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Electronic Supplementary Information on

Formation of iminium ions during the processing of metal halide perovskites

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Experimental procedures

General

Lead iodide (PbI₂), dimethylamine (Me₂NH, 40 % in water) and hydroiodic acid (HI, 57 % solution in water, stabilizer: 0.75 % H₃PO₂) were used as supplied from commercial sources. Dimethylammonium iodide (Me₂NH₂)I was prepared by reacting stoichiometric amounts of HI and Me₂NH in aqueous solution and drying at 10^{-3} mbar. Organic solvents were stored over molecular sieves for three days before distilling onto a fresh portion of molecular sieves and keeping under argon. Reactions were performed under inert conditions, but dried powders of the perovskite products were generally stable in air. For filtration cellulose filters with a pore size of 5 - 8 µm were used. CHN analysis was carried out on an Elementar CHN-analyzer. During more extended series of experiments, we also obtained single crystals of the simple iminium halide salt (C₅H₁₂N)I, which we have included here for the sake of completion.

 $(Me_2NH_2)PbI_3$. A total of 92 mg (0.2 mmol) of PbI₂ and 43 mg (0.25 mmol) of $[Me_2NH_2]I$ were suspended in 5 mL of acetonitrile (MeCN) and heated to 95 °C under reflux cooling. The resulting yellow powder was removed from the near colorless solution, washed with 3 mL of cold MeCN and dried at 10⁻³ mbar. Yield: 108 mg (85 %). CNH (calculated): C 3.72 (3.79), H 1.07 (1.27), N 2.14 (2.21).

 $(C_5H_{12}N)PbI_3$ (1). A total of 74 mg (0.2 mmol) of $(Me_2NH_2)PbI_3$ was suspended in 20 mL of acetone and stirred for 2 h at room temperature. To check the progress of the reaction, the stirring was stopped every 10 min and small sample of the settled down powder was taken. The final, faintly yellow powder was washed with 3 mL of acetone and dried at 10^{-3} mbar. CNH (calculated): C 9.06 (8.91), H 1.89 (1.79), N 2.16 (2.08).

Single crystals of **1** were grown by cooling down a hot saturated solution of the compound in acetone. **1** can also be prepared by using stoichiometric amounts of PbI_2 and $(Me_2NH_2)I$ instead of $(Me_2NH_2)PbI_3$.

($C_6H_{14}N$)Pbl₃ (2). A total of 150 mg (0.5 mmol) of (Me_2NH_2)Pbl₃ was suspended in 15 mL of butanone and stirred for 2 h at 80 °C. After cooling the resulting faintly yellow powder was removed from the solution, washed with 3 mL of butanone and dried at 10⁻³ mbar. Yield: 165 mg (97 %). CNH (calculated): C 10.66 (10.47), H 1.96 (2.05), N 2.13 (2.04).

Single crystals of **2** were grown by cooling down a hot saturated solution of the compound in butanone. **2** can also be prepared by using stoichiometric amounts of PbI_2 and $(Me_2NH_2)I$ instead of $(Me_2NH_2)PbI_3$. $(C_5H_{12}N)I$. A total of 33 mg (0.1 mmol) of TII and 17 mg (0.1 mmol) of $(Me_2NH_2)I$ were suspended in 10 mL of acetone and heated to 65 °C under reflux cooling for 1.5 h. The resulting yellow solution was filtered of the yellow precipitate while still hot. After three days colourless needle of $(C_5H_{12}N)I$ had formed. The yellow participate was identified as unreacted TII via PXRD.

Additional crystallographic details

Single crystal X-ray determination was performed on a STOE STADIVARI diffractometer with microfocus MoK_{α} radiation and a Pilatus 300K (Dectris) detector or a Bruker Quest D8 diffractometer with microfocus MoK_{α} radiation and a Photon 100 (CMOS) detector.

