Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information

Structural and chemical evolution of methylammonium lead halide perovskites during thermal processing from solution

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Table S1. Composition of the solutions used in perovskite preparation showing the mass, moles, and weight percent of each component

Solution Nomenclature	PbI_2 (g|mmol|%)	$PbCl_2$ (g|mmol|%)	CH_3NH_3I (g|mmol|%)	CH_3NH_3Cl (g|mmol|%)	DMF (g|%)	DMSO (g|%)	GBL (g|%)
1:1 MAI:PbI_2	0.693 | 1.5 | 18.82	--	0.239 | 1.5 | 6.49	--	2.75 | 74.69	--	--
1:1 MAI:PbI_2 (DMSO)	0.693 | 1.5 | 18.82	--	0.239 | 1.5 | 6.49	--	--	2.75 | 74.69	--
1:1 MAI:PbI_2 (GBL)	0.693 | 1.5 | 18.82	--	0.239 | 1.5 | 6.49	--	--	--	2.75 | 74.69
1:0.5:1 MAI:MACl:PbI_2	0.693 | 1.5 | 18.57	--	0.239 | 1.5 | 6.40	0.050 | 0.75 | 1.34	2.75 | 73.69	--	--
1:1:1 MAI:MACl:PbI_2	0.693 | 1.5 | 18.32	--	0.239 | 1.5 | 6.32	0.100 | 1.5 | 2.64	2.75 | 72.71	--	--
1:2:1 MAI:MACl:PbI_2	0.693 | 1.5 | 17.85	--	0.239 | 1.5 | 6.16	0.200 | 3 | 5.15	2.75 | 70.84	--	--
3:1 MAI:$PbCl_2$	--	0.477 | 1.7 | 13.52	0.822 | 5.2 | 23.29	--	2.75 | 63.19	--	--

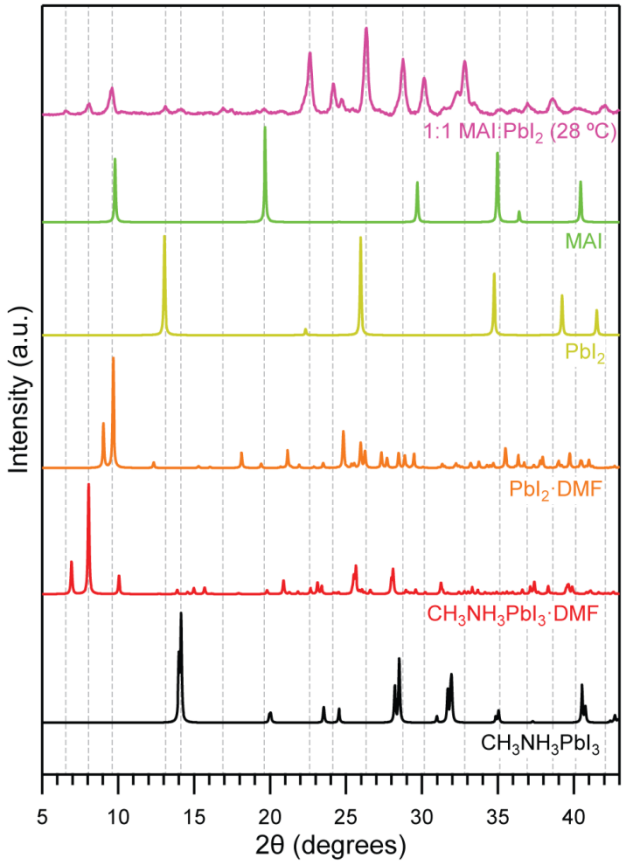

Figure S1. Comparison of the XRD pattern of the 1:1 MAI:PbI_2 precursor phase at 28 °C to other known crystal structures. Dashed vertical lines show the peak positions of the precursor phase.

