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# Single Crystal Purification Reduces Trace Impurities in Halide Perovskite Precursors, Alters Perovskite Thin Film Performance, and Improves Phase Stability

Supporting Information

Connor J. Dolan, Emma R. Yakel, Shiwei Liu, Ross A. Kerner, Jack R. Palmer, Kelly X.

Vences, Hendrik M. Vossler, Clark Han, Sean P. Dunfield\*, David P. Fenning\*

\*Corresponding Authors: seandunfield@gmail.com, dfenning@ucsd.edu

#### **EXPERIMENTAL SECTION**

#### **Solvent Orthogonality Induced Crystallization**

In a N<sub>2</sub>-filled glovebox (<1ppm O<sub>2</sub>, H<sub>2</sub>O), 1.5M formamidinium iodide (FAI, 99.99%, Greatcell Solar, lot number 255005) and 1.5M lead iodide (PbI<sub>2</sub>, 99%, Sigma Aldrich, lot number BCCF9314 or 99.99%, Tokyo Chemical Industry, lot number HQRPA-PD) were added to a 20mL vial (VWR) and solvated in dried and filtered gamma-butyrolactone (99.5%, Transene, lot number 080785). The FAPbI<sub>3</sub> solutions were stirred using a PTFE stir bar (VWR) for several hours until fully transparent and filtered into a fresh vial through a 0.2 $\mu$ m pore size PTFE filter (VWR). Once dissolved, the FAPbI<sub>3</sub> solutions were removed from the glovebox. In a fume hood, 5mL of filtered FAPbI<sub>3</sub> solution was added to a fresh 20mL vial for each growth and these vials were carefully placed uncapped into a 100mL glass bottle (VWR) containing 20mL of antisolvent (chlorobenzene, toluene, or methyl acetate). The cap to the 100mL glass bottle was then shut and the bottle was placed upright in a sand bath to mitigate thermal and vibrational changes to minimize nucleation sites. These growth solutions were left for a specified amount of time depending on the vapor pressure of the antisolvent used (3 days for methyl acetate, 1 week for toluene, 2 weeks for chlorobenzene).

To reclaim the crystals, which are typically 1-10mm in size, the inner (20mL) vial containing the FAPbI<sub>3</sub> single crystals was carefully removed from the outer (100mL) bottle with clean tweezers. All remaining liquid was removed from this vial with a pipette and crystals were rinsed twice with fresh, filtered methyl acetate (Sigma Aldrich, 99.5%) to remove excess unreacted precursor. The crystals were then gently scraped out onto weighing paper with a fresh disposable spatula (polypropylene, VWR) and left to dry for ~2 minutes. Crystals were then transferred to a fresh 20mL vial and washed in methyl acetate again. This process was repeated 3x for a total of 6

washes with methyl acetate in 3 separate vials. After the final drying step, crystals were transferred to a (4<sup>th</sup>) fresh 4mL vial and thoroughly crushed using a disposable pestle (VWR) for ~5 minutes by hand until powderized. Powders were then heated at 150°C under vacuum for 2 hours to remove residual solvent and convert to  $\alpha$ -FAPbI<sub>3</sub>. Following the heating step, powders were quickly placed into a N<sub>2</sub>-filled glovebox for storage. SONIC results in a yield of 60% +/- 10% by mass for a single crystallization.

#### **Retrograde Powder Crystallization**

RPC was performed as previously reported.<sup>19</sup> In an N<sub>2</sub>-filled glovebox (<1ppm O<sub>2</sub>, H<sub>2</sub>O), 0.8M of formamidinium iodide (FAI, 99.99%, Greatcell Solar, lot number 255005) and 0.8M of lead iodide (PbI<sub>2</sub>, 99%, Sigma Aldrich, lot number BCCF9314 or 99.99%, Tokyo Chemical Industry, lot number HQRPA-PD) were solvated in 2-methoxyethanol (Sigma Aldrich, 99.8%). Solutions were stirred using a PTFE magnetic stirring bar (VWR) for several hours until clear. Parafilmed solutions were then transferred outside of the glovebox into a fume hood. Solutions were placed in a silicone oil bath preheated to 120°C and stirred at 1000rpm for 45 minutes until a uniform black powder accumulated at the bottom of the vial. Solutions were then removed from the bath and quickly dumped into a disposable vacuum filter (VWR) before they were allowed to cool (< 5 seconds outside of the bath before the solution was dumped onto the vacuum filter). To ensure all excess powder stuck to the edges of the vial was recovered, the vial was continuously flushed with filtered methyl acetate (Sigma Aldrich, 99.5%) with a syringe.<sup>5</sup> The powder was then gently scraped from the vacuum filter with a disposable spatula (VWR) and placed in a fresh 4mL vial. The powder was then heated at 150°C under vacuum for 30 minutes and promptly transferred into the glovebox for storage.

