Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

# Amine Additive Reactions Induced by the Soft Lewis Acidity of $Pb^{2+}$ in Halide Perovskites. Part I: Evidence for Pb-Alkylamide Formation

Ross A. Kerner[a†], Tracy H. Schloemer[b†], Philip Schulz[c,d], Joseph J. Berry[c], Jeffrey Schwartz[e], Alan Sellinger[b,c,f], and Barry P. Rand[a,g]

[a.] Department of Electrical Engineering, Princeton University, Princeton, New Jersey 08544, United States

[b.] Department of Chemistry, Colorado School of Mines, Golden, Colorado 80401, United States

[c.] National Renewable Energy Laboratory, Golden, Colorado 80401, United States

[d.] CNRS, Institut Photovoltaïque d'Ile de France (IPVF), UMR 9006, Palaiseau, France.

[e.] Department of Chemistry, Princeton University, Princeton, New Jersey 08544, United States

[f.] Materials Science Program, Colorado School of Mines, Golden, Colorado 80401, United States

[g.] Andlinger Center for Energy and the Environment, Princeton University, Princeton, New Jersey 08544, United States

## Supplementary Information

## Experimental

The primary precursors used in this study are butylamine (99.5%, Sigma), methylamine (33 wt% in ethanol, Sigma), $PbI_2$ (98%, TCI), and N,N-dimethylformamide (anhydrous, 99%, Sigma), acetonitrile (anhydrous, 99.8%, Sigma) butylammonium iodide (Dyesol), and tetrabutylammonium iodide (Sigma). All other amines were purchased from Alfa Aesar. Linear PEI (MW = 10,000) was purchased from Sigma. The butylammonium iodide and tetrabutylammonium iodide were not exposed to atmosphere due to their hygroscopic nature. The solution chemistry and sample preparation were mainly performed inside of a $N_2$ filled glovebox to exclude the effects of moisture and oxygen. However, it was observed to proceed similarly in atmosphere. In addition to the precursors listed above, two different purities of $PbI_2$ from Alfa Aesar were also examined. The higher purity (99.999% by trace metals) $PbI_2$ also reacted readily with amines. Solutions where $PbI_2$ was reacted with methylamine:ethanol in DMF were allowed to react at room temperature for several days to ensure some amide formation.

The $PbI_2$/butylamine reaction product samples for XRD and XPS were prepared in a $N_2$ glovebox by drop casting 10 µL of solution onto a clean 1 cm x 2.5 cm glass substrate at 110 °C and annealing for 20 min. The $PbI_2$/PEI was fabricated in an $N_2$ glovebox by spin coating $PbI_2$ (200 mg/mL in DMF, 4000 rpm for 35 s), annealed at 75 °C for 15 min, followed by spin coating linear-PEI (~1 mg/mL in chlorobenzene, 4000 rpm for 60 s). The MAI:$PbI_2$ (0.8:1 ratio, 345 mg of $PbI_2$ per mL of DMF) with and without methylamine additive 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 75 °C for 15 min. 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 $5\times10^{-8}$ 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. A flood gun was used to neutralize the non-conductive, drop cast samples. $^1H$-NMR spectra were recorded using a JEOL ECA-500 at room temperature, and chemical shifts were referenced to the chloroform peak at 7.26 ppm and DMF at 8.0 ppm. The $PbI_2$•butylamine complex was prepared by reacting $PbI_2$ with butylamine for 2 hours at 65 °C. The mixture was then diluted in deuterated chloroform and filtered with a 450 nm PTFE syringe filter. The filtered solution continued to react forming more precipitates. After several filtrations, the solution was suitable to collect a $^1H$-NMR spectrum. TGA was performed in dynamic rate mode with a nominal rate of 50 °C/min, sensitivity of 1% mass change/min, and resolution of 4. Samples for TGA were prepared by reacting 200 mg of $PbI_2$ in 1 mL in DMF with 2 molar equivalents of butylamine at 65 °C for at least 2 hours to form a considerable amount of precipitate. The DMF containing excess $PbI_2$, BAI, and butylamine was decanted and the solid precipitate was washed 3 more times with 3 mL of ACN. The solid was dried under vacuum for 8 h before loading into the TGA where it was dried at 150 $^{o}$C for 10 min prior to starting a scan. Photoluminescence measurements were performed on an Edinburgh Instruments FLS980 photoluminescence spectrometer with an excitation wavelength of 550 nm.

