Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information for:

Chemically Controlled Crystal Growth of $(CH_3NH_3)_2AgInBr_6$

Thao T. Tran,[§] Michael A. Quintero,[§,⊥] Kathryn E. Arpino,[§,//] Zachary A. Kelly,[§] Jessica R. Panella,[§] Xiaoping Wang,[ζ,] and Tyrel M. McQueen[§,‡,*]*

[§]Department of Chemistry, Department of Physics and Astronomy, Institute for Quantum Matter, Johns Hopkins University, Baltimore, MD 21218, United States

[ζ] Neutron Scattering Division, Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, TN 39831, United States

[‡] Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, MD 21218, United States

CORRESPONDING AUTHOR EMAIL ADDRESS: wangx@ornl.gov and mcqueen@jhu.edu

Table of contents

Synthesis.

The starting material, MABr, was prepared by mixing stoichiometric amounts of methylamine solution (40 wt% in H_2O, Sigma-Aldrich) and HBr (48 wt % in H_2O, Sigma-Aldrich) at 0°C, then heating at 60°C to dryness, washing with acetone, and drying overnight under vacuum.

Crystals of $MAPbBr_3$ starting material was grown by mixing stoichiometric amounts of MABr and $PbBr_2$ (99.9% Alfa Aesar) in HBr (48% in H_2O, Sigma-Aldrich) at 100°C, followed by cooling to room temperature.

Single crystals of $(MA)_2AgInBr_6$ were grown hydrothermally at 150°C for 1 day by mixing stoichiometric amounts of 0.146 g MABr, 0.122g AgBr (99.9% Alfa Aesar) and 0.231 g $InBr_3$ (99.9% Alfa Aesar) and additional 0.0625 g (10 mol %) of $MAPbBr_3$ with 1.00 mL 48 wt % HBr solution in Teflon-lined stainless steel autoclaves, followed by slow cooling at 2°C/h. Crystals were then filtered out and washed with ethanol to separate $(MA)_2AgInBr_6$ from $MAPbBr_3$. To better understand the role of $MAPbBr_3$ in this synthesis, a series of additional experiments, where molar ratios of the starting materials and/or the presence (*in situ, ex situ*, or different amount) of $MAPbBr_3$ were changed, were performed (Table S1). At the optimum reaction condition (Exp 7, 9 Table S1), secondary phase is totally absent and $(MA)_2AgInBr_6$ was obtained at high yield (80%), indicating this synthesis selectively resulted in the target material $(MA)_2AgInBr_6$.

Single crystal X-ray diffraction. All reflection intensities were measured at T = 213(2) K and 90(2) K using a SuperNova diffractometer (equipped with Atlas detector) with Mo-Kα radiation (λ = 0.71073 Å) using the program CrysAlisPro (version 1.171.36.32 Agilent Technologies, 2013). The same program was used to refine the cell dimensions and for data reduction. The

crystal structures were solved with the program SHELXS-2013 and were refined on F^2 with SHELXL-2013.[1] The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments) (Table S3).

Powder X-ray diffraction. Laboratory powder X-ray diffraction (PXRD) patterns were collected using Cu Kα radiation (λavg = 1.5418 Å) on a Bruker D8 Focus diffractometer with LynxEye detector. Rietveld refinements of laboratory PXRD data were carried out using TOPAS (Bruker AXS) to determine the crystal structures.

Neutron diffraction. The TOPAZ neutron time-of-flight (TOF) single crystal Laue diffractometer at the Spallation Neutron Source, Oak Ridge National Laboratory was used to locate the MA cations in the crystal structures of $(MA)_2AgInBr_6$ at T = 295(2) K and 95(2) K. Neutrons with wavelengths in the range of 0.4 to 3.5 Å were used for the data collection. Sample orientations were optimized with CrystalPlan[2] to ensure full coverage of the asymetric unit in reciprocal space and a good redundancy for the low symmetry trigonal $P\bar{3}$ space group. The integrated raw Bragg intensities were obtained using the 3D ellipsoidal *Q*-space integration method.[3] Data reduction including Lorentz, absorption, TOF spectrum, and detector efficiency corrections were carried with the ANVRED3 program. The crystal is twinned by merohedry and the reduced data were transformed accordingly to SHELX[1] in HKLF 5 format as a merohedral twin. The twin laws, i.e., twofold rotation about [0 0 1], [1 2 0] and [0 -1 0] directions, were determined by the TwinRotMat progam in PLATON.[4] The atomic coordinates of the inorganic components were obtained from the X-ray data refinement. The atomic positions of the organic MA cation were determined from the difference Fourier map using neutron data.