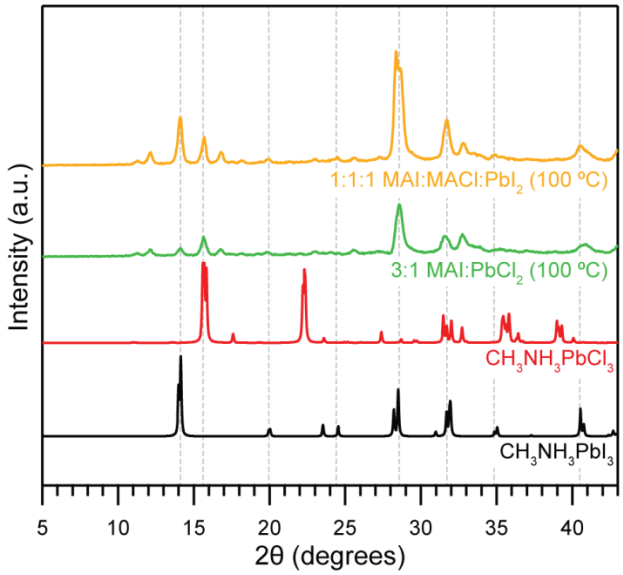

Figure S2. Comparison of the XRD pattern of the 1:1:1 MAI:MACl:PbI_2 and 3:1 MAI:$PbCl_2$ intermediate phase to simulated XRD patterns of $CH_3NH_3PbI_3$ and $CH_3NH_3PbCl_3$. Dashed vertical lines show the peak positions of the intermediate phase.

Table S2. 2θ angles at which the line cuts shown in **Figure 2** were made

1:1 MAI:PbI_2 Precursor Phase	**Cl^- Precursor Phase**	**Cl^- Intermediate Phase**	**Perovskite Phase**	**Degraded Phase**
6.56	7.04	11.21	14.12	12.7
8.00	8.11	12.15	24.41	39.1
9.55	10.07	15.61	28.27	--
13.06	20.96	16.8	31.72	--
16.79	23.22	18.16	40.34	--
17.41	25.60	28.81	--	--
19.52	--	32.80	--	--
20.64	--	--	--	--
22.59	--	--	--	--
24.04	--	--	--	--
26.27	--	--	--	--
28.70	--	--	--	--
30.00	--	--	--	--
32.73	--	--	--	--
36.80	--	--	--	--
38.47	--	--	--	--

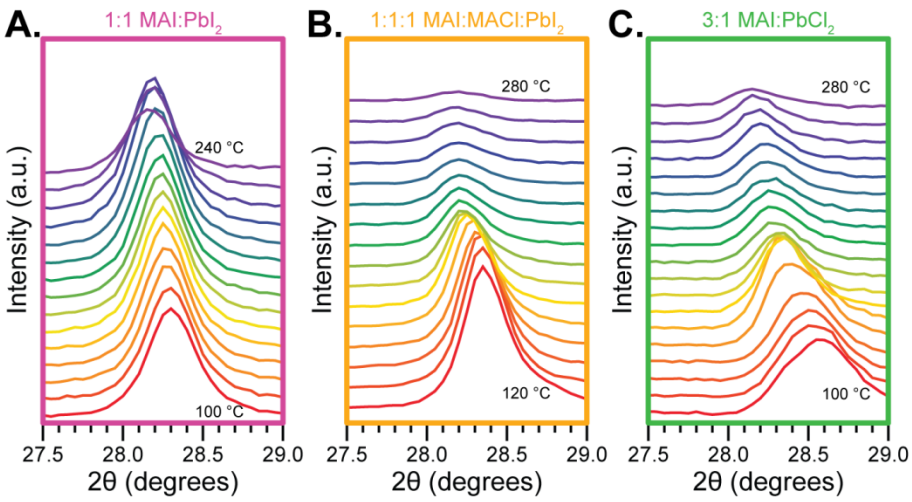

Figure S3. The shift of the perovskite (200) peak with increasing temperature for the samples A) 1:1 MAI:PbI_2, B) 1:1:1 MAI:MACl:PbI_2, and C) 3:1 MAI:$PbCl_2$. Temperature increases in 10 °C increments from the bottom to the top of the figure and traces are averages of all traces taken over a 5 °C window (*e.g.*, 100 °C is the sum of 97.5 – 102.5 °C).

