Amine Additive Reactions Induced by the Soft Lewis Acidity of Pb^{2+} in Halide Perovskites. Part II: Impacts of Amido Pb Impurities in Methylammonium Lead Triiodide Thin Films

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Supplementary Information

Experimental

The precursors used were methylammonium iodide (Dyesol), methylamine (anhydrous, 33 wt% in ethanol, Sigma), PbI_2 (98%, TCI), N,N-dimethylformamide (anhydrous, 99%, Sigma), and linear PEI (Sigma, MW = 10,000). All sample preparation was performed inside of a N_2 filled glovebox to exclude the effects of moisture and oxygen.

Samples for XPS were prepared in a N_2 glovebox by spin coating. Films of PbI_2 were fabricated by spin coating PbI_2 (200 mg/mL in DMF, 4000 rpm for 35 s), annealed at 75 °C for 15 min. Methylamine exposure of PbI_2 was performed inside of the glovebox by placing a PbI_2 film and an open vial of methylamine:ethanol solution under a beaker for 5 min. The PbI_2/PEI heterojunction was prepared by spin coating linear-PEI (~1 mg/mL in chlorobenzene, 4000 rpm for 60 s). All MAI:PbI_2 solutions were prepared with 345 mg of PbI_2 per 1 mL of DMF. Methylamine:ethanol solution was added to the perovskite inks in a ratio of 50 µL per mL of DMF and monitored as a function of aging time at room temperature. Perovskite films with and without methylamine additives were spin coated onto a 3 cm x 3 cm ITO substrate at 5300 rpm for 35 s also in an N_2 glovebox. A solvent exchange with toluene was performed at 4 s after the start of spinning, and the films were annealed at 70 °C for 20 min. For PL measurements, some films were encapsulated in PMMA (MW = 950,000, 50 mg/mL in CB, 4000 rpm to give approximately 300-400 nm).

A Bruker D8 Discover X-ray Diffractometer with a Cu X-ray tube, monochromating Göebel mirror, scintillation detector, and 0.6 mm divergence slits was used to obtain Bragg-Brentano geometry XRD patterns. A Thermo-Scientific K-Alpha X-ray Photoemission Spectrometer at a base pressure of $5x10^{-8}$ mbar using an Al anode at a power of 72 W, hemispherical analyzer, pass energy of 50 eV, and 400 µm X-ray beam spot size was used to obtain XPS spectra. The films were fabricated in a N_2 glovebox and transferred to the XPS under vacuum in order to exclude reactions with oxygen. Photoluminescence measurements were performed in atmosphere using an Edinburgh Instruments FLS980 photoluminescence spectrometer with 635 nm wavelength laser diode, pulse width of 100 ps, and pulse energy density of approximately 2 nJ/cm^2 (5 mW max power output).