## Supplementary Figures

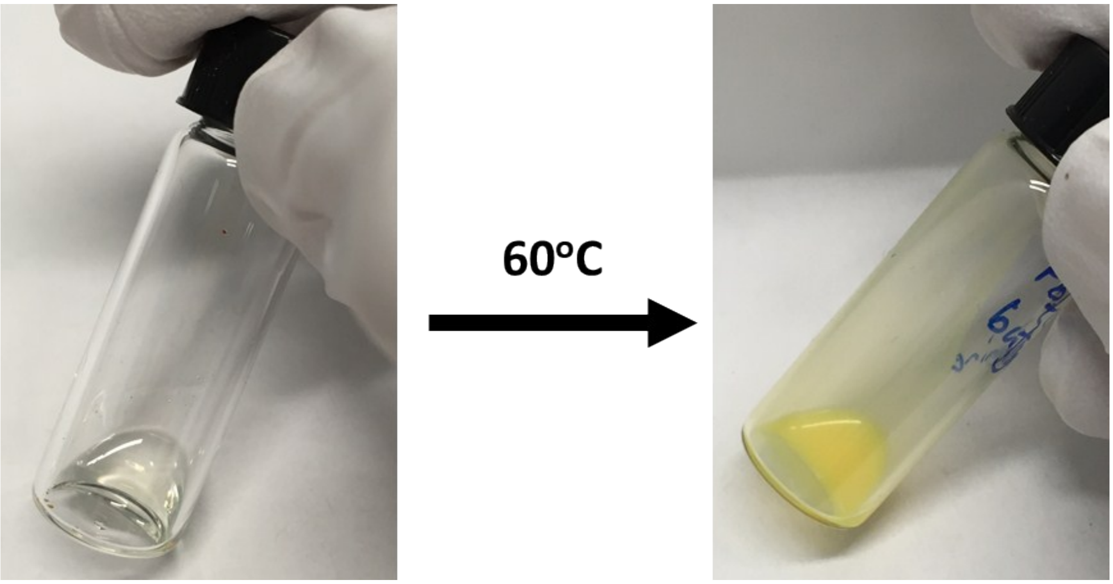

Figure S1. $PbI_2$ dissolved in butylamine (~500 mg/mL) stored at low temperature in a refrigerator (left) and then precipitated when brought to 60 °C (right). The precipitate did not redissolve upon cooling.

*Acid/Base Chemistry of a variety of Pb salts*. A variety of primary and secondary amines reacted with $PbX_2$ salts (X = Cl, Br, I, and $NO_3$). Tertiary amines and salts of PbX (such as X = $SO_4$) were not observed to react. Salient observations include azobenzene formation between aqueous $Pb(NO_3)_2$ and aniline and gelation when $PbBr_2$ was reacted with butylamine in DMF under certain conditions.

