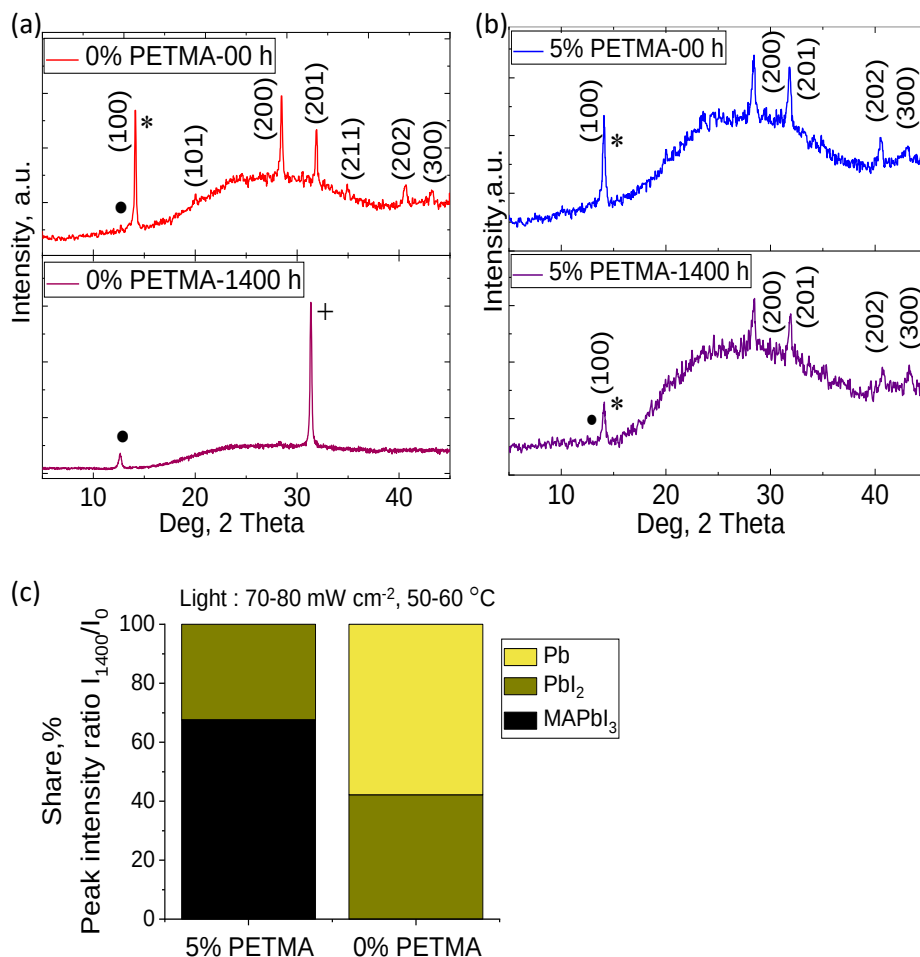


Figure S3 XRD patterns of fresh and photoaged films: (a) pristine, (b) MAPbI₃+PETMA films. (c) XRD qualitative phase analysis: “*” represents the perovskite phase, “•” represents PbI₂, and “+” represents Pb.

The XRD patterns of fresh pristine MAPbI₃ in Figure S3 (a) correspond to cubic perovskite phase with characteristic peaks at 14.12°, 28.52°, 31.93°, 40.62° and 43.26°. The XRD patterns of photoaged pristine film validate the UV-Vis results (Figure 1) and show peaks corresponding to PbI₂ at 12.6° (minor byproduct) and Pb at 31.3° (major byproduct)⁴. While MAPbI₃+PETMA films show perovskite XRD peaks unchanged upon photoaging, with lower intensity (Figure S3(b)). Besides, the lower intensities of XRD peaks indicate that the film becomes less crystalline. The qualitative XRD analysis of phase composition does not show the formation of metallic lead in MAPbI₃+PETMA (Figure S3 (c)). Note that the XRD phase composition analysis is done by finding the XRD peak intensity ratio of MAPbI₃, PbI₂ and Pb in the photoaged state to the fresh state and represents only qualitative results to visualise degradation dynamics. It does not represent quantitative phase analysis.