Supplementary Figures

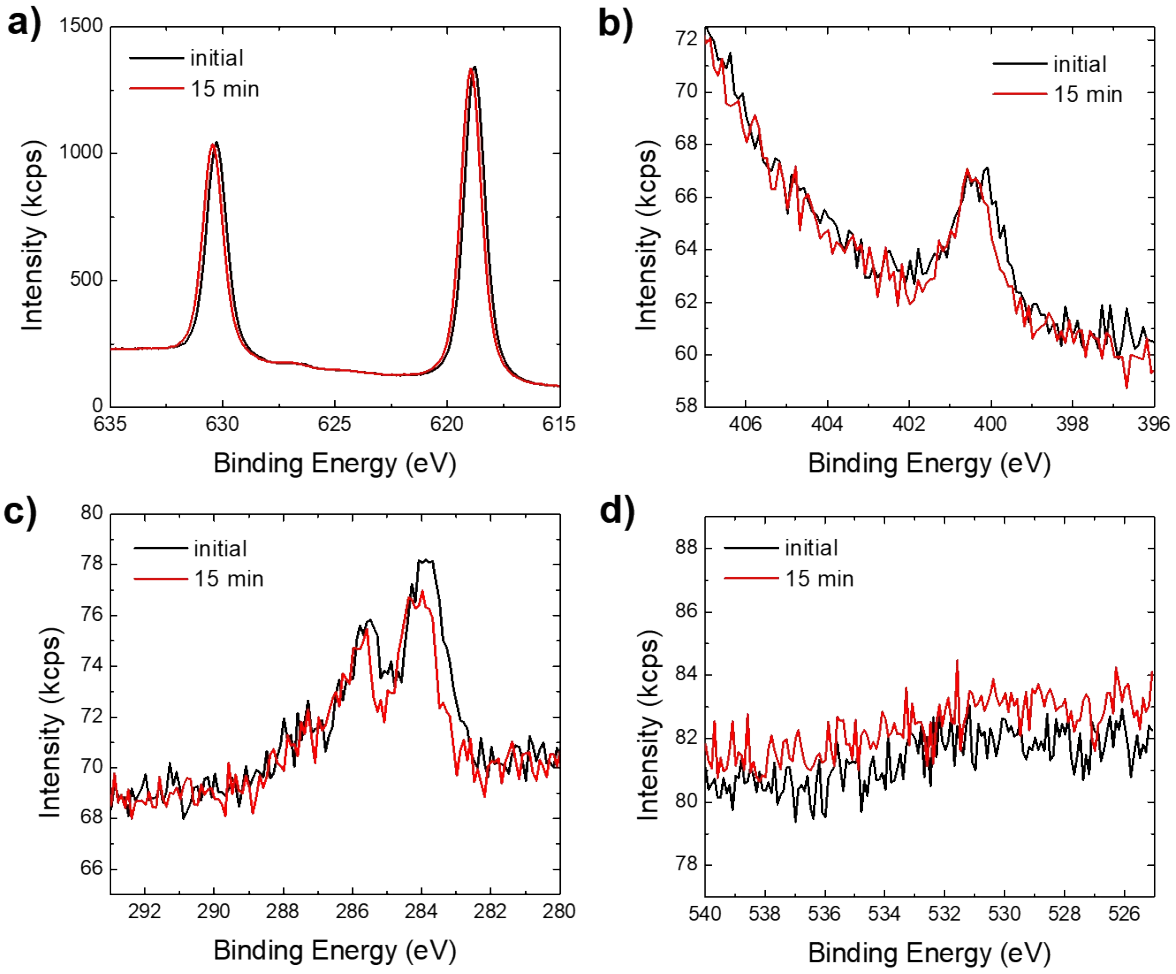

Figure S1. XPS of (a) I 3d, (b) N 1s, (c) C 1s, and (d) O 1s spectra for a thin film of PbI_2 reacted with methylamine:ethanol in DMF (corresponding to Fig. 1b of the main text).