Infrared (IR) spectroscopy. The Fourier transform infrared spectroscopy (FTIR) spectra were collected in reflectance mode using Thermo Scientific Nicolet iS 10 FTIR spectrometer (spectral resolution 4 cm^{-1}) in the range 4000 – 400 cm^{-1}.

Ultra-violet visible (UV-Vis) spectroscopy. UV-Vis data were collected on an Agilent Cary 60 UV-Vis spectrometer over the 200 – 800 nm spectral range at room temperature.

Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) measurements. TGA and DSC data were collected on TA Instruments SDT Q600 from 50 – 700 °C under Ar atmosphere.

Heat capacity measurements. Heat capacity was measured on a crystal using the semiadiabatic pulse technique, with three repetitions at each temperature (2 K – 300 K) in a Physical Property Measurement System (PPMS, Quantum Design).

Figure S1. Powder XRD showing $(CH_3NH_3)_2AgInBr_6$ decomposition into $(CH_3NH_3)_4InBr_7$ and AgBr after heating in the absence of $PbBr_2$/(MA)$PbBr_3$.

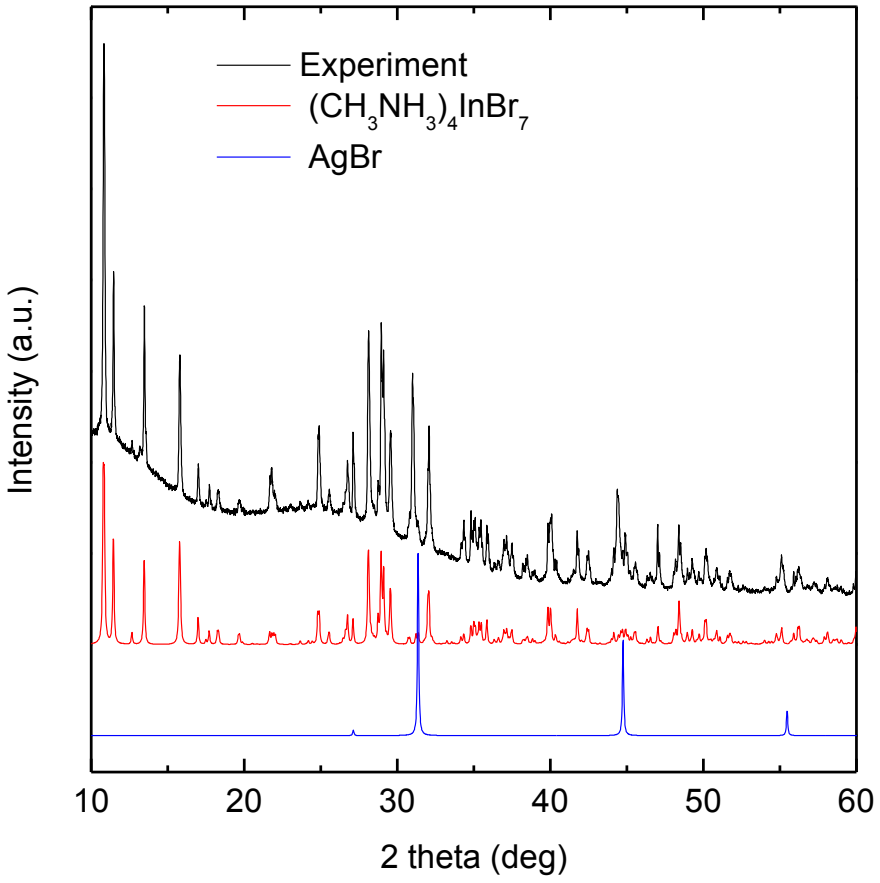

Figure S2. Raw spectra used for Jobs analysis for chemical compositions of activated complex.