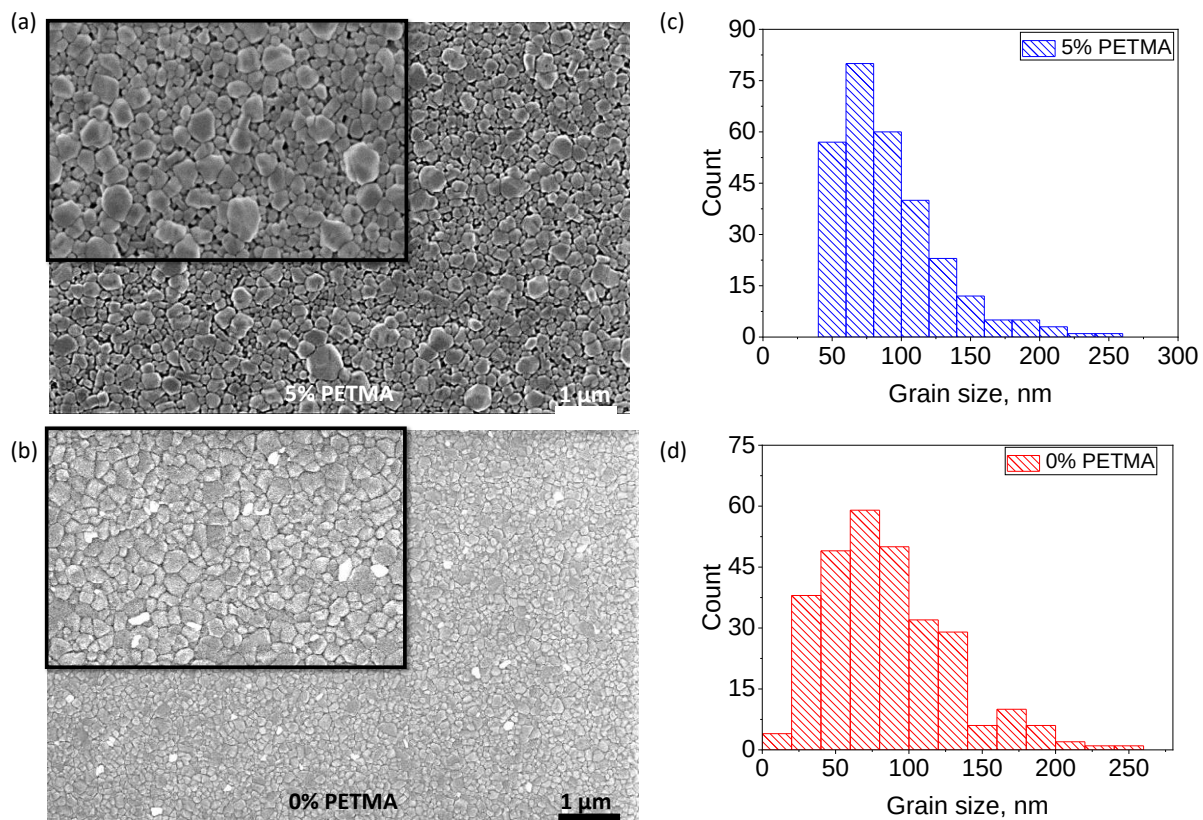


Figure S4 SEM images (a) pristine MAPbI_3 film. (b) MAPbI_3 +PETMA film. Grain-size distribution (c) pristine MAPbI_3 film (d) MAPbI_3 +PETMA film.