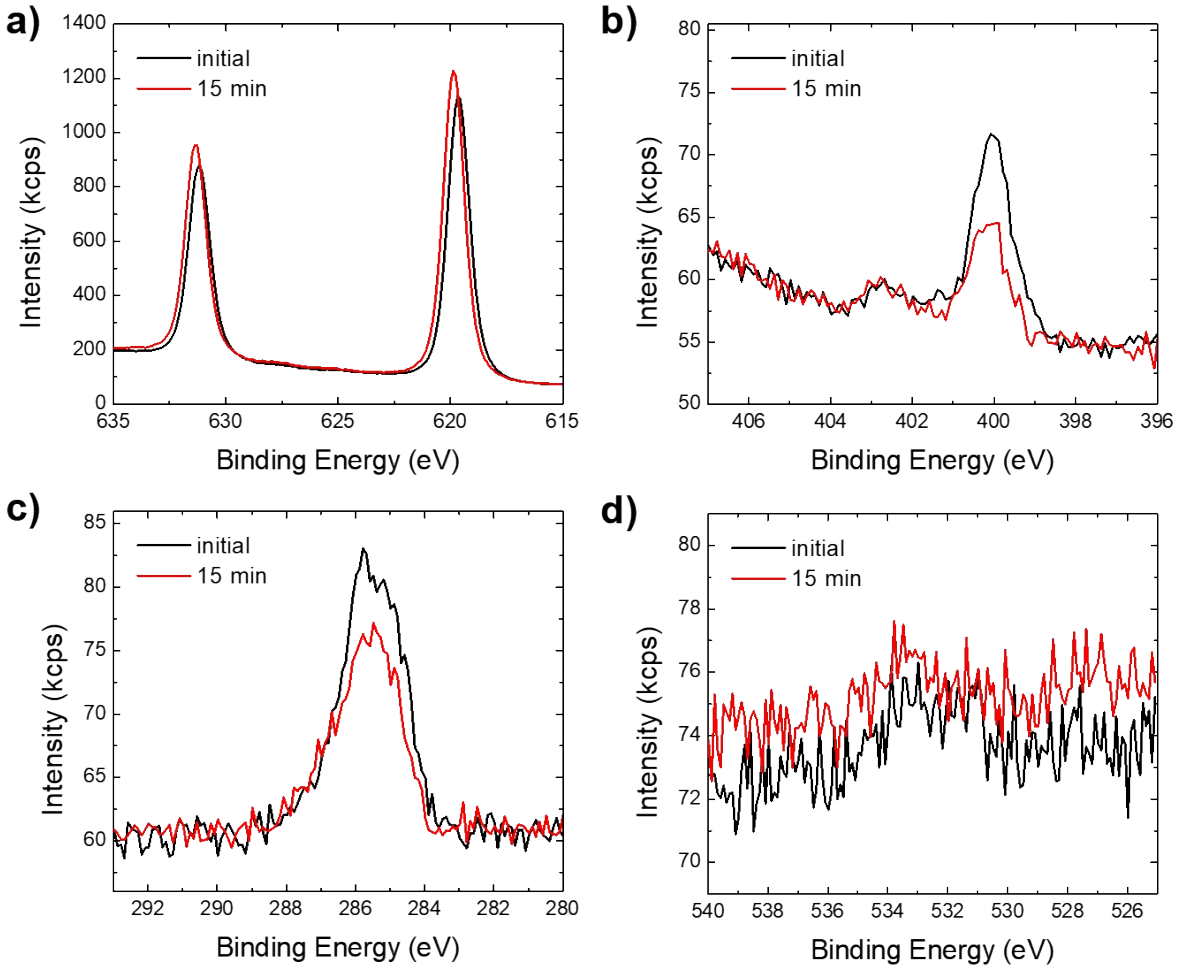

Figure S2. XPS of (a) I 3d, (b) N 1s, (c) C 1s, and (d) O 1s spectra for a thin film of PbI_2 reacted with methylamine vapor in a N_2 glovebox (corresponding to Fig. 1c of the main text).