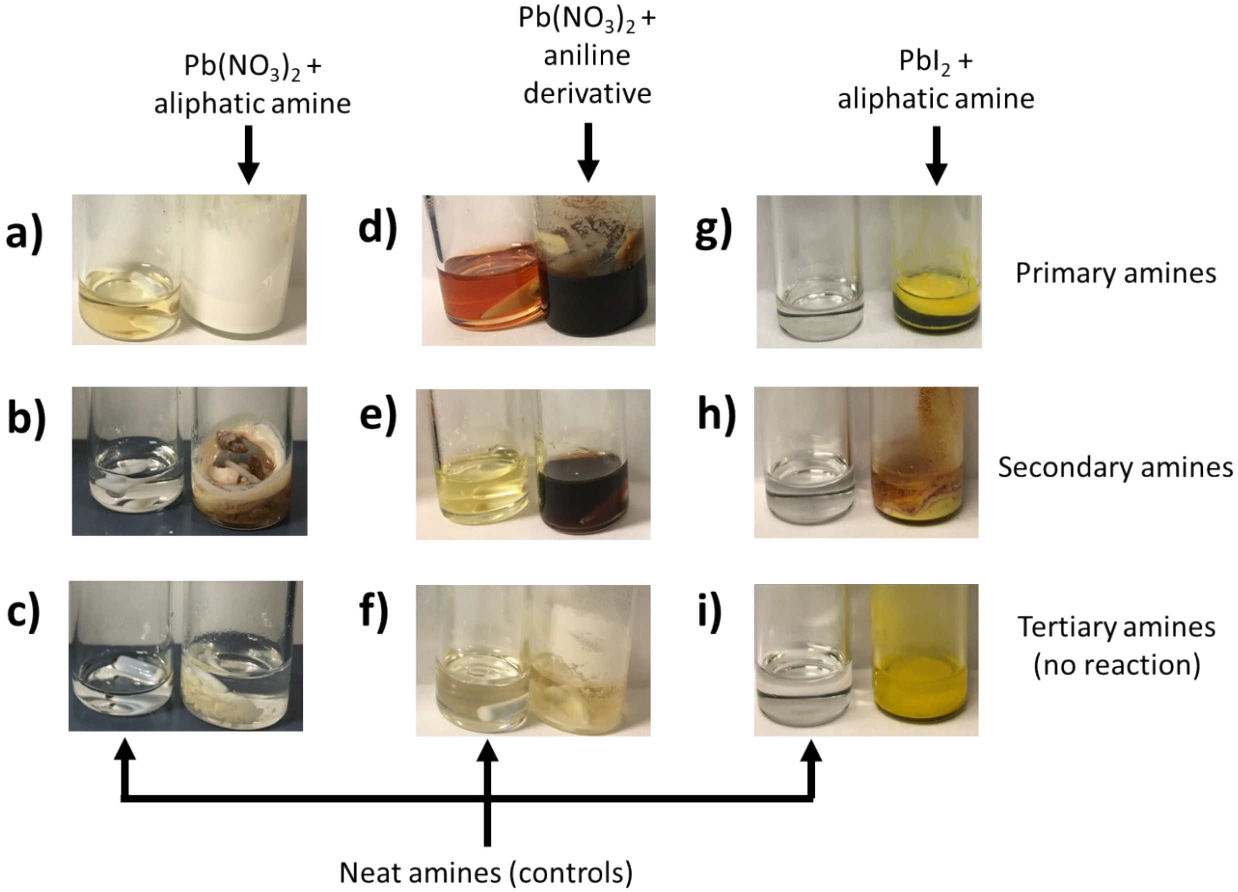

Figure S2. (vials on the right in each image) Days old mixtures of $Pb(NO_3)_2$ and an excess of (a) butylamine, (b) diethylamine, (c) triethylamine, (d) aniline, (e) N, methylaniline, and (f) N,N dimethylaniline alongside (vials on the left in each image) a control of the neat amine liquid reacted at 50 $^{o}$C. Days old mixtures of $PbI_2$ with an excess of (g) butylamine, (h) diethylamine, and (i) triethylamine alongside the control of the neat amine liquid reacted at 50 $^{o}$C.

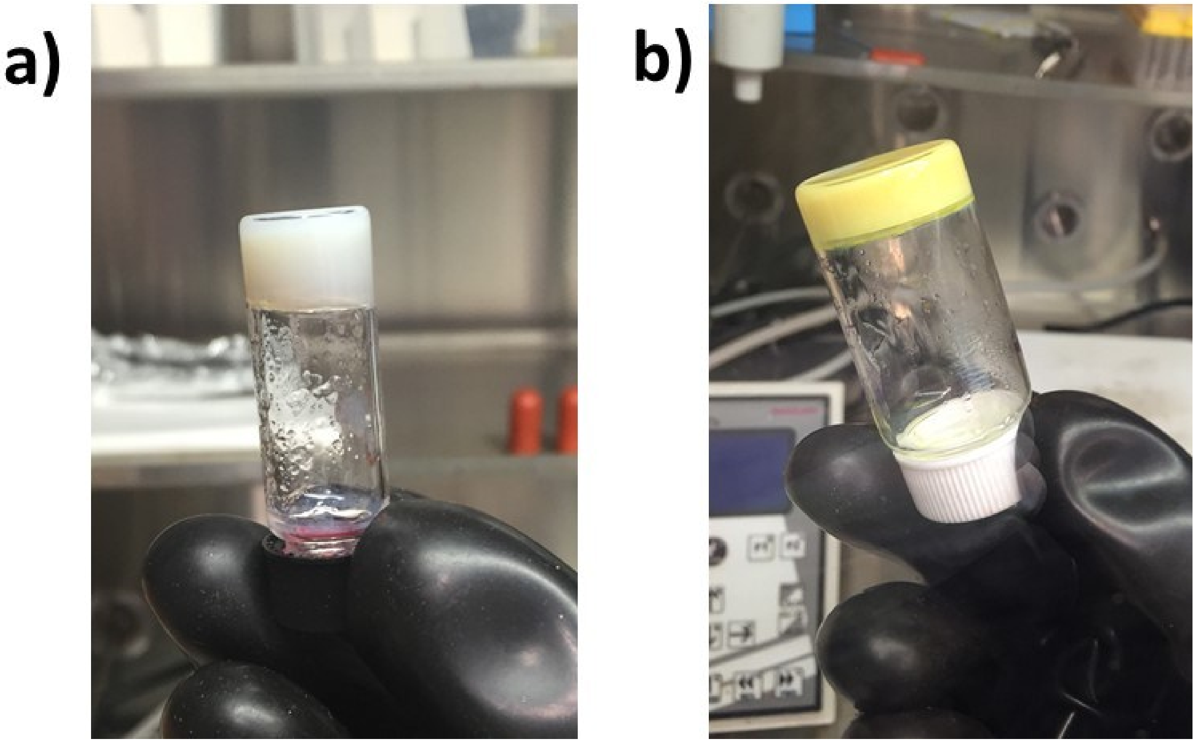

Figure S3. A reaction of 4 equivalents of butylamine with (a) $PbBr_2$ in DMF (~183 mg/mL) and (b) $PbI_2$ (200 mg/mL) completely gelled after 1 day at 55 $^oC$.