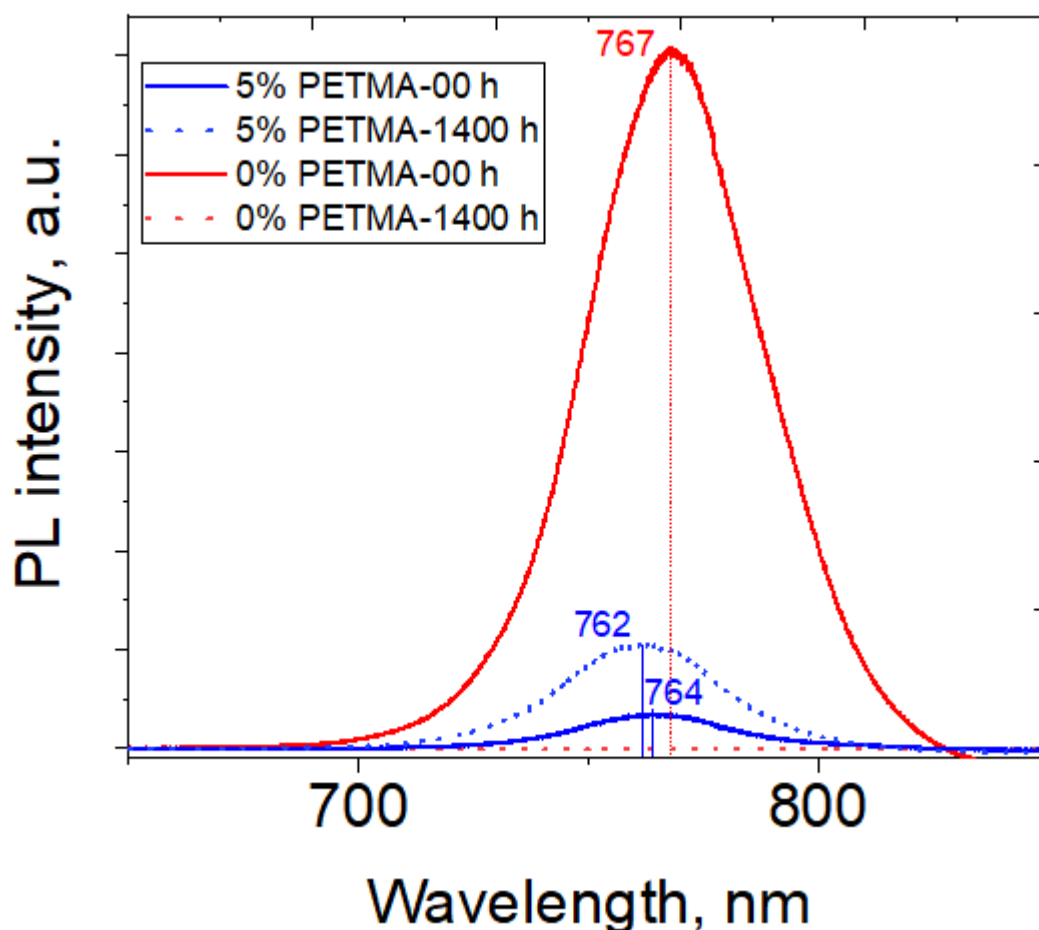


Figure S5 Reduced PL peak emission intensity upon PETMA incorporation in MAPbI₃.

Figure S5 Comparison of PL emission peak spectra of pristine MAPbI₃ to MAPbI₃+PETMA film. MAPbI₃+PETMA film (764 nm) illustrates a blue shift compared to pristine (767 nm)⁵. Additionally, MAPbI₃+PETMA film demonstrates diminished PL peak intensity in the fresh film. The diminished PL peak intensity can be correlated with the PETMA distribution near the surface, where the new grains/clusters appear as seen in SEM images, and the gaps between the grains do not allow radiative recombination⁶⁻⁸. It has been reported that distortion between Pb-I bonds could also affect the grain size, resulting in PL blue shift for ~100 nm crystal size. Here, this could be caused by bond alteration due to PETMA incorporation that contains multiple functional groups known to chelate with Pb²⁺^{7,8}. Upon photoaging of films, pristine MAPbI₃ degrades and does not show any PL peak. In comparison, MAPbI₃+PETMA film exhibits higher PL peak intensity than the fresh state with a further blue shift upon light soaking⁸.