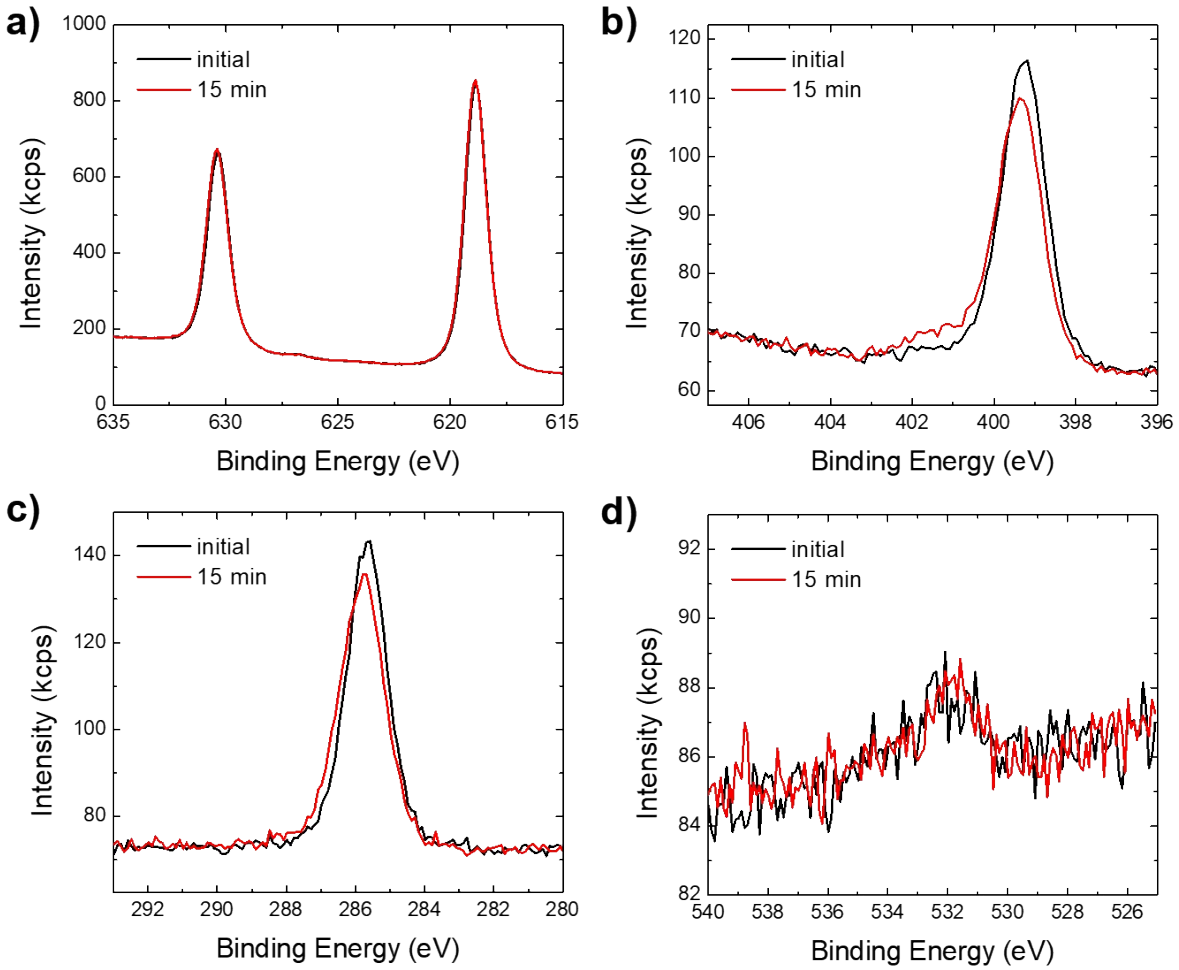

Figure S3. XPS of (a) I 3d, (b) N 1s, (c) C 1s, and (d) O 1s spectra for a thin film of PbI_2/linear-PEI (corresponding to Fig. 1d of the main text).

Table S1. Changes in elemental peak areas for thin films of PbI_2 reacted with methylamine in solution, with methylamine in vapor phase, and with linear-PEI in the solid phase after degradation by X-rays measured *in situ* by XPS (samples in Figures S1-S3). The C and N decrease the most significantly except in PbI_2/linear-PEI sample for which the C and N species are tethered to the non-volatile polymer.

Sample	% change in peak area after X-ray degradation			
	Pb	**I**	**N**	**C**
PbI_2/methylamine solution reaction	5.9	-0.03	-25.5	-11.8
PbI_2/methylamine vapor reaction	3.3	3.7	-25.2	-19.9
PbI_2/linear-PEI	-2.6	2.5	-1.9	-0.7

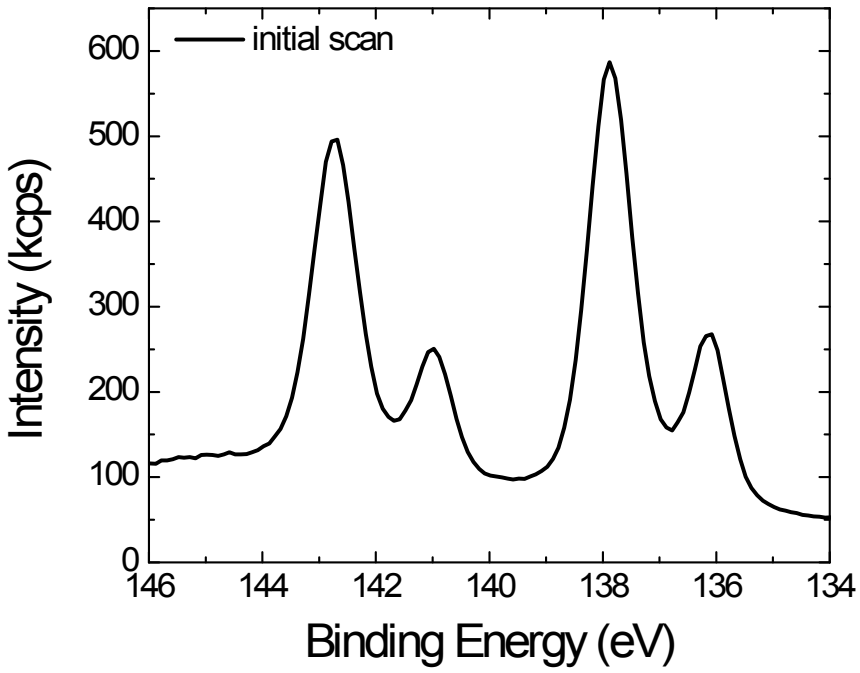

Figure S4. Initial XPS scan of the Pb 4f region of a film of PbI_2 reacted with methylamine in DMF (the same sample in Fig. 1b of the main text) at a location which had not seen x-rays but was exposed to visible illumination by the chamber analysis lights in UHV for approximately 60 minutes. X-rays were not required to induce Pb^0 formation from Pb-iodo-amides in UHV.