Figure S4. Equimolar tetra-BAI:$PbI_2$ in DMF after adding 2 equivalents of butylamine and storing at room temperature for 2 months.

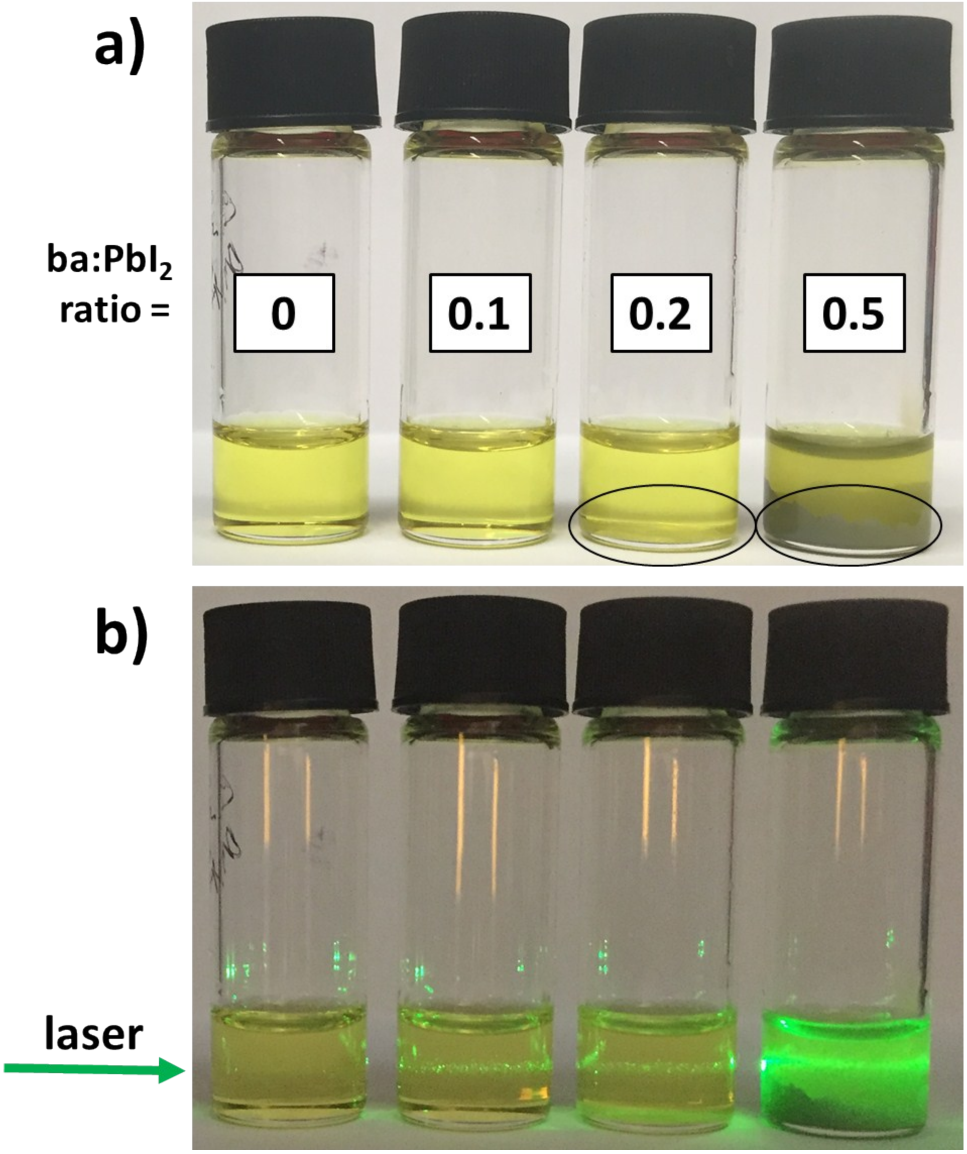

Figure S5. (a) Solutions of 200 mg/mL of PbI$_2$ in DMF with (from left to right) 0, 0.1, 0.2, and 0.5 molar equivalents of butylamine (ba) after reacting for 1 week at 55 $^o$C. Visible precipitates are observed to form even for small additions of butylamine down to 0.2 molar equivalents. (b) Tyndall effect helps to visualize precipitates forming for butylamine ratios down to 0.1 whereas no precipitates are observed in the control solution.