Structure solutions and refinements were carried out using the SHELX-software suite¹ within Olex2²

	1
Empirical formula	C ₅ H ₁₂ I ₃ NPb
Formula weight	674.05
Temperature/K	100
Crystal system	hexagonal
Space group	P6 ₃ /m
a/Å	16.4064(4)
b/Å	16.4064(4)
c/Å	8.3883(3)
α/°	90
β/°	90
γ/°	120
Volume/ų	1955.38(12)
Z	6
$\rho_{calc}g/cm^3$	3.434
µ/mm⁻¹	19.999
Absorption correction (T _{min} /T _{max})	multi-scan (0.1337/0.3179)
F(000)	1740.0
Crystal size/mm ³	0.057 × 0.033 × 0.028
Radiation	Μο Κα (λ = 0.71073)
20 range for data collection/°	4.966 to 66.682
Index ranges	$-23 \le h \le 25, -25 \le k \le 24, -11 \le l \le 12$
Reflections collected	38204
Independent reflections	2586 [R _{int} = 0.0959, R _{sigma} = 0.0630]
Data/restraints/parameters	2586/0/58
Goodness-of-fit on F ²	1.026
Final R indexes [I>=2σ (I)]	$R_1 = 0.0342$, $wR_2 = 0.0541$
Final R indexes [all data]	$R_1 = 0.0772$, $wR_2 = 0.0610$
Largest diff. peak/hole / e Å ⁻³	1.84/-1.75

Table S1: Crystallographic data for **1**, measured on a STOE STADIVARI at 100 K, CCDC 2346575.

Details of crystal structure measurement and refinement: The crystal was merohedrally twinned according to $(0\ 1\ 0\ 1\ 0\ 0\ 0\ -1)$ with the smaller domain making up 38.9 % of the crystal. The position of nitrogen atom could not by assigned reliably to one of the two potential atomic positions of the

cationic site. Due to the symmetry of the cation a disorder is likely and a mixture of N and C was refined for the two respective positions using EXYZ and EADP commands. The occupancies for N1/C1 and C2/N2 are 61 %/39 %, respectively. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized geometric positions and included in structure factors calculations.



Figure S1: Asymmetric unit of **1** at 100 K, ellipsoids at 50 % probability. Hydrogen atoms are omitted for clarity.

	1
Empirical formula	C ₅ H ₁₂ I ₃ NPb
Formula weight	674.05
Temperature/K	273.00
Crystal system	hexagonal
Space group	P6 ₃ /m
a/Å	16.745(4)
b/Å	16.745(4)
c/Å	8.387(3)
α/°	90
β/°	90
γ/°	120
Volume/ų	2036.5(12)
Z	6
$\rho_{calc}g/cm^3$	3.298
µ/mm⁻¹	19.202
Absorption correction (T_{min}/T_{max})	multi-scan (0.5866/ 0.7457)
F(000)	1740.0
Crystal size/mm ³	$0.108 \times 0.029 \times 0.027$
Radiation	ΜοΚα (λ = 0.71073)
20 range for data collection/°	4.866 to 51.998
Index ranges	-20 ≤ h ≤ 20, -20 ≤ k ≤ 20, -10 ≤ l ≤ 10
Reflections collected	21901
Independent reflections	1438 [R _{int} = 0.1402, R _{sigma} = 0.0768]
Data/restraints/parameters	1438/40/68
Goodness-of-fit on F ²	1.029
Final R indexes [I>=2σ (I)]	$R_1 = 0.0406$, $wR_2 = 0.0859$
Final R indexes [all data]	$R_1 = 0.0917$, $wR_2 = 0.0981$
Largest diff. peak/hole / e Å ⁻³	1.67/-0.87

Table S2: Crystallographic data for 1, measured on a BRUKER D8 QUEST at 273 K, CCDC 2346574.

Details of crystal structure measurement and refinement: Compared to the measurement at 100 K only the *a*- and *b*-axes are elongated, while the *c*-axis is practically identical. There is no phase transition to be observed. However, the disorder of the cation is more severe at the higher temperature. It was modelled as two differently oriented parts with occupancies of 75 %/25 % using the Fragment DB³. It was not possible to refine anisotropic displacement parameters for the affected atoms and SADI and FLAT commands were necessary to ensure a stable refinement. All other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized geometric positions and included in structure factors calculations.