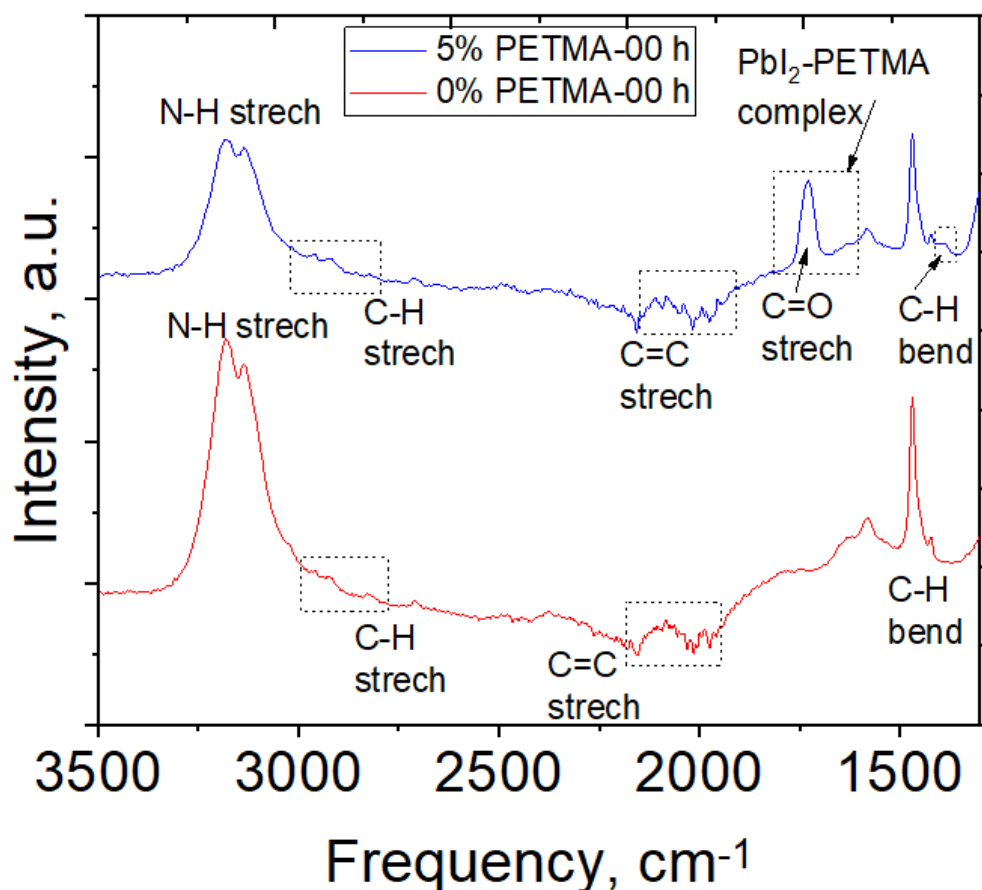


Figure S6 FTIR spectra of fresh films with 0% and 5% PETMA in MAPbI₃.

The FTIR spectra of the fresh, pristine film illustrate peaks at C-H bend at 1378 cm⁻¹ and 1421 cm⁻¹, N-H bending at 1468 cm⁻¹ and 1579 cm⁻¹, C-H stretch at 2828 cm⁻¹ and N-H stretch at 3136 cm⁻¹ and 3180 cm⁻¹. These peaks for pristine MAPbI₃ are consistent with literature data ¹¹. In the case of MAPbI₃+PETMA film, an additional peak at 1728 cm⁻¹ belonging to the C=O stretch from esters is noticed ¹². This serves as the basis of the hypothesis of Pb²⁺ chelation. Besides, the C-H bend is shifted to 1386 cm⁻¹. N-H bend is also slightly shifted to 1583 cm⁻¹. Moreover, changes in the region from 1935 cm⁻¹ to 2085 cm⁻¹ are also noticeable in the C=C stretch. Also, the C-H stretch is slightly shifted to 2823 cm⁻¹ ¹³. It can be associated with chelation of Pb²⁺, through C=O bonding, resulting in the complex formation ¹⁴⁻¹⁶.