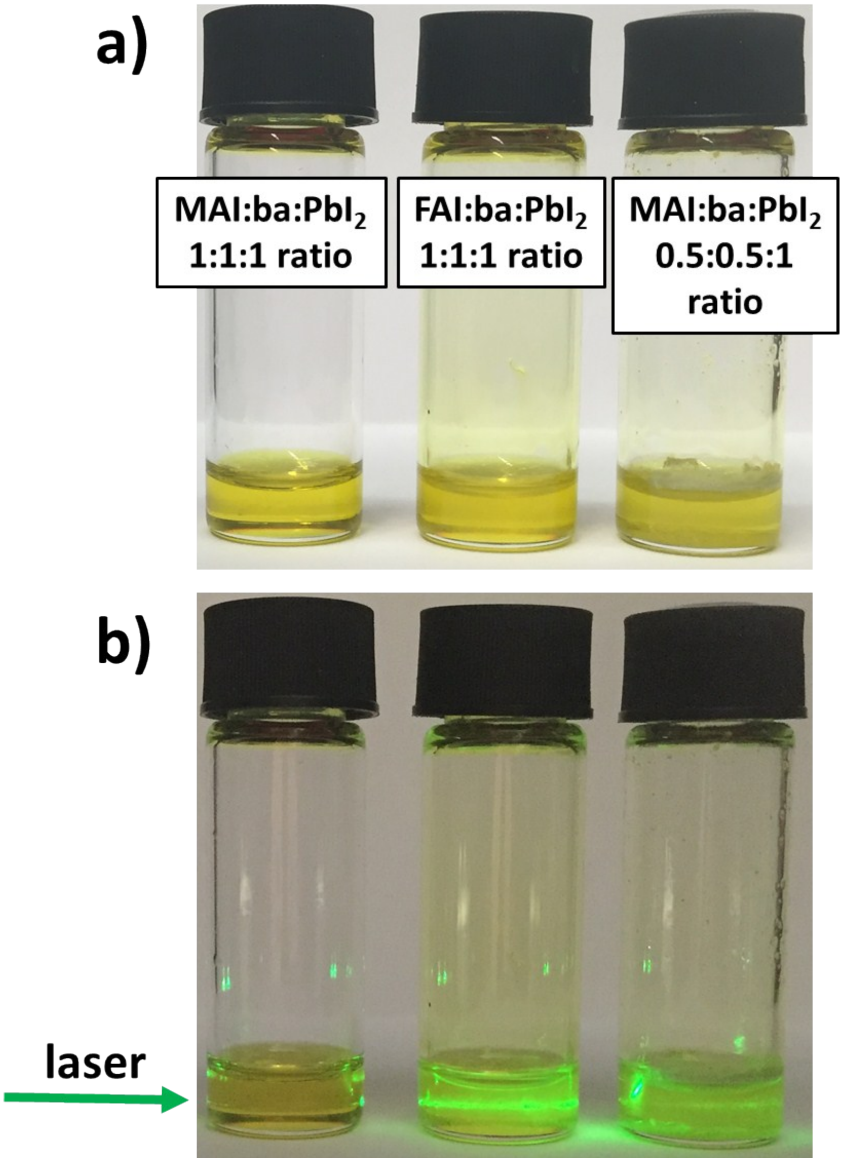

Figure S6. (a) Solutions of $PbI_2$ in DMF (200 mg/mL) with additives ratios from left to right: methylammonium iodide (MAI):butylamine (ba):$PbI_2$ (molar ratio 1:1:1), formamidinium iodide (FAI):ba:$PbI_2$ (molar ratio 1:1:1), and ba:MAI:$PbI_2$ (molar ratio 0.5:0.5:1) in DMF at a concentration of 200 mg/mL with respect to $PbI_2$. The solutions were reacted for one month at room temperature. The FAI and MAI deficient solutions produced an insoluble product which is clearly illustrated by the Tyndall effect (b). The ba:MAI:$PbI_2$ 0.5:0.5:1 solution illustrates that any excess of $PbI_2$ w.r.t. MAI in solution is available participate in acid-base reactions with free amines.