Figure S2: Asymmetric unit of **1** at 273 K, ellipsoids at 50 % probability, C and N atoms displayed as balls with a radius of 0.3 Å, only the higher occupied part of the cation is shown. Hydrogen atoms are omitted for clarity.

	2
Empirical formula	C ₆ I ₃ NPb
Formula weight	673.96
Temperature/K	230
Crystal system	orthorhombic
Space group	Pnma
a/Å	7.8521(4)
b/Å	11.3081(8)
c/Å	15.9901(9)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	1419.80(15)
Z	4
$\rho_{calc}g/cm^3$	3.153
µ/mm⁻¹	18.363
Absorption correction (T_{min}/T_{max})	multi-scan (1/1)
F(000)	1136.0
Crystal size/mm ³	0.09 × 0.035 × 0.022
Radiation	Μο Κα (λ = 0.71073)
20 range for data collection/°	5.096 to 56.948
Index ranges	-5 ≤ h ≤ 10, 0 ≤ k ≤ 15, 0 ≤ l ≤ 21
Reflections collected	13193
Independent reflections	1887 [R _{int} = 0.0874, R _{sigma} = 0.0418]
Data/restraints/parameters	1887/0/57
Goodness-of-fit on F ²	1.003
Final R indexes [I>=2σ (I)]	$R_1 = 0.0421$, $wR_2 = 0.1084$
Final R indexes [all data]	$R_1 = 0.0740$, $wR_2 = 0.1181$
Largest diff. peak/hole / e Å ⁻³	1.42/-2.33

Table S3: Crystallographic data for 2, measured on a BRUKER D8 QUEST at 230 K, CCDC 2346572.

Details of crystal structure measurement and refinement: The measurement was carried out at 230 K as the crystals tended to spilt when cooled down further. The crystal was partial-merohedrally twinned and the dataset was processed using the hklf5tools⁴. Non-overlapping reflections of the smaller domain were deleted. Reflections were merged in point group mmm (non-overlapping) and point group 1 (overlapping). To give correct statistics the number of reflections was extracted before merging. The final refinement was carried out against fully de-twinned data (hklf4-format) that was extracted from the SHELXL .fcf-file. The cationic site is subject to disorder with the atoms N1 and C3 being distributed over two equally occupied positions linked by symmetry, each. For both atoms no anisotropic displacement parameters could be refined. All other non-hydrogen atoms were refined anisotropically. The size and shape of the ellipsoids of the other carbon atoms points towards

additional disorder. However, this could not be modelled in a better way. Due to the disorder the atomic positions for hydrogen atoms could not be assigned sensibly and were omitted. A significant level of residue electron density of -2.53 e/Å^3 was left after the final refinement. It is, however, situated reasonably close to the lead position and therefore most likely an effect of not ideal absorption correction due to the twinning.



Figure S3: Asymmetric unit of **2** at 230 K, ellipsoids at 50 % probability, N1 and C3 atoms displayed as balls with a radius of 0.3 Å. Hydrogen atoms are omitted for clarity.

	(C ₅ H ₁₂ N)I
Identification code	jmx114
Empirical formula	C ₅ H ₁₂ IN
Formula weight	213.06
Temperature/K	100
Crystal system	tetragonal
Space group	I4/m
a/Å	7.38460(10)
b/Å	7.38460(10)
c/Å	7.2299(2)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	394.263(15)
Z	2
$\rho_{calc}g/cm^3$	1.795
Absorption correction (T_{min}/T_{max})	multi-scan (0.2828/0.8036)
F(000)	204.0
Crystal size/mm ³	0.148 × 0.055 × 0.037
Radiation	Μο Κα (λ = 0.71073)
20 range for data collection/°	7.804 to 85.254
Index ranges	-14 ≤ h ≤ 13, -14 ≤ k ≤ 13, -13 ≤ l ≤ 9
Reflections collected	12242
Independent reflections	755 [R _{int} = 0.0172, R _{sigma} = 0.0121]
Data/restraints/parameters	755/68/61
Goodness-of-fit on F ²	1.092
Final R indexes [I>=2σ (I)]	$R_1 = 0.0172$, $wR_2 = 0.0365$
Final R indexes [all data]	$R_1 = 0.0205$, $wR_2 = 0.0375$
Largest diff. peak/hole / e Å ⁻³	0.80/-1.56