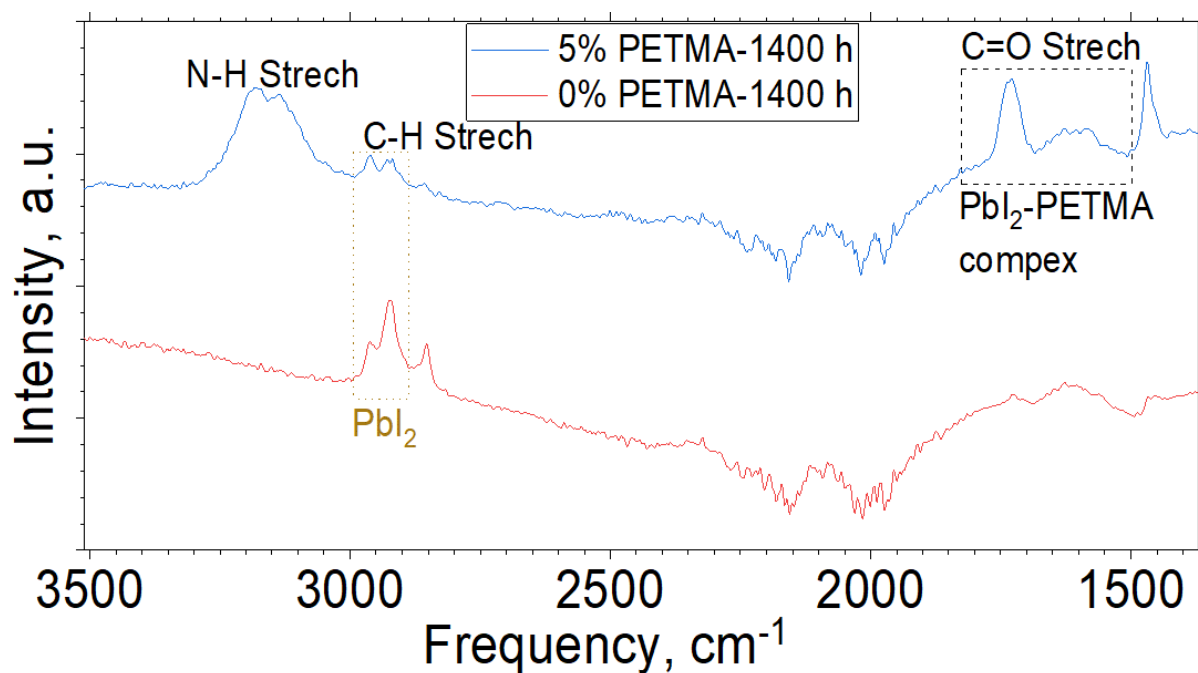
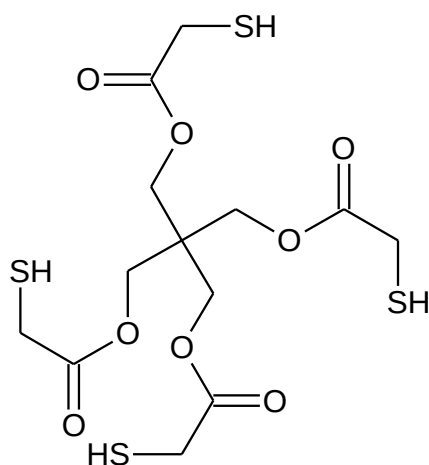


Figure S7 FTIR spectra of photoaged pristine and MAPbI_3 +PETMA films.

The photoaged pristine MAPbI_3 film degrades, and the corresponding PbI_2 peak in FTIR spectra can be seen at 2920 cm^{-1} and 2962 cm^{-1} ¹⁷. In comparison, photoaged MAPbI_3 +PETMA film shows peaks at 2913 and 2926 cm^{-1} corresponding to Pb^{2+} , indicating a change in bonding related to the Pb atom. Further, the C=O is now observed 1732 cm^{-1} . In addition, a lower frequency below 1700 cm^{-1} (i.e. 1510 cm^{-1} - 1680 cm^{-1}) shows changes compared to pristine photoaged perovskite film, suggesting the strong presence of the carbonyl group from esters is effective, further supporting the notion of Pb^{2+} chelation¹³.



PETMA

Figure S8 Chemical structure of pentaerythritol tetrakis(2-mercapto acetate) (PETMA).