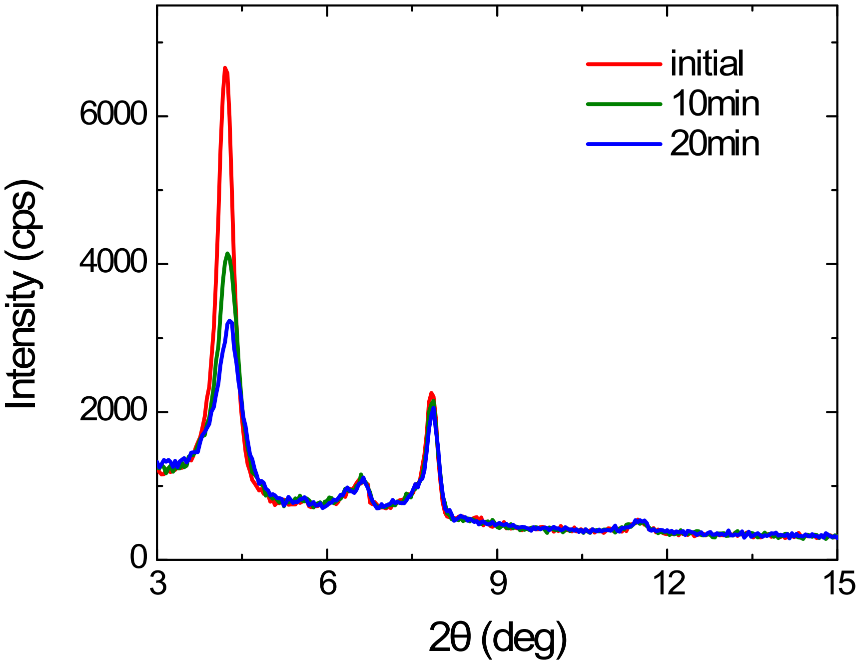

Fig. S7. XRD versus time of a drop cast film of $PbI_2$ solvated in a butylamine atmosphere and subsequently encapsulated in PMMA by spin coating (50 mg/mL in chlorobenzene at 4000 rpm giving roughly 300 nm of PMMA). The peak at low angle decreases over time as the solvate loses butylamine at room temperature which is only slowed by the PMMA. The peaks near $2\theta \approx 6.4^{o}$ are very near to that of $BA_2PbI_4$ which is expected to form from a $PbI_2$•butylamine solvate exposed to atmosphere due to a reaction with water.[1]

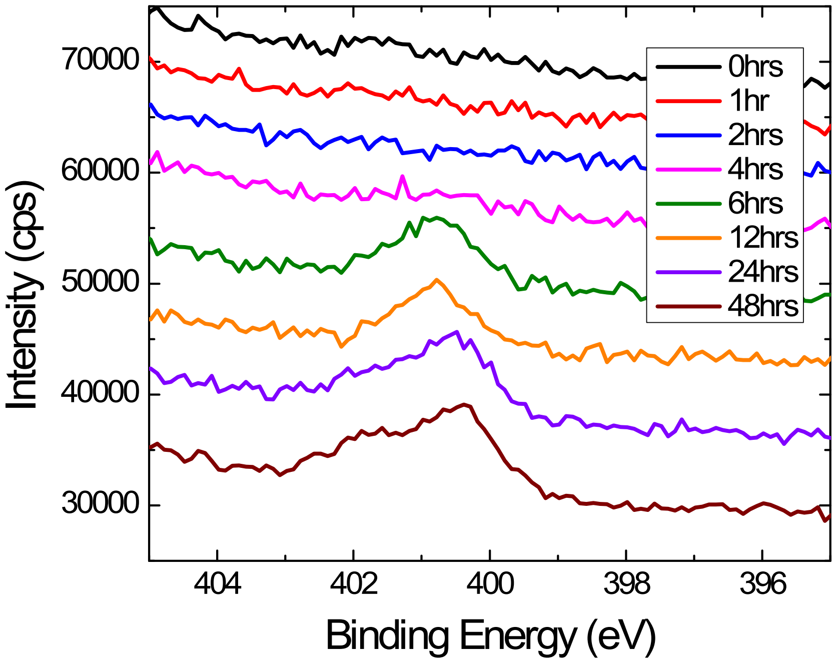

Fig. S8. Evolution of the N 1s XPS of $PbI_2$/butylamine reaction in DMF versus time. The lowest measurable N content is approximately 1-2 atomic % *via* XPS.

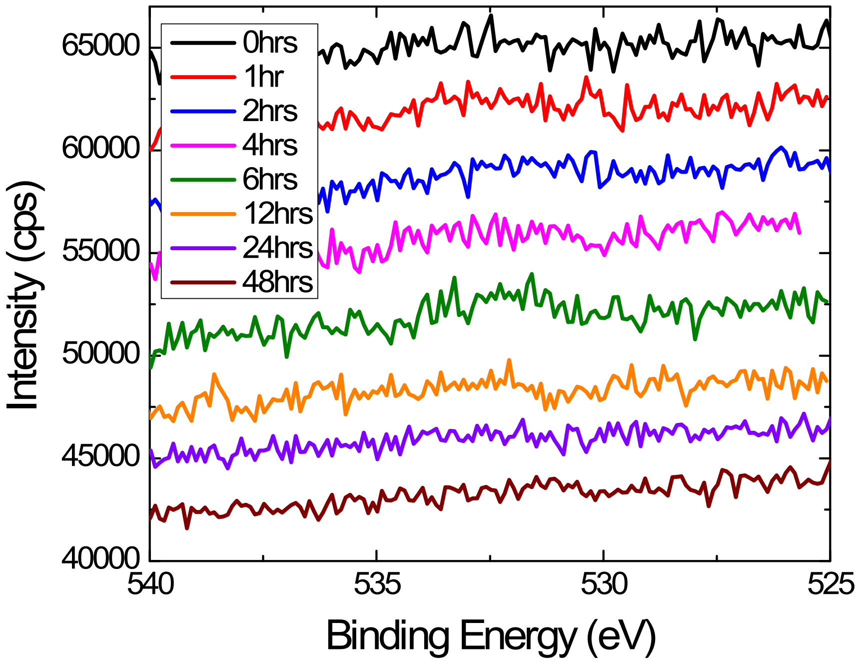

Fig. S9. O 1s XPS of $PbI_2$/butylamine reaction in DMF versus time showing negligible oxygen content.