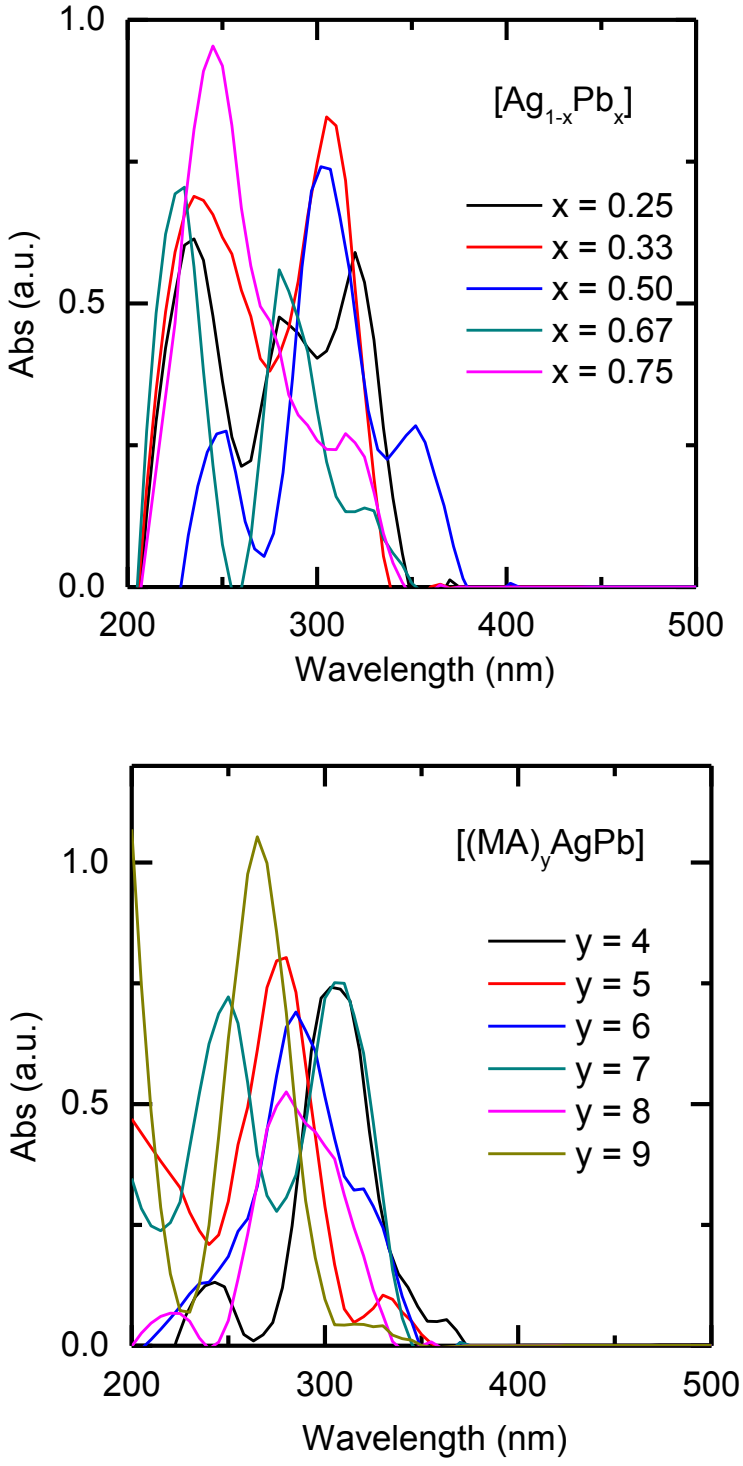

Figure S3. Rietveld refinements of the laboratory PXRD pattern of phase-pure $(CH_3NH_3)_2AgInBr_6$**.**