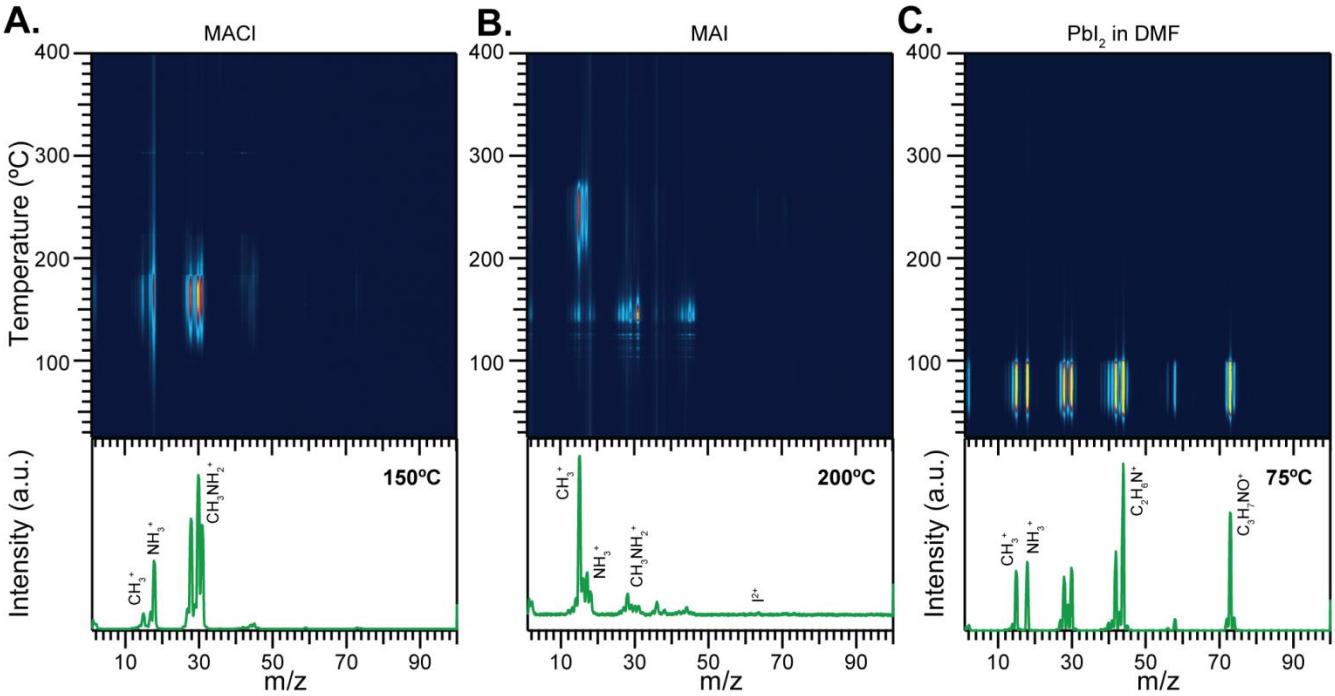

Figure S4. TPD-MS plots and labeled horizontal line cuts at the indicated temperature for control samples of pure A) MACl, B) MAI, and C) PbI_2 in DMF.