#### **Powder X-Ray Diffraction**

Samples for powder X-ray diffraction were prepared by taking crystallized powders from the RPC and SONIC processes and crushing them thoroughly with a disposable pestle then spreading them out over a glass substrate with double sided carbon tape on top to create a continuous layer of powder over the surface. Measurements were taken using an Anton-Paar XRDynamic diffractometer using a Cu-K $\alpha$  X-ray source with the samples under vacuum during the measurement to eliminate the possibility of oxygen or moisture-induced degradation. Measurements were taken in a parallel beam geometry using a coupled omega-two theta scanning geometry with no omega offset.

#### **Inductively Coupled Plasma Mass Spectrometry**

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) measurements were taken using a Thermo iCAP RQ single-quadrupole ICP-MS system at the Environmental and Complex Analysis Laboratory (ECAL) at the University of California, San Diego. Samples were prepared by solvating a small amount (~10mg) of each powder in 2% aqueous HNO<sub>3</sub> (VWR, 67-70% Aristar Plus diluted in Milli-Q water) in clean 15mL centrifuge tubes. Samples were heated at 60°C for 24 hours to fully digest.

ICP-MS measurements were taken in two steps to ensure maximum sensitivity to impurity elements. First, a relatively high concentration of each sample (100ppm weight/weight) was prepared. In the 100ppm samples, all cations of interest except for Pb were measured to avoid matrix effects from measurement of Pb, which is far more concentrated than any of the impurity species detected. Each of these 100ppm solutions were then diluted to 10ppb weight/weight and remeasured exclusively to accurately quantify Pb. The impurity concentrations quantified in the 100ppm samples were then normalized based on the measured concentration of Pb in the 10ppb

samples. All samples were measured 5 times successively to improve statistics of the measurements.

Standards for quantification were prepared by diluting a standard mix (Periodic Table Mix 1 for ICP, Sigma Aldrich) in 2% aqueous HNO<sub>3</sub>. Standards were measured at concentrations of 1ppt, 10ppt, 10ppt, 1ppb, 10ppb, and 100ppb weight/weight in 2% aqueous HNO<sub>3</sub> for both measurements. Standards were measured in order of low to high concentration. To maximize the sensitivity of measurements to trace impurities, all measurements were taken in "Kinetic Energy Discrimination" mode, where a collision cell in the ICP-MS is filled with helium. This removes polyatomic interference with overlapping mass-to-charge ratios with elemental isotopes due to their larger scattering cross sections. Statistical limits of detection (LoD) were calculated by measuring a blank sample (2% aqueous HNO<sub>3</sub>) 5 times. The LoD for each element was set to the mean concentration from these measurements added to three times the standard deviation from these measurements.

#### **Proton Nuclear Magnetic Resonance**

Inside of a N<sub>2</sub>-filled glovebox (<1ppm O<sub>2</sub>, H<sub>2</sub>O), 0.5M of FAPbI<sub>3</sub> was solvated in deuterated DMSO (DMSO-d6, Sigma Aldrich, 99.9%) and vortexed for several hours to fully dissolve. The samples were transferred into glass NMR tubes (NORELL) using clean single use glass pipettes. Pure DMSO-d6 was measured as a control for all NMR measurements. All NMR tubes were filled to a solution height of 4 cm and sealed with a cap and tightly parafilmed before removal from the glovebox. <sup>1</sup>H-NMR measurements were carried out using a Jeol ECZ 400MHz NMR Spectrometer at room temperature. 64 scans were measured and averaged for each sample with an acquisition time of 2 seconds and a relaxation time of 4 seconds, employing force tune. The pure DMSO-d6

was analyzed first to ensure the absence of contaminants in the solvent. The NMR data was processed using MestReNova software. The central peak of DMSO was calibrated to 2.5 ppm.