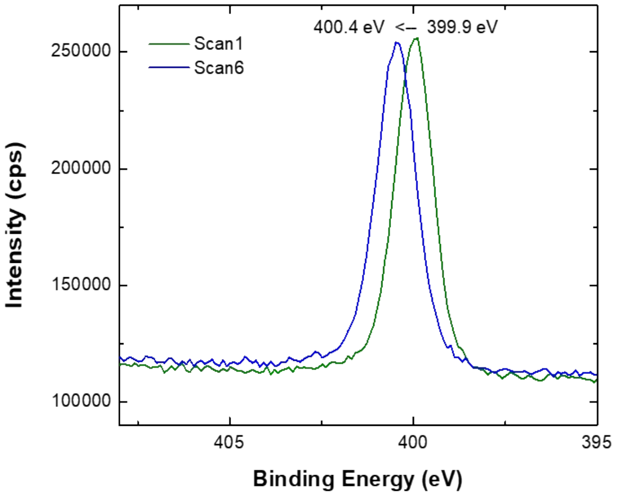

Figure S10. XPS of a thin film of linear-PEI on a glass/Au substrate.

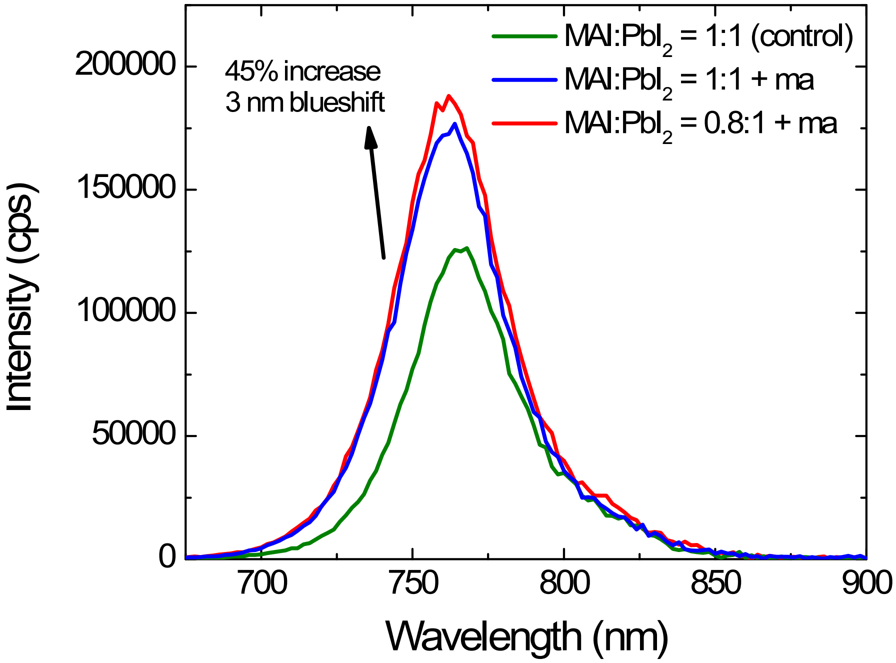

Fig. S11. Photoluminescence of thin films spin coated from stoichiometric and non-stoichiometric (MAI:PbI$_2$ = 0.8:1) reacted with methylamine in solution showing improved emission and blue-shift compared to the stoichiometric control film. Films were encapsulated in a layer of PMMA (50 mg/mL in chlorobenzene).