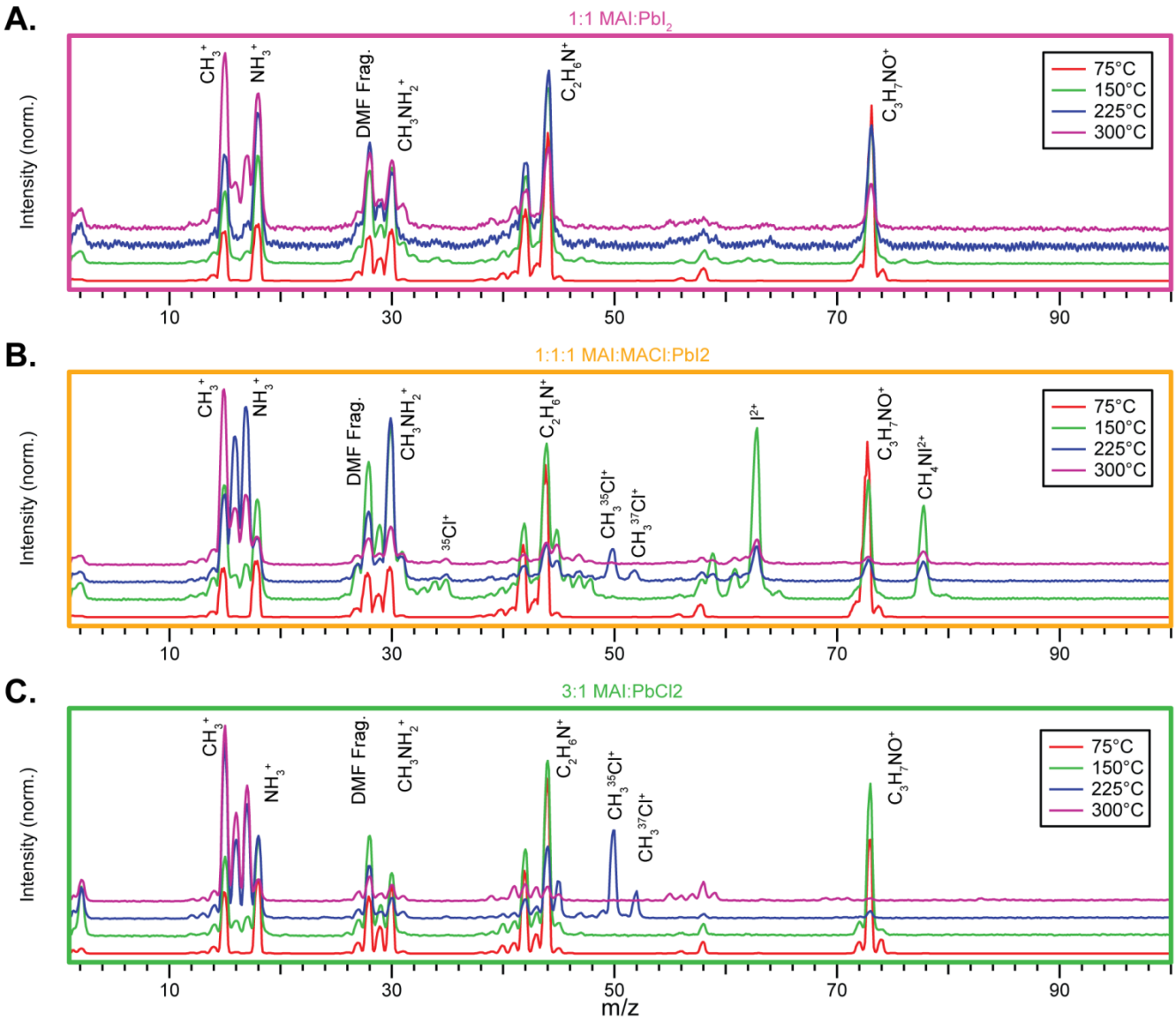

Figure S5. Normalized line cuts, including peak assignment, of TPD-MS data for A) 1:1 MAI:PbI_2, B) 1:1:1 MAI:MACl:PbI_2, and C) 3:1 MAI:$PbCl_2$.