Table S4: Crystallographic data for (C₅H₁₂N)I, measured on a STOE STADIVARI at 100 K, CCDC 2346573.

Details of crystal structure measurement and refinement: All non-hydrogen atoms were refined anisotropically. The cationic moiety is disordered over eight symmetry equivalent positions and was modelled using the fragment DB³. SADI, FLAT, SIMU and RIGU commands needed to be used to ensure a stable refinement. Hydrogen atoms were assigned to idealized geometric positions and included in structure factors calculations.



Figure S4: Asymmetric unit of $(C_5H_{12}N)I$ at 100 K, ellipsoids at 50 % probability. Hydrogen atoms are omitted for clarity.

UV-Vis spectroscopy

Optical absorption spectra were recorded on a *Varian Cary 5000* UV/Vis/NIR spectrometer in the range of 200-800 nm in diffuse reflectance mode employing a Praying Mantis accessory (*Harrick*) with automatic baseline correction. $BaSO_4$ was used as white standard and the compounds were ground together with $BaSO_4$ (5 % of the compound by weight) prior to the measurement to dilute the sample and reduce artefacts.

To determine the optical band gaps the raw data was transformed from reflectance R to absorption according to the Kubelka-Munk function

$$F(R) = \frac{\left(1 - R\right)^2}{2R}$$

and then plotted as a Tauc-plot, where $(F(R) \cdot hv)^{1/n}$ is plotted against radiation energy. For a direct band gap n would be $\frac{1}{2}$, for an indirect band bap 2.5 Since the transition in the region of interest was generally more pronounced when choosing n = 2, we assume that all analysed substances feature a direct band gap. In addition to the classical absorption edge, all compounds show a distinct absorption band at energies below the edge, which we associate with an excitonic transition.

The following figures show the Tauc-plots of the measurements with linear fits to determine the bandgaps as well as Gaussian fits for the excitonic band.



Figure S5. Tauc-Plot and fit curves of $(Me_2NH_2)PbI_3$. The Gaussian function was fitted to the range of 2.5 - 3.4 eV. The value assigned to the excitonic peak is the centre of the Gaussian fit.



Figure S6. Tauc-Plot and fit curves of $(C_5H_{12}N)PbI_3$ (1). The Gaussian function was fitted to the range of 2.5 - 3.45 eV. The value assigned to the excitonic peak is the centre of the Gaussian fit.



Figure S7. Tauc-Plot and fit curves of $(C_6H_{14}N)PbI_3$ **2**. The Gaussian function was fitted to the range of 2.5 - 3.45 eV. The value assigned to the excitonic peak is the centre of the Gaussian fit.

Photoluminescence spectroscopy

Photoluminescence spectra were recorded on an *Avantes AvaSpec-ULS2048CL-EVO-RS-UA* spectrometer featuring a 2048 pixel CMOS detector in the range of 450 - 1100 nm under excitation with a 405 nm laser. The measurements were carried out at room temperature and 85 K (\pm 5 K) using the pure compounds ground to a fine powder. Spectra were corrected for systematic errors of the setup and transformed from wavelength to energy using the *Jacobian* conversion.⁶

To determine the centre and FWHM of the emission Gaussian fits were applied to the spectra.



Figure S8. Photoluminescence spectrum and Gaussian fit curve of (Me₂NH₂)Pbl₃ at 85 K (± 5 K).



Figure S9. Photoluminescence spectrum and Gaussian fit curve of (Me₂NH₂)PbI₃ at room temperature.