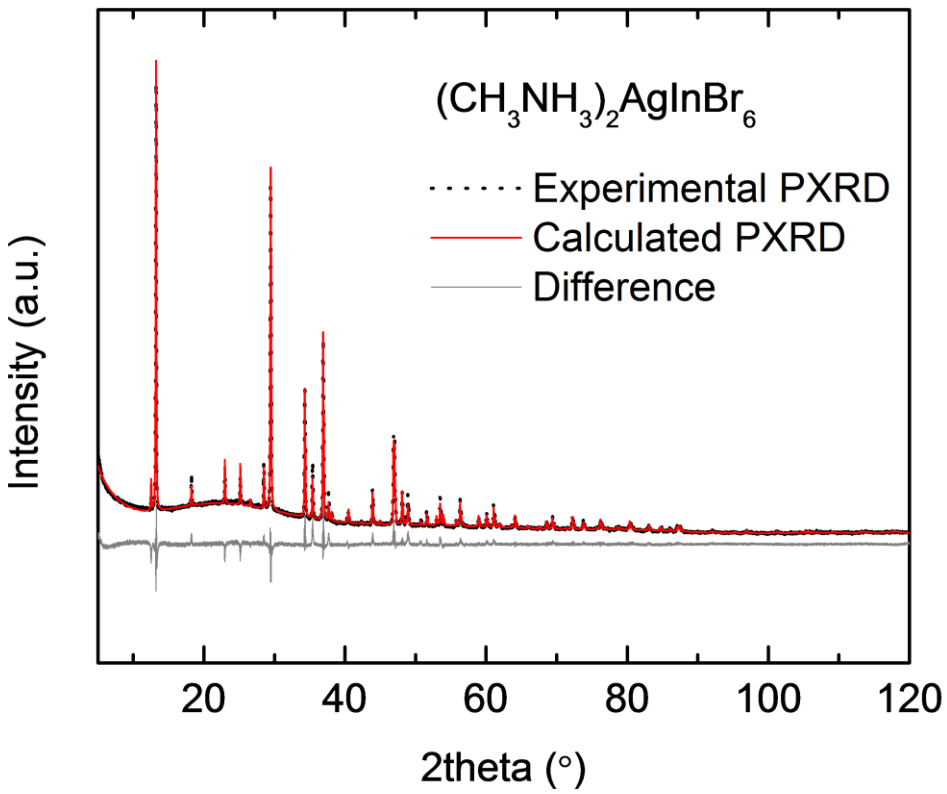

Figure S4. IR spectrum of $(MA)_2AgInBr_6$.

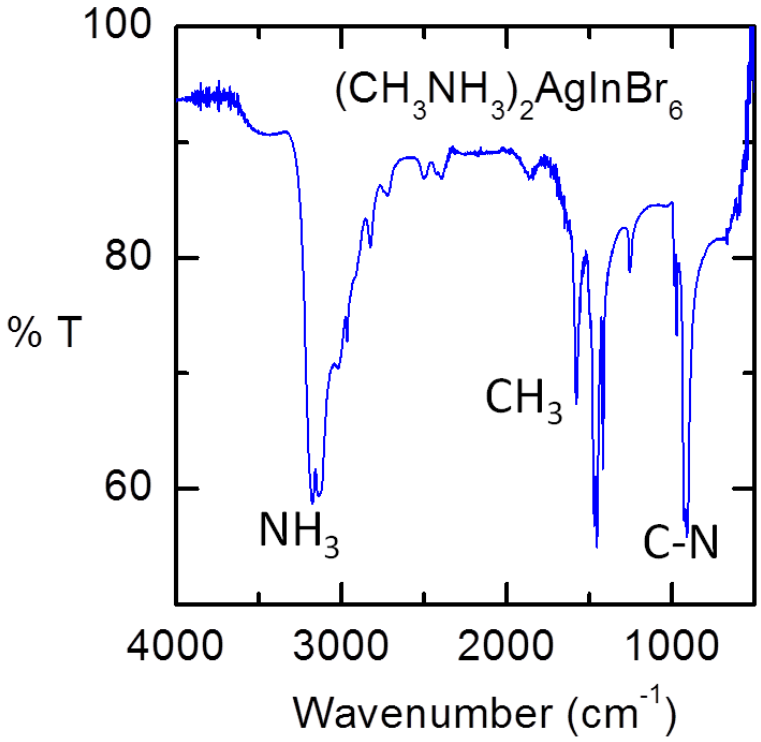

Figure S5. UV spectrum of $(MA)_2AgInBr_6$.