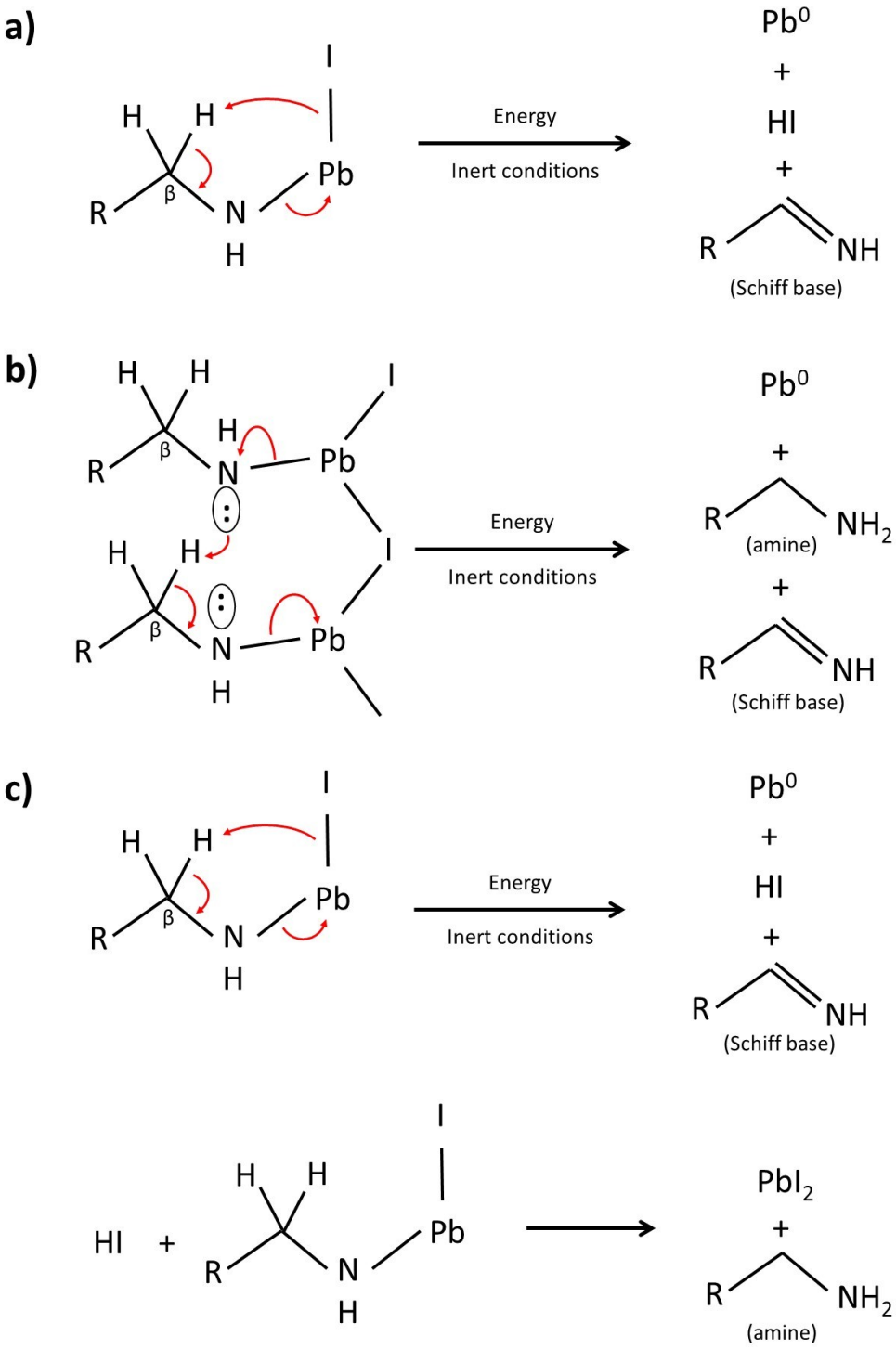

Figure S5. Possible mechanisms of β-C-H proton transfer to form Pb^0 and the Schiff base. In (a), iodide acts as the kinetic base to deprotonate the β-C-H to form HI. In (b), a second alkylamide group acts as both the kinetic base and thermodynamic base deprotonating an amide group to reform an alkylamine molecule. Case (c) is a combination of the former where iodide acts as the kinetic base but protonates a distant amide species forming the thermodynamic base. We have characterized this for R = H (i.e. methylamine as in the main text) and R = $(CH_2)_2CH_3$ (butylamine) as well. This is also applicable for secondary amines such as linear-PEI (not depicted).