Figure S10. Photoluminescence spectra of $(Me_2NH_2)PbI_3$ at different temperatures. PL intensities decrease significantly with rising temperature, spectra are normalised to the emission peak. Spectra at 203 K and 233 K are smoothed with a *Savitzky-Golay* filter. Spectrum at 293 K recorded with longer integration time than the rest.



Figure S11. Photoluminescence spectrum and Gaussian fit curve of $(C_5H_{12}N)PbI_3$ (1) at 85 K (± 5 K).



Figure S12. Photoluminescence spectrum and Gaussian fit curve of $(C_5H_{12}N)PbI_3$ (1) at room temperature.



Figure S13. Photoluminescence spectrum and Gaussian fit curves of $(C_6H_{14}N)PbI_3$ **2** at 85 K (± 5 K). In this case two emission peaks were observed that could be fitted with a Gaussian function each, independently of one another.



Figure S14. Photoluminescence spectrum and Gaussian fit curve of $(C_6H_{14}N)PbI_3$ (2) at room temperature. Here the two emission peaks are strongly overlapping. To de-convolute the spectrum, a first fit was applied to the region of the spectrum not influenced by the second emission. The fit curve was then subtracted from the measurement and a second fit applied to the result.

Powder diffraction

Powder patterns were either recorded on a *STADI MP* (*STOE* Darmstadt) powder diffractometer with CuK_{a1} radiation with $\lambda = 1.54056$ Å at room temperature in transmission mode or a *X'Pert Pro PW3040/60* (*Philips/PANalytical*) with CoK_{a1/2} radiation with $\lambda = 1.7890 / 1.7929$ Å at room temperature in Bregg-Brentano geometry. The patterns confirm the presence of the respective phase determined by SCXRD measurements and the absence of any major crystalline by-products unless otherwise indicated.

For the investigation of the conversion of $(Me_2NH_2)PbI_3$ to **1**. The samples were dried on air, stuck between two pieces of scotch tape and measured on the *STADI MP* in flat-transmission mode.

Rietveld refinements were performed using TOPAS-Academic Version 7.⁷ Preferred orientation was modelled using a spherical harmonics function for each phase. No significant correlations of parameters were observed, where not expected.



Figure S15. Results of a Rietveld refinement of (Me₂NH₂)PbI₃.



Figure S16. Results of a Rietveld refinement of a mixture of $(Me_2NH_2)PbI_3$ and **1**. Sample taken after 10 min of stirring pure $(Me_2NH_2)PbI_3$ in acetone at room temperature.



Figure S17. Results of a Rietveld refinement of a mixture of $(Me_2NH_2)PbI_3$ and **1**. Sample taken after 20 min of stirring pure $(Me_2NH_2)PbI_3$ in acetone at room temperature.



Figure S18. Results of a Rietveld refinement of a mixture of $(Me_2NH_2)PbI_3$ and **1**. Sample taken after 30 min of stirring pure $(Me_2NH_2)PbI_3$ in acetone at room temperature.



Figure S19. Results of a Rietveld refinement of a mixture of $(Me_2NH_2)PbI_3$ and **1**. Sample taken after 40 min of stirring pure $(Me_2NH_2)PbI_3$ in acetone at room temperature.



Figure S20. Results of a Rietveld refinement of a mixture of $(Me_2NH_2)PbI_3$ and **1**. Sample taken after 50 min of stirring pure $(Me_2NH_2)PbI_3$ in acetone at room temperature.



Figure S21. Results of a Rietveld refinement of a mixture of $(Me_2NH_2)PbI_3$ and **1**. Sample taken after 60 min of stirring pure $(Me_2NH_2)PbI_3$ in acetone at room temperature.



Figure S22. Results of a Rietveld refinement of bulk product of **1**. Sample taken after 70 min of stirring pure $(Me_2NH_2)PbI_3$ in acetone at room temperature.



Figure S23. Powder diffractogram of bulk product of three **3**. Although showing significant effects of preferred orientation, the pattern confirms the presence of the respective phase determined by SCXRD measurements and the absence of any major crystalline by-products.

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