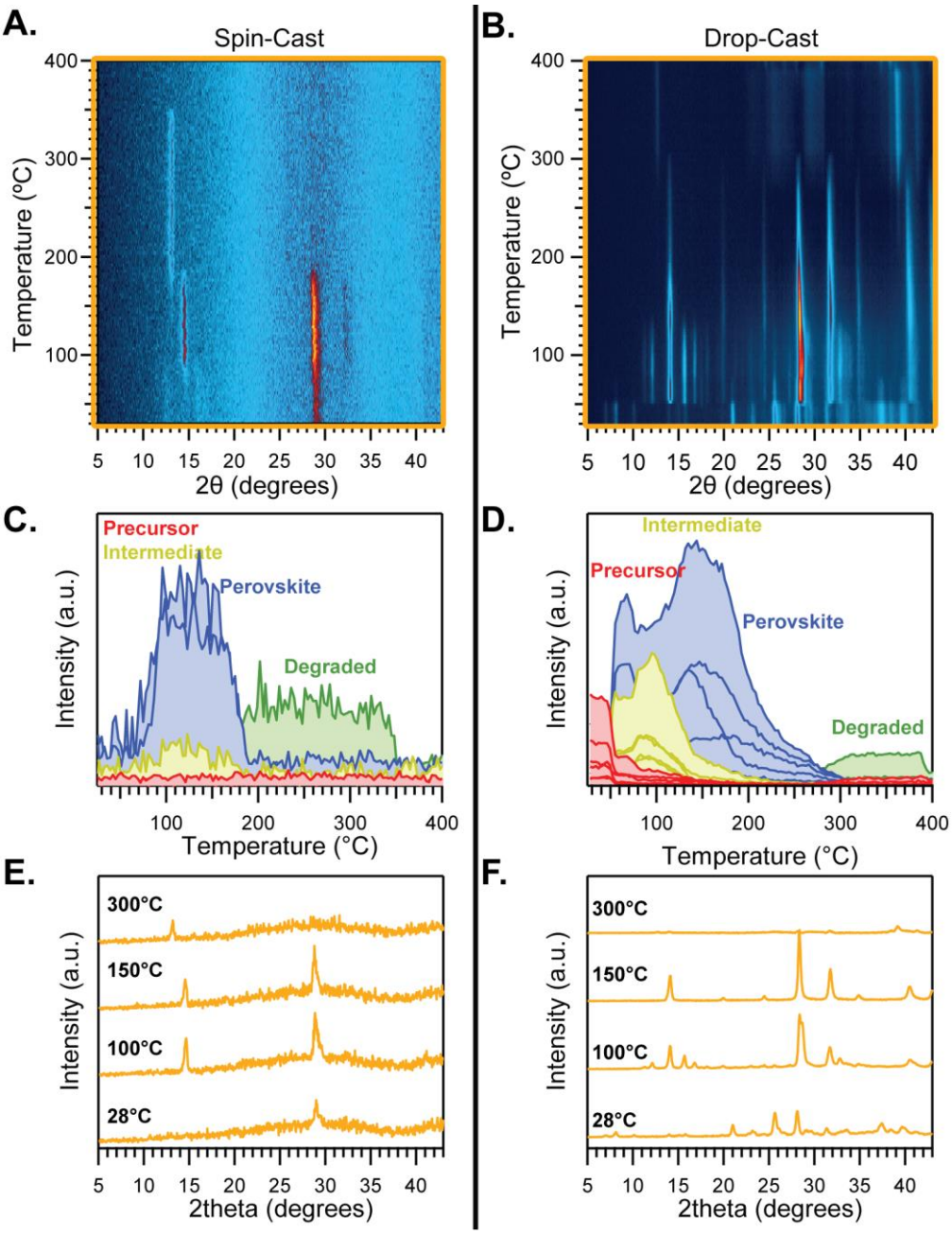

Figure S6. T-XRD spectra obtained from A) spin-cast and B) drop-cast samples obtained from the precursor solution 1:1:1 MAI:MACl:PbI_2. A constant temperature ramp of 2 °C/min was used in each case. Vertical line cuts of the 2-dimensional T-XRD patterns of C) spin-cast and D) drop-cast films taken at the characteristic 2θ angles shown in **Table S2**; some 2θ angles were omitted in C) because no signal was observed. XRD line cuts taken at 28, 100, 150, and 300 °C for E) spin-cast and F) drop-cast films.