#### Thin Film/Solar Cell Fabrication

FAPbI<sub>3</sub> thin films were fabricated using solvent self-volatilization as previously reported.<sup>29</sup> Solar cell devices were fabricated in a P-I-N inverted architecture with a device stack of indium-doped tin oxide (ITO)/Aluminum Oxide (AlOx)/MeO-2PACz/FAPbI<sub>3</sub>/C<sub>60</sub>/BCP/Ag.

Substrates (glass for thin films, pre-patterned ITO (Biotain) for solar cells) were cleaned by sonication in acetone, isopropanol, and deionized water for 15 minutes each. They were placed in a convection drying oven at 170°F for >1 hour to thoroughly remove all residual water from the substrates. For solar cells, one atomic layer of AlOx was then deposited at 150°C substrate temperature using a Veeco Savannah Thermal Atomic Layer Deposition setup to mitigate interfacial reactivity of the ITO.<sup>30</sup> They were then treated with ultraviolet-ozone for 20 minutes immediately prior to bringing into the glovebox for deposition. Inside of a N<sub>2</sub>-filled glovebox, 0.6mg/mL of [2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid (MeO-2PACz, 98%, TCI) was solvated in ethanol (Sigma Aldrich, 99.5%) and vortexed for 1 hour to fully dissolve. 100µL of MeO-2PACz solution was then spin-coated on the cleaned glass substrates at 3000rpm for 30 seconds and annealed at 100°C for 10 minutes. MeO-2PACz was utilized to mitigate the impact of interfacial recombination at the bottom interface on photoluminescence behavior.<sup>31</sup>

FAPbI<sub>3</sub> solutions were prepared by first dissolving 1.33M of FAPbI<sub>3</sub> precursor in 2methoxyethanol (Sigma Aldrich, 99.8%) and vortexed for several hours until clear. Raw (not purified) FAPbI<sub>3</sub> precursor consisted of equimolar formamidinium iodide (FAI, 99.99%, Greatcell Solar, batch number 255005) and lead iodide (PbI<sub>2</sub>, 99%, Sigma Aldrich, lot number BCCF9314 or 99.99%, Tokyo Chemical Industry, lot nRumber HQRPA-PD). For the second batch of degradation experiments at 0.6-sun light intensity, the precursors used were formamidinium iodide (FAI, 99.99%, Greatcell Solar, batch number 485105) and lead iodide (PbI<sub>2</sub>, 99%, Sigma Aldrich, lot number BCCH3275 or 99.99%, Tokyo Chemical Industry, lot number 2XUQD-LV. 0.2M MACl (Greatcell Solar, 99.99%) was then added to the FAPbI<sub>3</sub> solution and was vortexed < 5 min to dissolve. 7.5% N-methyl-2-pyrrolidone (NMP, Sigma Aldrich, 99.5%) by volume was then added in and the solution was quickly vortexed to mix. 100µL of perovskite solution was then spin-coated at 8000rpm for 30s and annealed at 150°C for 10 minutes.

For solar cells, films were transferred to an evaporator where 30nm of  $C_{60}$  (0.1 Å/s), 12nm of BCP (0.1 Å/s), and 100nm of Ag (0.5 Å/s for first 5nm, then 2 Å/s) were deposited in vacuum <1e-8 mbar.

### **Thin Film X-Ray Diffraction**

X-ray diffraction measurements were taken using an Anton-Paar XRDynamic diffractometer with the samples under vacuum during the measurement to eliminate the possibility of oxygen or moisture-induced degradation. Measurements were taken with a Cu-Kα X-ray source in a parallel beam geometry using a coupled omega-two theta scanning geometry with no omega offset.

#### **Scanning Electron Microscopy**

Scanning Electron Microscopy (SEM) images were taken using a FEI Apreo SEM in with 2kV accelerating voltage, 0.1nA current, and a working distance of 2.5-3mm using a backscattered electron detector at 10,000x magnification.

#### **Photoluminescence Spectra**

Photoluminescence spectra were taken using a home-built setup. Samples were excited with a 520nm laser and spectra were measured with a Stellarnet Silver-Nova Super Range TEC fiber coupled spectrometer.