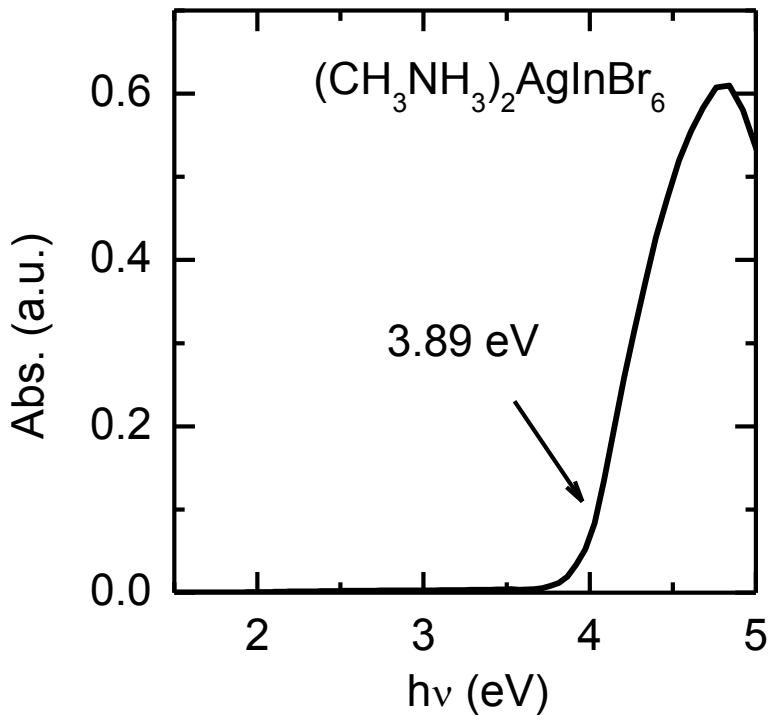

Figure S6. TGA and DSC measurements of $(MA)_2AgInBr_6$.

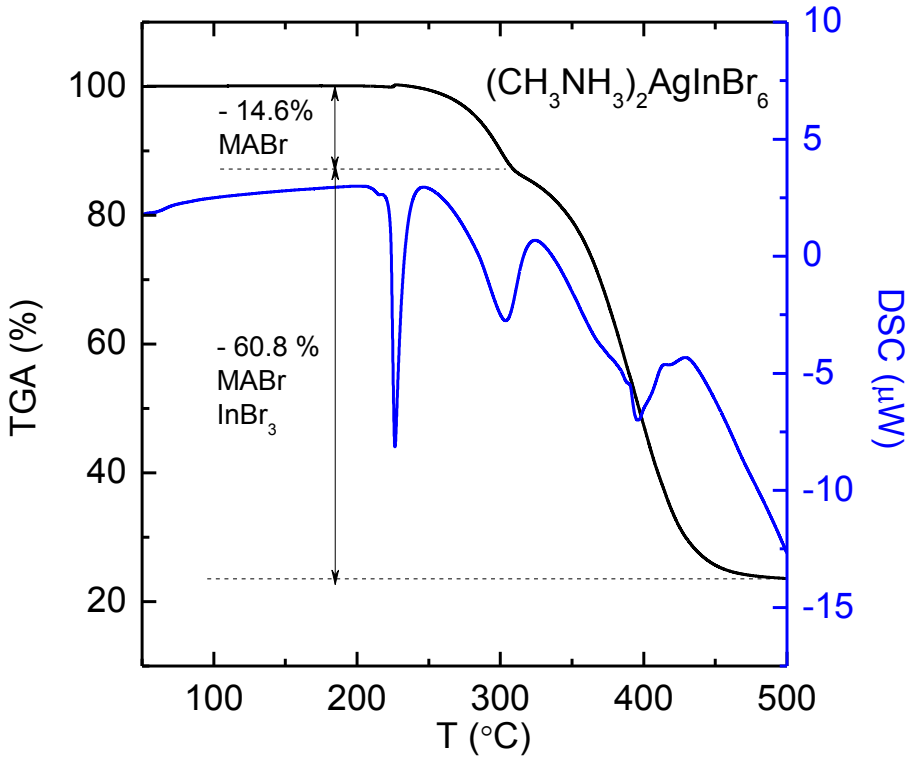

Figure S7. PXRD of the residue after the TGA and DSC measurements.