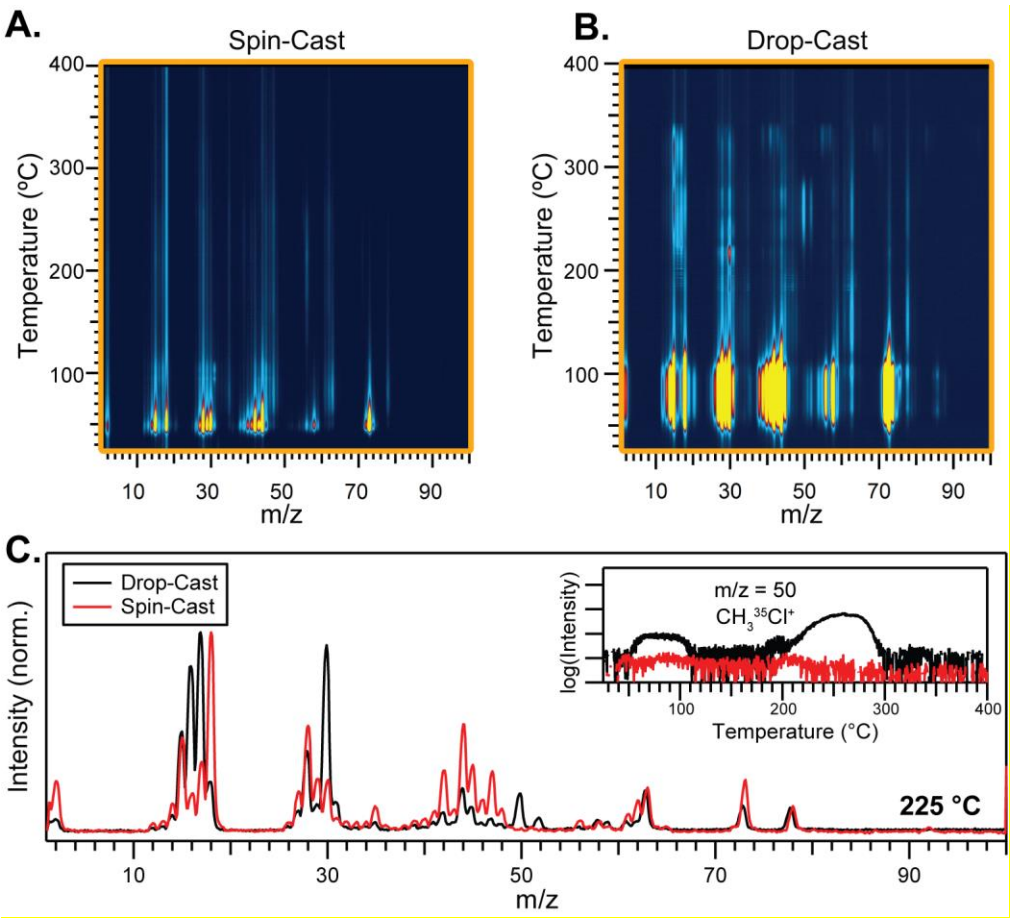

Figure S7. TPD-MS spectra obtained from A) spin-cast and B) drop-cast samples obtained from the precursor solution 1:1:1 MAI:MACl:PbI_2. A constant temperature ramp of 5 °C/min was used in each case. C) Normalized horizontal line cuts of the 2-dimensional TPD-MS spectra obtained from the drop- and spin-cast samples taken at 225 °C. Inset shows vertical line cuts of these samples taken at an m/z ratio of 50.