#### Photoluminescence Quantum Yield and Implied Current-Voltage Curves

Implied current-voltage (implied-JV) curves of APTES-passivated perovskite films were calculated from injection-dependent photoluminescence quantum yield (PLQY) measurements as previously reported.<sup>32</sup> PLQY measurements were performed on each sample using a home-built setup consisting of an integrating sphere and using the three-measurement approach.<sup>33</sup> Samples were excited with a continuous wave diode pumped solid state DPSS laser module controlled by a laser diode controller (SRS, Model LDC502) coupled into an integrating sphere (Newport, Model 819C-SF-4). The sphere was fitted with a switchable-gain Si photodetector (Thorlabs, PDA100A2) with an automated filter slider (Thorlabs, ELLK6) loaded with a 600nm longpass filter (Thorlabs, FELH600, O.D. 6). The laser was modulated at 993Hz and photodetector signal was read using a lock-in amplifier (SRS, SR830). To determine the implied voltage (iV) values, we initially calculated the ideal open-circuit voltage ( $V_{oc,ideal}$ ) using the formula:

$$V_{oc, ideal} = \frac{k_B T}{q} ln \left( \frac{\int a(\lambda) \phi_{exc}(\lambda) d\lambda}{\int a(\lambda) \phi_{BB}(\lambda, T) d\lambda} + 1 \right)$$

where  $k_B$  is the Boltzmann constant, T is the temperature of the sample in Kelvin, q is the elementary charge,  $\lambda$  is the wavelength,  $a(\lambda)$  is the sample's absorptance,  $\phi_{BB}(\lambda,T)$  is the blackbody photon current, and  $\phi_{exc}(\lambda)$  is the excitation photon current. Through PLQY measurements, we determined the implied voltage (iV) of the semiconductors. Implied voltage is directly proportional to the quasi-Fermi level splitting (QFLS), a parameter limited by non-radiative recombination, which is quantified through PLQY. We calculate the QFLS from the relation:

$$QFLS = k_B T ln(PLQY)$$

iV is defined as:

$$iV = \frac{QFLS}{e}$$

$$iV = V_{oc, ideal} - \frac{k_B T}{e} |ln(PLQY)|$$

Implied current density (iJ) at each iV value was assumed to be:

$$iJ = J_{sc}(1 - Suns)$$

where  $J_{sc}$  is the detailed balance limit short circuit current density of the solar cell, and Suns is the injection condition relative to 1-sun intensity for each measurement. The implied current density values were scaled down to 90% to represent 10% losses of photocurrent due to reflection.

## **Solar Cell Testing**

To measure current-voltage characteristics, solar cells were masked with an 0.07cm<sup>2</sup> aperture area and measured with a scan rate of 50mV/s under 1-sun illumination calibrated using a KG2-filtered silicon reference cell.



Figure S1: Photos of Growths With Different Antisolvents

Figure S1: Photographs of completed growths prior to reclamation (top) and reclaimed single crystals after washing steps in methyl acetate prior to crushing step. Antisolvent conditions from left to right: Methyl Acetate (MA), methyl acetate + 2% formic acid in precursor solution, Toluene (Tol), toluene + 2% formic acid in precursor solution, Chlorobenzene (CB), chlorobenzene + 2% formic acid in precursor solution.

Figure S2: SONIC Growth at Elevated Temperature



Figure S2: Photographs of single crystal grown using SONIC method at 60°C, resulting in growth of a cm-scale single crystal in  $\sim$ 2 hours.



Figure S3: Changing Exposed Surface Areas to Alter Growth Rate

Figure S3: Pictures of SONIC single crystals grown with different surface areas exposed after 1 week growth time. Left: 13mm inner diameter, 28mm outer diameter. Right: 28mm inner diameter, 56mm outer diameter.



Figure S4: Full XRD Patterns of Reclaimed Powders

Figure S4: Full powder XRD patterns of reclaimed powders from 10-45 degrees 2-theta.



Figure S5: Williamson-Hall of Powder XRD

Figure S5: Williamson-Hall Analysis of Powder XRD for SONIC and RPC purified precursors, with best fits plotted as solid lines and 95% confidence intervals plotted as shaded areas.



Figure S6: Growth Attempt Using Alcohol Antisolvent

Figure S6: Unsuccessful attempt at growing single crystals using isopropanol (IPA) as the antisolvent. IPA solubilizes FAI, making it unsuitable as an antisolvent for SONIC purification.



Figure S7: Growth Attempts Using NMP as Solvent

Figure S7: Photograph of growth attempt utilizing NMP as the perovskite solvent.



Figure S8: SEM of reclaimed powders and single crystals

Figure S8: SEM of RPC powders (top) and SONIC single crystals (bottom).