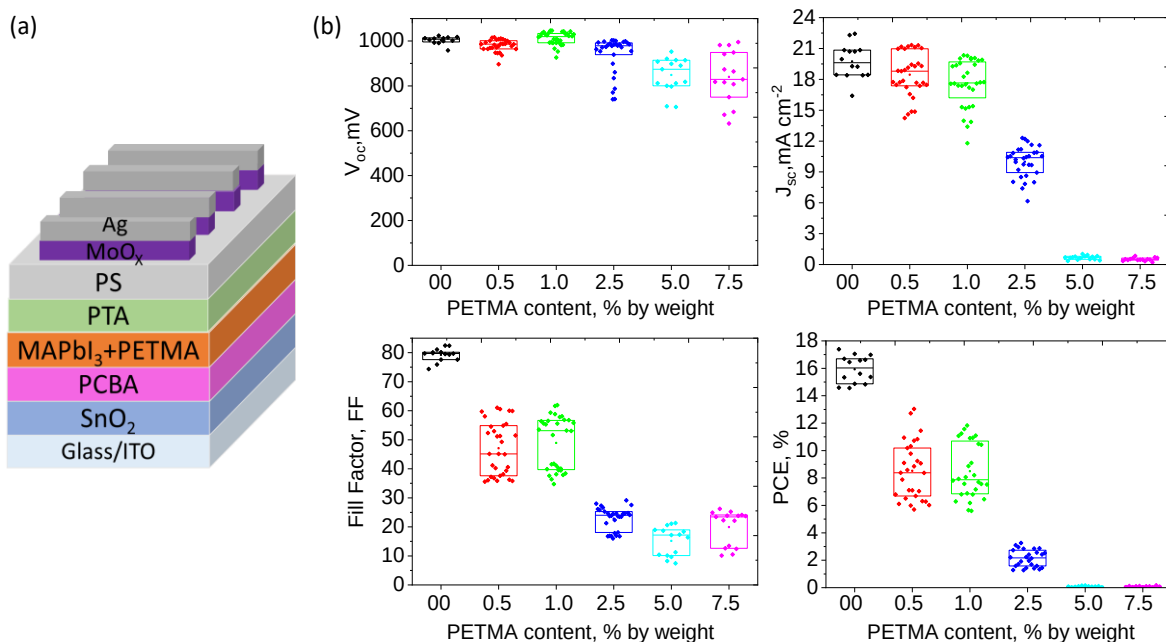


Figure S9 (a) Device architecture. (b) Impact of PETMA incorporation on solar cell device performance.

Table S1 Dependence of best and average I–V parameters of the MAPbI₃+PETMA-based solar cells on PETMA concentration

PETMA concentration (wt%)		V _{oc} , mV	J _{sc} , mA cm ⁻²	Fill factor	Power conversion efficiency (PCE), %
0%	Best	1001.75	22.43	75.90	17.05
	Avg	1002.61±16.09	19.73±1.68	79.27±2.26	15.92±1.00
0.5%	Best	1016.44	21.33	61.03	13.04
	Avg	987.07±26.01	18.44±2.13	48.54±9.1	8.52±2.04
1%	Best	1046.62	20.33	61.94	11.83
	Avg	1019.7±28.91	17.67±2.29	53.11±9.15	8.7±1.98
2.5%	Best	1003.28	12.3	29.11	3.25
	Avg	978.56±82.45	10.38±1.50	23.98±3.92	2.22±0.59
5%	Best	952.85	1.02	21.32	0.16
	Avg	874.16±76.38	0.69±0.19	17.19±5.01	0.08±0.04
7.5%	Best	991	0.83	26.22	0.18
	Avg	850.79±113.85	0.5±0.15	23.45±6.05	0.09±0.04

Figure S9 (a) depicts the architecture used to fabricate solar cell devices. PETMA concentrations range from 0% (reference) to 0.5%, 1%, 2.5%, 5%, and 7.5%, % by weight (Figure S9 (b) and Table S1). The best PCE achieved with 0.5% PETMA is slightly lower than that of pristine-based solar cells. The addition of a small quantity of PETMA additive into the perovskite precursor results in an increase in the

open circuit voltage. While the short circuit current density lies in similar range. However, the fill factor decreases. The lower fill factors could indicate trap states due to increased film thickness, hindering smooth charge extraction, resulting in no increase in current. This could be associated with KPFM and FIB-SEM results, signifying that PETMA incorporation creates a barrier/trap state. Further, as the PETMA concentration increases beyond 2.5%, the open circuit voltage, short circuit current density and fill factor sharply decline, suggesting that excessive concentration of PETMA may block charge transport and result in poor device performance.