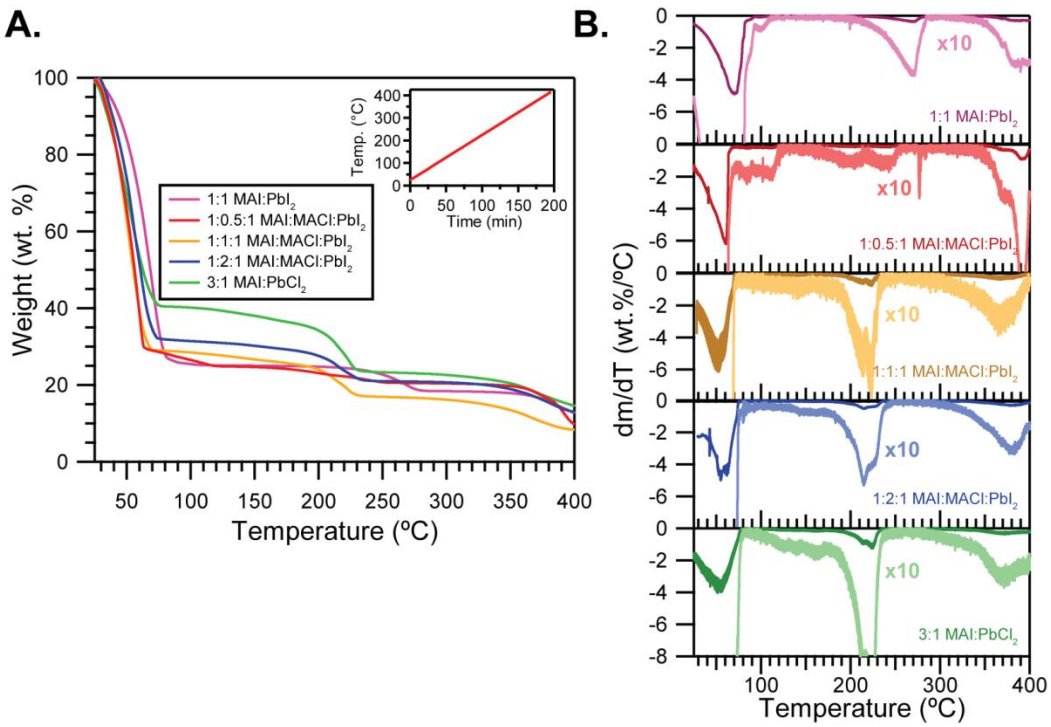

Figure S8. A) TGA heating curves of solutions with varying amounts of Cl^- added and B) the first derivative of the TGA curves. The molar composition of the solutions are 1:1 MAI:PbI_2, 1:0.5:1 MAI:MACl:PbI_2, 1:1:1 MAI:MACl:PbI_2, 1:2:1 MAI:MACl:PbI_2, and 3:1 MAI:$PbCl_2$. The TGA figure inset shows the heating profile used in the experiments. The lighter traces in the first derivatives show the data multiplied by 10 to highlight smaller features.