Figure S9: ICP-MS of 5 repeats from different SONIC growths for both 99%  $PbI_2$  (gray, pink), and 99.99%  $PbI_2$  (black, red). Normalized impurity concentrations are plotted in the right hand boxplots for each growth.

## Figure S9: Repeatability of SONIC Purification



Figure S10: Reproducibility of RPC Purification

Figure S10: ICP-MS of 3 repeats from different RPC growths for both 99%  $PbI_2$  (gray, lavender), and 99.99%  $PbI_2$  (black, purple). Normalized impurity concentrations are plotted in the right hand boxplots for each growth.

	Raw 99%	RPC 99%	SONIC 99%	Raw	RPC	SONIC	Detection
				99.99%	99.99%	99.99%	Limit
Na	1.69 x 10 <sup>-5</sup>	8.20 x 10 <sup>-6</sup>	1.16 x 10 <sup>-5</sup>	3.19 x 10 <sup>-5</sup>	1.33 x 10 <sup>-5</sup>	1.07 x 10 <sup>-5</sup>	2.30 x 10 <sup>-6</sup>
Κ	9.90 x 10 <sup>-4</sup>	$< 1.89 \text{ x } 10^{-5}$	< 1.89 x 10 <sup>-5</sup>	5.98 x 10 <sup>-5</sup>	< 1.89 x 10 <sup>-5</sup>	< 1.89 x 10 <sup>-5</sup>	1.89 x 10 <sup>-5</sup>
Co	6.21 x 10 <sup>-8</sup>	1.08 x 10 <sup>-7</sup>	1.22 x 10 <sup>-7</sup>	2.56 x 10 <sup>-7</sup>	< 3.44 x 10 <sup>-8</sup>	1.01 x 10 <sup>-7</sup>	3.44 x 10 <sup>-8</sup>
Cu	1.99 x 10 <sup>-6</sup>	6.22 x 10 <sup>-7</sup>	5.04 x 10 <sup>-7</sup>	1.26 x 10 <sup>-5</sup>	4.17 x 10 <sup>-6</sup>	3.86 x 10 <sup>-6</sup>	1.26 x 10 <sup>-7</sup>
Zn	2.13 x 10 <sup>-5</sup>	8.24 x 10 <sup>-6</sup>	3.82 x 10 <sup>-6</sup>	1.23 x 10 <sup>-4</sup>	5.95 x 10 <sup>-5</sup>	1.66 x 10 <sup>-4</sup>	7.28 x 10 <sup>-7</sup>
Ag	3.17 x 10 <sup>-6</sup>	5.25 x 10 <sup>-7</sup>	1.06 x 10 <sup>-7</sup>	2.78 x 10 <sup>-7</sup>	7.12 x 10 <sup>-8</sup>	< 1.25 x 10 <sup>-8</sup>	1.25 x 10 <sup>-8</sup>
Cs	5.92 x 10 <sup>-8</sup>	6.24 x10 <sup>-8</sup>	2.42 x 10 <sup>-8</sup>	1.38 x 10 <sup>-8</sup>	6.57 x 10 <sup>-8</sup>	7.10 x 10 <sup>-9</sup>	1.31 x 10 <sup>-8</sup>
Ba	8.33 x 10 <sup>-6</sup>	1.25 x 10 <sup>-5</sup>	3.08 x 10 <sup>-6</sup>	1.69 x 10 <sup>-7</sup>	1.39 x 10 <sup>-7</sup>	1.08 x 10 <sup>-7</sup>	3.15 x 10 <sup>-8</sup>
T1	3.94 x 10 <sup>-6</sup>	3.35 x 10 <sup>-6</sup>	8.08 x 10 <sup>-8</sup>	2.42 x 10 <sup>-7</sup>	1.67 x 10 <sup>-7</sup>	1.25 x 10 <sup>-7</sup>	1.98 x 10 <sup>-8</sup>
Bi	1.22 x 10 <sup>-5</sup>	5.87 x 10 <sup>-6</sup>	9.64 x 10 <sup>-6</sup>	1.52 x 10 <sup>-6</sup>	1.25 x 10 <sup>-6</sup>	7.88 x 10 <sup>-7</sup>	4.45 x 10 <sup>-9</sup>

Supplementary Table 1: Impurity Concentrations (atomic, normalized to Pb)



Figure S11: ICP-MS of raw precursors and SONIC precursors using different antisolvents with and without 2% formic acid (FAH) incorporated into the precursor solution for 99.99% PbI<sub>2</sub> (top) and 99% PbI<sub>2</sub> (bottom). Antisolvents used are methyl acetate (MeOAc), toluene, and chlorobenzene (CB).