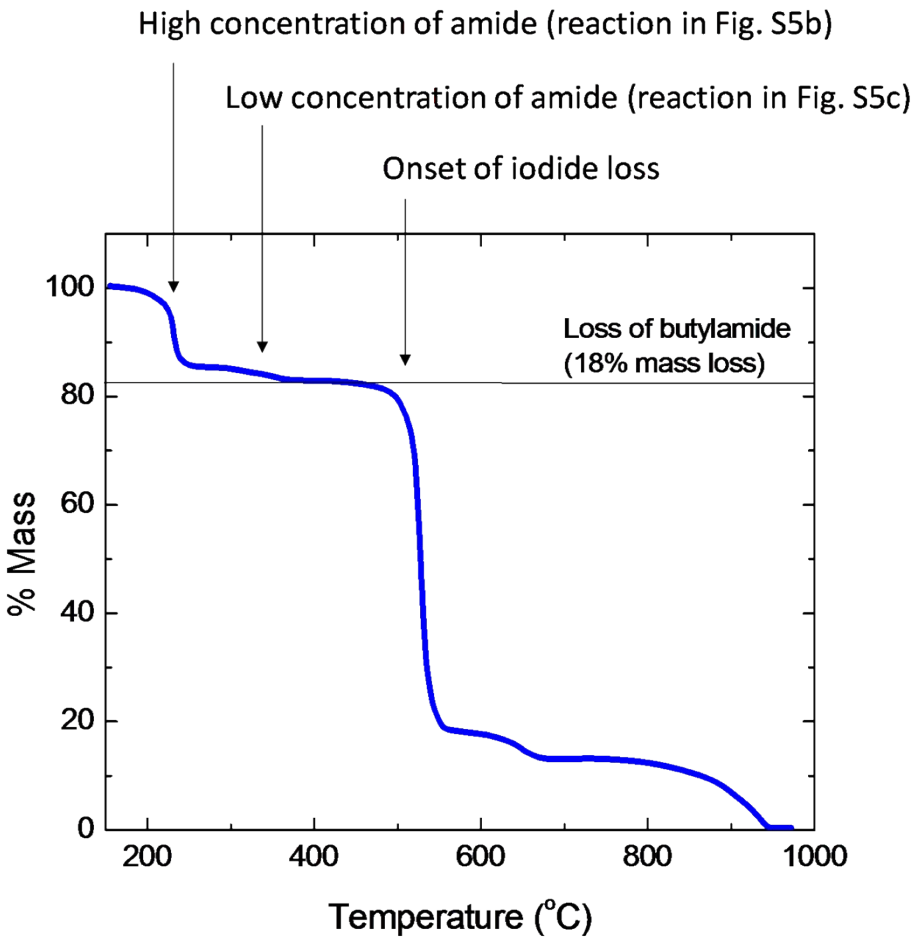

Figure S6. Thermal gravimetric analysis (TGA) of isolated PbI(butylamide) product showing two important features. The butylamide groups are eliminated prior to iodide loss. Butylamide loss occurs in two different steps which we attribute to a transition in mechanism when the concentration of butylamide becomes low.