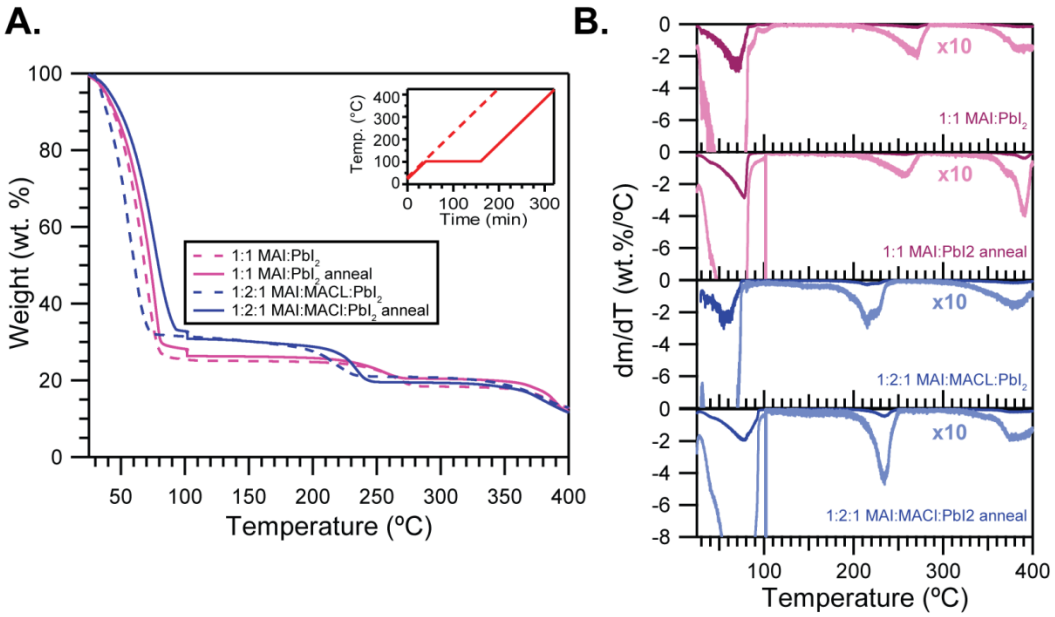

Figure S9. A) TGA heating curves and B) the corresponding first derivatives comparing the results of a constant temperature ramp (dashed lines) and a 90 min, 100°C anneal (solid lines) for 1:1 MAI:PbI_2 and 1:2:1 MAI:MACl:PbI_2 in DMF. The inset shows the heating profile used in the experiments. The lighter traces in the first derivatives show the data multiplied by 10 to highlight smaller features.

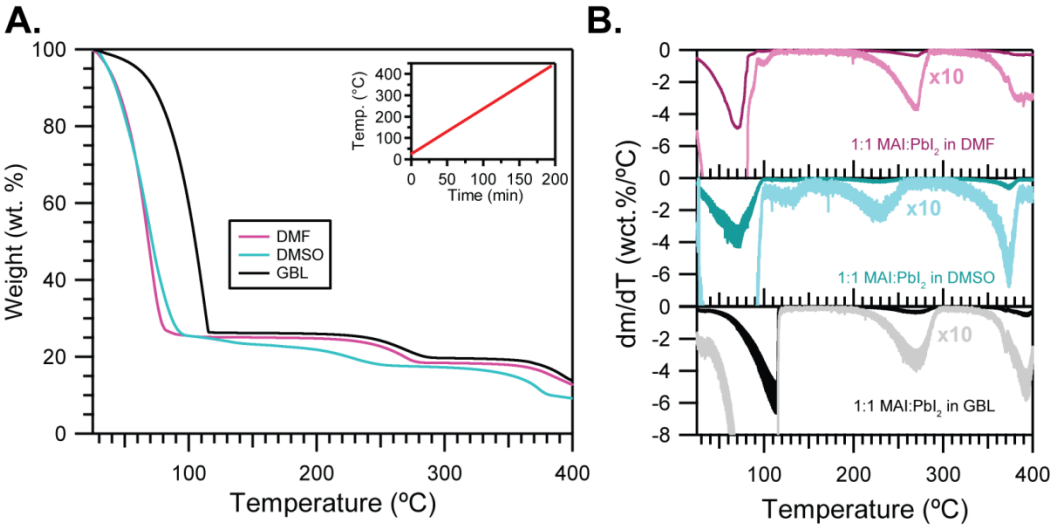

Figure S10. A) TGA heating curves and B) the corresponding first derivatives for 1:1 MAI:PbI_2 solutions in DMF, DMSO, and GBL. The inset shows the heating profile used in the experiments. The lighter traces in the first derivatives show the data multiplied by 10 to highlight smaller features.