#### Supplementary Discussion 1: Details of Difference of Means Test

To calculate the difference of means, the negative of the base 10 logarithm of the concentration of each element remaining following SONIC purification was subtracted from the negative of the base 10 logarithm of the concentration of each element in the raw precursor (Supplementary Table 2) or remaining following RPC purification (Supplementary Table 3):

 $\Delta = -\ln [Raw \text{ or } RPC] - (-\ln [SONIC])$ 

This set of 9 values at each purity – one for each of the quantified elements (omitting K because measured values in crystallized samples were below the statistical limit of detection) - was then compared against a set of 9 0s, which is equivalent to an identical concentration for each element in raw or RPC purified and SONIC purified samples. These values were compared using a one-sided t-test assuming a null hypothesis. This resulted in p-values for the assertion that there are more impurities in the raw samples than in SONIC purified samples of 0.0002 for 99.99% PbI<sub>2</sub> and 0.014 for 99% PbI<sub>2</sub>. When testing the assertion that more impurities remain in RPC purified samples than in SONIC purified samples, p-values were 0.099 for 99.99% PbI<sub>2</sub> and 0.034 for 99% PbI<sub>2</sub>. Thus, SONIC removes a statistically significant amount impurities from both purifies of raw PbI<sub>2</sub> and is better at removing these impurities than RPC.

99% PbI <sub>2</sub>	t-statistic	p-value	99.99% PbI <sub>2</sub>	t-statistic	p-value
Na	2.771931	1.26E-02	Na	2.32E+01	7.55E-15
K	inf	0.00E+00	К	inf	0.00E+00
Со	-1.527979	1.44E-01	Со	3.98E-01	6.96E-01
Cu	85.21831	6.41E-25	Cu	1.21E+01	4.38E-10
Zn	17.3347	1.12E-12	Zn	-1.13E+00	2.72E-01
Ag	64.70264	8.98E-23	Ag	inf	0.00E+00
Cs	6.481898	4.27E-06	Cs	4.85E+00	1.29E-04
Ba	9.161846	3.38E-08	Ba	3.17E+00	5.26E-03
T1	1116.471	5.06E-45	T1	6.51E+01	8.09E-23
Bi	4.880175	1.20E-04	Bi	7.96E+01	2.19E-24

Supplementary Table 2: Difference of Means Tests of SONIC Purification vs. Raw

Supplementary Table 2: Difference of Mean Tests (1 sided) comparing the amount of impurity remaining in raw vs. SONIC purified precursors for each element in each purity PbI<sub>2</sub>.

99% PbI <sub>2</sub>	t	р	99.99% PbI <sub>2</sub>	t	р
Na	-3.149306	6.204232e-03	Na	1.805939	8.977476e-02
K	N/A	N/A	K	N/A	N/A
Со	-0.463496	6.492513e-01	Со	-2.133398	4.872270e-02
Cu	1.026451	3.199480e-01	Cu	0.141932	8.889055e-01
Zn	0.933532	3.644205e-01	Zn	-4.007829	1.015179e-03
Ag	6.474549	7.670696e-06	Ag	9.667183	4.389966e-08
Cs	4.362837	4.831442e-04	Cs	19.700780	1.207124e-12
Ba	13.271417	4.720640e-10	Ba	0.762862	4.566467e-01
T1	120.583015	4.186697e-25	T1	8.371786	3.060938e-07
Bi	-21.158713	4.008617e-13	Bi	14.509032	1.257241e-10

Supplementary Table 3: Difference of Mean Tests of SONIC vs. RPC Purification

Supplementary Table 3: Difference of Mean Tests (1 sided) comparing the amount of impurity remaining in RPC purified vs. SONIC purified precursors for each element in each purity PbI<sub>2</sub>.

#### Supplementary Discussion 2: Bonferroni Correction

To avoid type 1 errors (rejecting the null hypothesis when it should not be rejected) in a multiple correlation test, we perform a Bonferroni correction<sup>1</sup> for n=9 correlations performed at each purity starting with an accepted initial error rate of  $\alpha = 0.05$ :

$$\alpha_{altered} = \frac{0.05}{9} \approx 5.56 \times 10^{-3}$$

Thus, p-values greater than  $5.56 \times 10^{-3}$  are not statistically significant and may be due to random error.