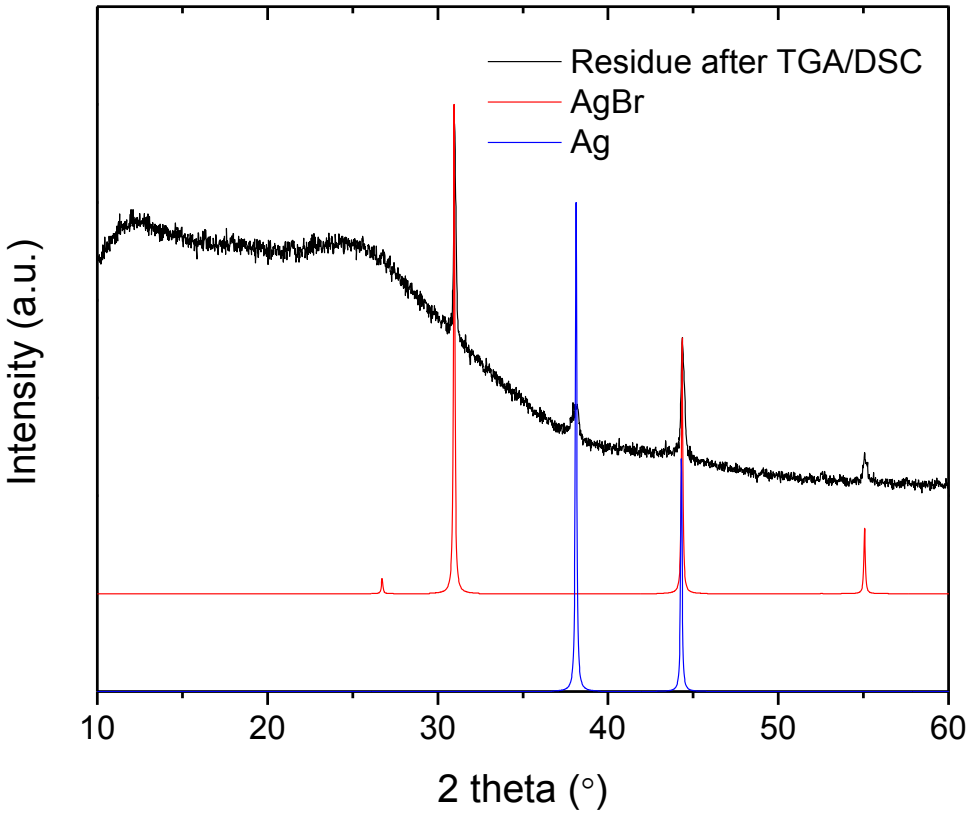

Figure S8. Heat capacity of $(MA)_2AgInBr_6$.

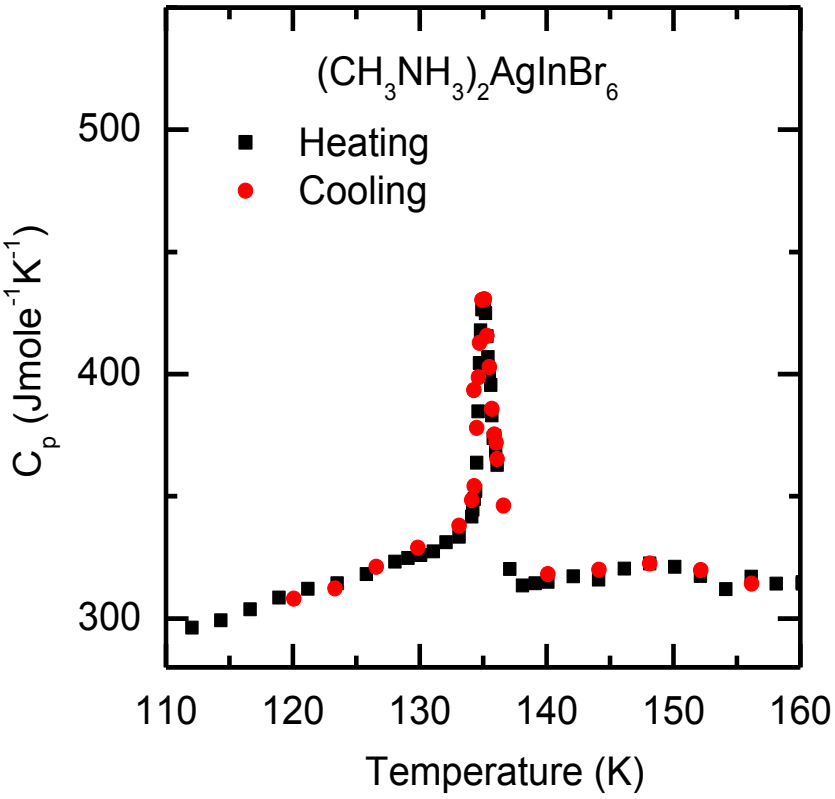

Table S1. Results of experiments (at 150°C) with different ratios of starting materials and in the presence (*in situ* or *ex situ*) or absence of $PbBr_2$/$MAPbBr_3$.