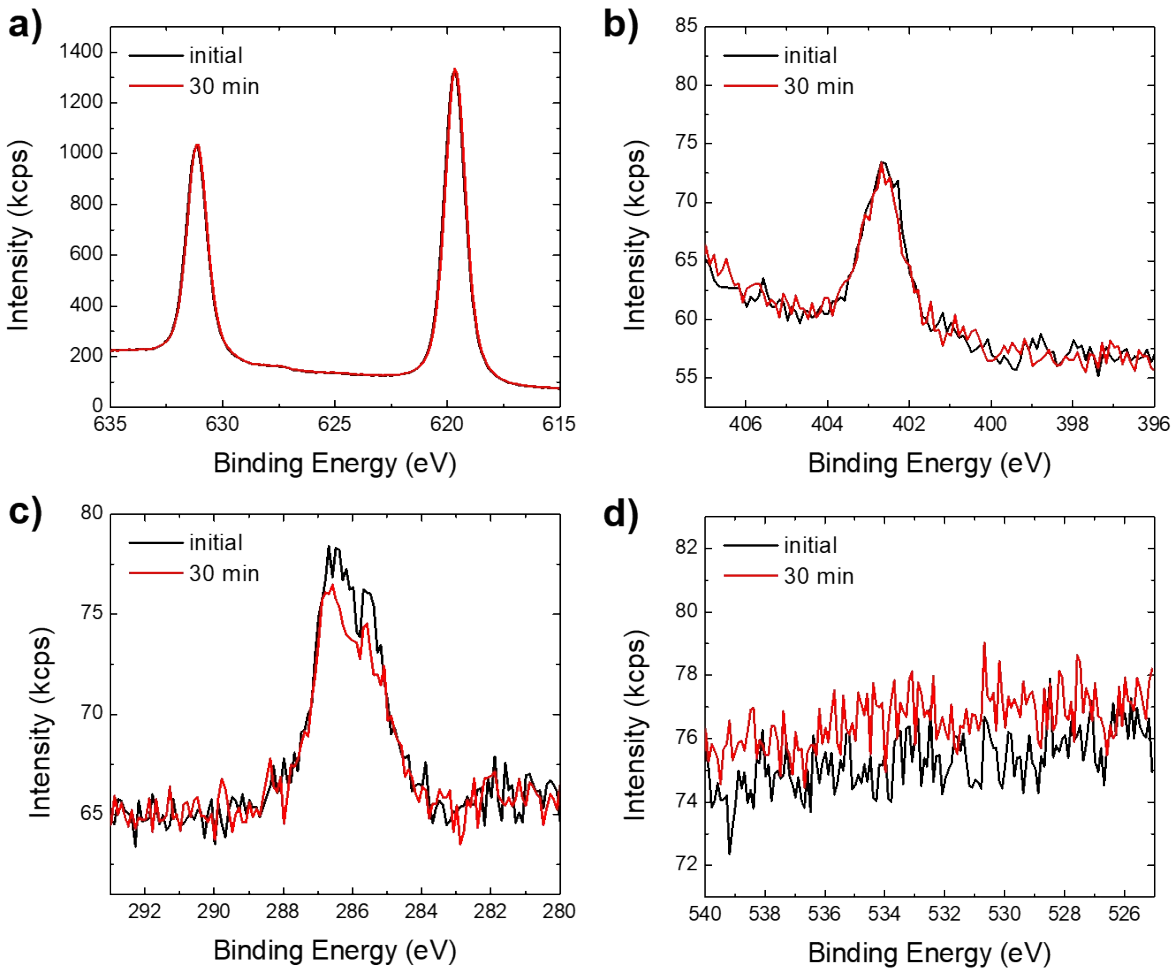

Figure S7. XPS of (a) I 3d, (b) N 1s, (c) C 1s, and (d) O 1s spectra for a thin film of PbI_2/$MAPbI_3$ cast from an MAI:PbI_2 = 0.5:1 precursor solution (corresponding to Fig. 2c of the main text).

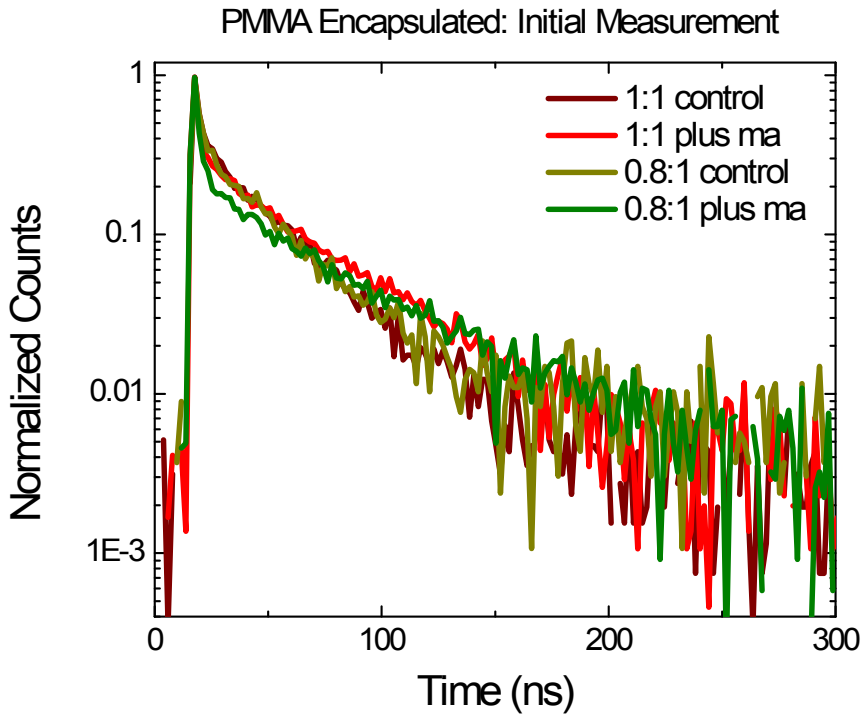

Figure S8. Initial time-resolved photoluminescence measurements of stoichiometric and sub-stoichiometric $MAPbI_3$ films with and without methylamine additives (reacted 24 hrs) and encapsulated by PMMA (50 mg/mL in chlorobenzene). The PL lifetimes are relatively short but there is a modest improvement from methylamine/methylamide. Decay curves were fit to a bi-exponential with lifetimes given by Table S1.