Figure S12: ICP-MS of SONIC Supernatant



Figure S12: ICP-MS of the SONIC supernatant liquid from a SONIC growth starting with 99.99% PbI<sub>2</sub>. Data points not shown are below the statistical limit of detection (horizontal limes).



Figure S13: 1H-NMR of FAI

Figure S13: 1H-NMR of FAI in DMSO-d6.



Figure S14: 1H-NMR Spectra of Raw and Crystallized Precursor, 99% PbI<sub>2</sub>

Figure S14: Raw 1H-NMR Spectra of raw (black), RPC (purple), and SONIC (red) samples, beginning with 99% PbI<sub>2</sub> (Sigma Aldrich) and 99.99% FAI (Greatcell Solar).



Figure S15: 1H-NMR Spectra of Raw and Crystallized Precursor, 99.99% PbI<sub>2</sub>

Figure S15: Raw 1H-NMR Spectra of raw (black), RPC (purple), and SONIC (red) samples, beginning with 99.99% PbI<sub>2</sub> (TCI) and 99.99% FAI (Greatcell Solar).



Figure S16: 1H-NMR of All SONIC Antisolvent Growth Conditions (99% PbI<sub>2</sub>)

Figure S16: Raw 1H-NMR spectra of raw (black) and SONIC films using methyl acetate (blue), methyl acetate + 2% formic acid (pale blue), toluene (green), toluene + 2% formic acid (pale green), chlorobenzene (red), and chlorobenzene + 2% formic acid (salmon), beginning with 99%  $PbI_2$  (Sigma Aldrich) and 99.99% FAI (Greatcell Solar).



Figure S17: 1H-NMR of All SONIC Antisolvent Growth Conditions (99.99% PbI<sub>2</sub>)

Figure S17: Raw 1H-NMR spectra of raw (black) and SONIC films using methyl acetate (blue), methyl acetate + 2% formic acid (pale blue), toluene (green), toluene + 2% formic acid (pale green), chlorobenzene (red), and chlorobenzene + 2% formic acid (salmon), beginning with 99.99% PbI<sub>2</sub> (TCI) and 99.99% FAI (Greatcell Solar).

Figure S18: ICP-MS of Film Additives + Solvents



Figure S18: ICP-MS of cationic impurities present in solvents and additives used without further purification in the fabrication of all films and devices.

Figure S19: <sup>1</sup>H-NMR of Film Additives



Figure S19: <sup>1</sup>H-NMR of organic impurities present in solvents and additives used without further purification in the fabrication of all films and devices. Left: zoomed-in NMR spectra. Right: integrated intensity of identified solvent impurities, normalized to integrated intensity of precursor/solvent.



Figure S20: Full X-Ray Diffraction Patterns of raw (gray/black), RPC (purple), and SONIC (red) films fabricated with 99% PbI<sub>2</sub> (left) and 99.99% PbI<sub>2</sub> (right).

Figure S21: Photoluminescence Quantum Yield



Figure S21: Photoluminescence Quantum Yield (PLQY) of APTES-passivated films fabricated with raw, RPC, and SONIC precursors starting from 99.99% PbI<sub>2</sub>.



	Raw	RPC	SONIC
iJ <sub>sc</sub> (mA/cm²)	25.2	25.2	25.2
iV <sub>oc</sub> (V)	1.18	1.17	1.18
iFF	0.878	0.878	0.878
iPCE (%)	26.1	25.9	26.1

Figure S22: Implied current density-voltage curves of APTES-passivated film fabricated from 99.99% PbI<sub>2</sub> using Raw, RPC purified, and SONIC purified precursors, including implied device parameters.

Figure S23: Champion Photovoltaic J-V Curves



Figure S23: Photovoltaic performance for champion devices fabricated with raw and SONICpurified precursors starting with 99.99% purity PbI<sub>2</sub>. Left: current density-voltage curves. Right: stabilized power output (SPO).

Figure S24: Photovoltaic Statistics



Figure S24: Boxplots of photovoltaic performance for devices fabricated with raw and SONIC-purified precursors starting with 99.99% purity  $PbI_2$ . n = 13 samples for each condition.