These device performance results show, there is a trade-off between efficiency and stability. To overcome this trade-off, an optimum concentration of PbI_2 can be added to enhance efficiency. It is known that excessive PbI_2 can increase device performance and stability¹⁸.

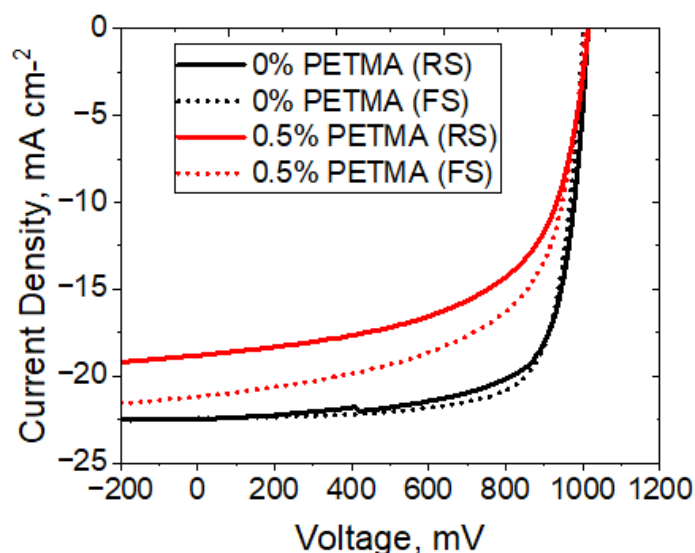


Figure S10 J–V curves of pristine MAPbI₃ and the best-PCE MAPbI₃ with 0.5% PETMA.

Table S2 J–V characteristics and hysteresis factor of the best solar cells made of pristine MAPbI₃ or 0.5% MAPbI₃+PETMA.

PETMA concentration (wt %)		V _{oc} , mV	J _{sc} , mA cm ⁻²	Fill factor	Power conversion efficiency (PCE), %	Hysteresis factor (HF)
0%	(RS)	1013.64	22.46	73.22	16.67	0.02
	(FS)	1001.75	22.43	75.90	17.05	
0.5%	(RS)	1016.44	21.33	61.03	13.04	0.12
	(FS)	1015.01	18.8	58.99	11.44	

Figure S10 demonstrates the current density-voltage curve of pristine MAPbI₃ and 0.5 % PETMA incorporated MAPbI₃ solar cell devices. Table S2 presents the best device performance and corresponding hysteresis factor of pristine and 0.5% PETMA-containing MAPbI₃ solar cells. The hysteresis factor is obtained with the formula reported elsewhere ¹:

$$\text{Hysteresis factor (HF)} = \frac{\text{PCE (Reverse)} - \text{PCE(Forward)}}{\text{PCE (Reverse)}}$$

The hysteresis observed in the solar cell incorporating 0.5% PETMA is comparable to that of the pristine-based device, suggesting its potential in perovskite based photovoltaic applications.

It is generally expected that stabilizing a device decreases hysteresis. However, under certain conditions, hysteresis can increase as the device is stabilized. PETMA incorporation in MAPbI₃ leads to increased film thickness, shown in FIB-SEM results (Figure 2), and creates a barrier that acts as trap states, as shown by KPFM results (Figure 3) and PL results (Figure S5). The barriers can slow down the extraction of charges or the redistribution of ions, thereby increasing the magnitude of the hysteresis. While these trap states may allow for binding with Pb-I antisites, Pb vacancies, or undercoordinated Pb²⁺ sites, they show a stabilising effect in thin films.

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