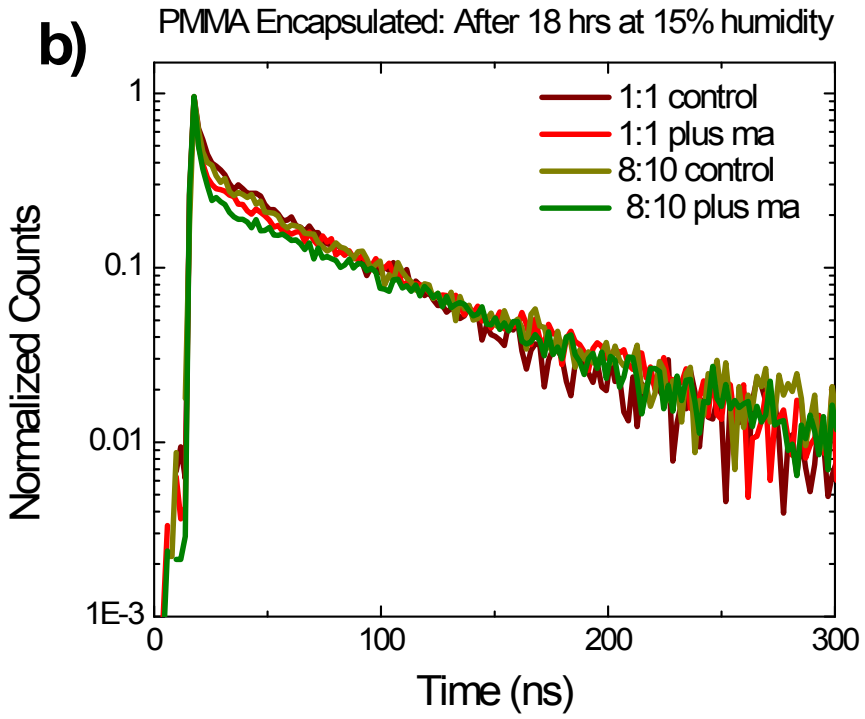

Figure S9. Time-resolved photoluminescence measurements after aging in ambient for 6 h during initial measurements followed by storage in a drybox at ~ 15% humidity of samples in Fig. S7. The relative improvements from methylamine/methylamide are retained for an extended period of time by encapsulation. Decay curves were fit to a bi-exponential with lifetimes given by Table S1.

Table S2. Lifetime components of bi-exponential fit to TRPL decay measurements of stoichiometric and sub-stoichiometric $MAPbI_3$ films with and without methylamine additives (reacted 24 h) and encapsulated by PMMA (50 mg/mL in chlorobenzene). Both initial and aged measurements are shown. The relative percentages of the total emission (rel. %) are also provided.

	Initial Measurement				After H_2O/O_2 Exposure			
Sample	τ_1 (ns)	τ_1 rel. %	τ_2 (ns)	τ_2 rel. %	τ_1 (ns)	τ_1 rel. %	τ_2 (ns)	τ_2 rel. %
1:1 Control	**3.5**	10.4	**33**	89.6	**4.7**	7.5	**58**	92.5
1:1 + ma	**2.6**	7.5	***45***	92.5	**3.9**	5.6	***75***	94.4
8:10 Control	**3.1**	11.5	**33**	88.5	**4.4**	7.7	**65**	92.3
8:10 + ma	**2.9**	11.6	***52***	88.4	**3.3**	7.1	***83***	92.9

Table S3. Lifetime components of bi-exponential fit to TRPL decay measurements of un-encapsulated stoichiometric and sub-stoichiometric $MAPbI_3$ films with and without methylamine additives (reacted 24 h). Both initial and atmosphere aged measurements are shown. The relative percentages of the total emission (rel. %) are also provided. Some samples were fit equally well to a mono-exponential fit and thus only one lifetime is given with a rel. % = 100 %.

	Initial Measurement				After H_2O/O_2 Exposure			
Sample	τ_1 (ns)	τ_1 rel. %	τ_2 (ns)	τ_2 rel. %	τ_1 (ns)	τ_1 rel. %	τ_2 (ns)	τ_2 rel. %
1:1 Control	**44**	1.9	**467**	98.1	**-**	-	**349**	100
1:1 + ma	**8.7**	3.4	***507***	96.6	**68**	6.8	***409***	93.2
8:10 Control	**-**	-	**487**	100	**-**	-	**477**	100
8:10 + ma	**72**	3.3	***953***	96.7	**78**	5.8	***586***	94.2