Figure S25: ICP-MS of 99.9985% PbI<sub>2</sub> + 99.99% FAI



Figure S25: ICP-MS of Raw and SONIC purified precursors starting from ultra-high purity 99.9985%  $PbI_2$  + 99.99% FAI.



Figure S26: XRD of perovskite films fabricated with 99.9985% PbI<sub>2</sub>

Figure S26: XRD patterns of perovskite films fabricated with raw and SONIC purified precursors starting from 99.9985% purity PbI<sub>2</sub>.

Figure S27: Passivated photoluminescence spectra of perovskite films fabricated with 99.9985%  $PbI_2$ 



Figure S27: Photoluminescence spectra of APTES-passivated perovskite films fabricated with raw and SONIC purified precursors starting from 99.9985% purity PbI<sub>2</sub>.



Figure S28: TRPL of perovskite films fabricated with 99.9985% PbI<sub>2</sub>

Figure S28: Time-resolved photoluminescence (TRPL). Left: representative TRPL traces of films fabricated with Raw, RPC, and SONIC purified precursors made from high purity (99.999%) PbI<sub>2</sub> with biexponential decay fits. Right: boxplots of the radiative lifetime fitted by a biexponential model with errorbars corresponding to the standard deviation of a set of samples.





Figure S29: Intensity Spectrum of LEDs used for illumination during degradation experiments.



Figure S30: Full XRD Spectra of Degraded Films

Figure S30: Full XRD spectra of unencapsulated films after exposure to continuous 1-sun illumination at  $85^{\circ}$ C in N<sub>2</sub> for 750 hours.

#### Supplementary Discussion 3: Quantification of Remaining Phase Fraction

Phase fractions remaining in each film following degradation experiments were determined from the patterns shown in Figure S29 (aged samples) and Figure S19 (fresh samples). We identified only two phases present in each of the degraded samples – PbI<sub>2</sub> and  $\alpha$ -FAPbI<sub>3</sub>. The equation used to determine remaining  $\alpha$ -FAPbI<sub>3</sub> phase fraction is as follows:

$I_{\alpha - FAPbI_3(aged)}$ –	$w_{\alpha - FAPbI_3} \left( \frac{\mu_{\alpha - FAPbI_3}}{\rho_{\alpha - FAPbI_3}} \right)$				
$\frac{I_{\alpha - FAPbI_3(fresh)}}{I_{\alpha - FAPbI_3(fresh)}} =$	$\overline{w_{\alpha - FAPbI_3}} \frac{\mu_{\alpha - FAPbI_3}}{\rho_{\alpha - FAPbI_3}} - \frac{\mu_{PbI_2}}{\rho_{PbI_2}}$				

Where:  $I_x$  is the integrated diffraction intensity from phase x,  ${}^{w_x}$  is the weight fraction of phase x,  $\mu_x$  is the linear x-ray absorption coefficient of phase x, and  ${}^{\rho_x}$  is the density of phase x.<sup>2</sup>

In this calculation, we assume that the degraded samples contain only  $PbI_2$  and  $\alpha$ -FAPbI<sub>3</sub> and that fresh samples contain only  $\alpha$ -FAPbI<sub>3</sub>.



#### Figure S31: Photographs of Degraded Films

Figure S31: Images of films degraded under light and heat from two different bottles of PbI<sub>2</sub>. Left column: images of fresh/undegraded films starting with 99% PbI<sub>2</sub> (all films appear black by visual inspection prior to degradation). 2<sup>nd</sup> and 3<sup>rd</sup> columns, highlighted in green: images of films degraded under 85°C at 1-sun illumination in N<sub>2</sub> for 750 hours, showing minimal visible degradation but still showing measurable degradation via XRD and photoluminescence. 4<sup>th</sup> and 5<sup>th</sup> (right-most) columns, highlighted in red: images of films degraded under 85°C at 0.6-sun illumination for 250 hours (99% PbI<sub>2</sub>, 4<sup>th</sup> column) and 720 hours (99.99% PbI<sub>2</sub>, 5<sup>th</sup>/right-most column) from separate bottles of precursors, highlighting the difference in stability based on bottle-to-bottle variations in impurities.

Figure S32: Photos of Ambiently Aged of Perovskite Films Fabricated with 99% PbI<sub>2</sub>



Figure S32: Ambient stability of films (left in air for 3 weeks, uncontrolled humidity) fabricated with 99% PbI<sub>2</sub>.

# References

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