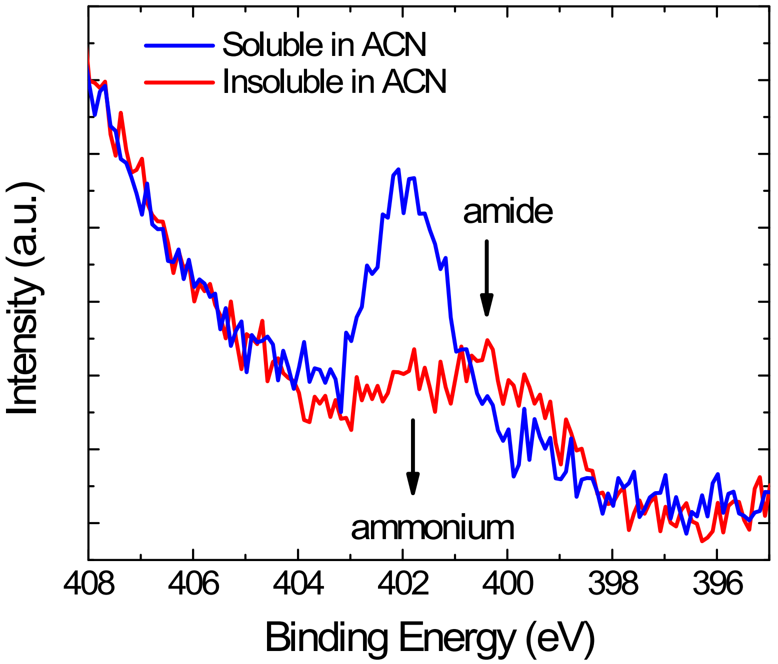

Fig. S12. N 1s XPS of the products of the neat reaction of $PbI_2$ with butylamine (4 equivalents, 24 hours at 60 °C) which were soluble or insoluble in ACN. The butylammonium iodide was selectively extracted due to its solubility in ACN whereas the amide product remained in the precipitate.

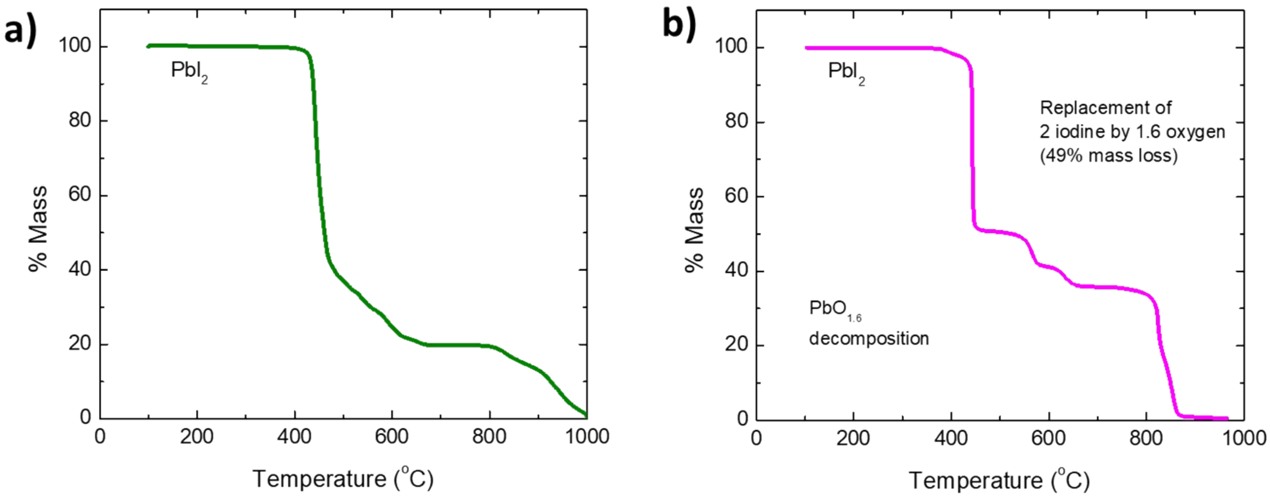

Fig. S13. TGA under (a) $N_2$ and (b) ambient air flow of $PbI_2$ powder.

Table S1. Theoretical mass losses of PbI(butylamide) and $PbI_2$ solvated by 1 or 2 butylamine molecules. The $PbI_2$•butylamine solvation complexes would be expected to gain mass in air due to a reaction with water as reported in reference 1 and were not considered here.

| Starting Material | Fragment | Percent Mass Loss in $N_2$ | Percent Mass Loss in Atmosphere (replacement by oxygen) | |
|---|---|---|---|---|
| $PbI_2$ | 2I | 55 | 53 | |
| $PbI \bullet [NH(CH_2)_3CH_3]$ | $[NH_2(CH_2)_3CH_3]$ | **18** | **14** | |
| $PbI_2 \bullet [NH_2(CH_2)_3CH_3]$ | $[NH_2(CH_2)_3CH_3]$ | 14 | mass gain expected | (mono solvate) |
| | I | 24 | 21 | |
| $PbI_2 \bullet [NH_2(CH_2)_3CH_3]_2$ | $[NH_2(CH_2)_3CH_3]_2$ | 24 | mass gain expected | (bi solvate) |

## References

1. Raga, S. R.; Ono, L. K.; Qi, Yabing. Rapid Perovskite Formation by $CH_3NH_2$ Gas-Induced Intercalation and Reaction of $PbI_2$. *J. Mater. Chem. A*. **2016**, *4*, 2494-2500