Exp	Starting materials (molar ratios)	Target product		Side products	
		% weight portion	% yield	% weight portion	% yield
1	$AgBr : InBr_3 : MABr$ 1 : 1 : 2	-		$(MA)_4InBr_7$ 60% AgBr 40%	70% 90%
2	$AgBr : InBr_3 :$ ***MABr*** 1 : 1 : ***2.2***	$(MA)_2AgInBr_6$ 10%	5%	$(MA)_4InBr_7$ 30% AgBr 60%	60% 80%
3	$AgBr : InBr_3 :$ ***MABr*** 1 : 1 : ***2.4***	-		$(MA)_4InBr_7$ 60% AgBr 40%	80% 60%
4	$AgBr : InBr_3 :$ ***MABr*** 1 : 1 : ***2.6***	-		$(MA)_4InBr_7$ 70% AgBr 30%	85% 50%
5	$AgBr : InBr_3 :$ ***MABr*** 1 : 1 : ***1.8***	$(MA)_2AgInBr_6$ 15%	10%	AgBr 85%	90%
6	$AgBr : InBr_3 :$ ***MABr*** 1 : 1 : ***1.6***	$(MA)_2AgInBr_6$ 10%	5%	AgBr 90%	95%
7	$AgBr : InBr_3 :$ ***MABr : PbBr2*** 1 : 1 : ***2.2 : 0.2***	$(MA)_2AgInBr_6$ 90%	80%	$MAPbBr_3$ 10%	70%
8	$AgBr : InBr_3 :$ ***MABr : PbBr2*** 1 : 1 : ***2.4 : 0.4***	$(MA)_2AgInBr_6$ 80%	80%	$MAPbBr_3$ 20%	80%
9	$AgBr : InBr_3 :$ ***MABr : MAPbBr3*** 1 : 1 : ***2 : 0.2***	$(MA)_2AgInBr_6$ 90%	80%	$MAPbBr_3$ 10%	70%
10	$AgBr : InBr_3 : MABr :$ ***$(MA)_2AgInBr_6$*** 1 : 1 : 2 : ***0.2***	$(MA)_2AgInBr_6$ 20% (only ~1/5th of the quantity added at the beginning of the reaction)	20%	$(MA)_4InBr_7$ 40% AgBr 40%	80% 70%

Table S2. Reactions involved in the formation of $(MA)_2AgInBr_6$.

Reaction	Reaction quotient Q	
$(MA)_2AgInBr_{6(s)} \leftrightarrow 2MA^+_{(aq)} + [Ag^+_{(aq)}]^* + In^{3+}_{(aq)} + 6Br^-_{(aq)}$	$Q_1 = [MA^+]^2[Ag^+]^*[In^{3+}][Br^-]^6$	(1)
$(MA)_4InBr_{7(s)} \leftrightarrow 4MA^+_{(aq)} + In^{3+}_{(aq)} + 7Br^-_{(aq)}$	$Q_2 = [MA^+]^4[In^{3+}][Br^-]^7$	(2)
$AgBr_{(s)} + 4MA^+_{(aq)} + 4Br^-_{(aq)} \leftrightarrow (MA)_4AgBr_{5(aq)}$	$Q_3 = \frac{[(MA)_4AgBr_5]}{[MA^+]^4[Br^-]^4}$	(3)
$(MA)_4AgBr_{5(aq)} + Pb^{2+}_{(aq)} + 2MA^+_{(aq)} + 4Br^-_{(aq)} \leftrightarrow [(MA)_6AgPb]Br_{9(aq)}$	$Q_4 = \frac{[[(MA)_6AgPb]Br_9]}{[(MA)_4AgBr_5][Pb^{2+}][MA^+]^2[Br^-]^4}$	(4)
$MAPbBr_{3(s)} \leftrightarrow MA^+_{(aq)} + Pb^{2+}_{(aq)} + 3Br^-_{(aq)}$	$Q_4 = [MA^+][Pb^{2+}][Br^-]^3$	(5)

$[Ag^+(aq)]^* = [(MA)_4AgBr_{5(aq)}] + [(MA)_6AgPbBr_{9(aq)}]$

Table S3. Crystallographic data for the high temperature (HT) and low temperature (LT) structures of $(MA)_2AgInBr_6$ from single crystal X-ray and neutron time-of-flight (TOF) diffraction.

	HT-$(MA)_2AgInBr_6$		LT-$(MA)_2AgInBr_6$	
	X-ray	Neutron TOF	X-ray	Neutron TOF
M/gmol^{-1}	766.24	766.24	766.24	766.24
T/K	213(2)	295(2)	95(2)	95(2)
Wavelength (Å)	0.71073	0.40 - 3.49	0.71073	0.40 - 3.49
Crystal system	Trigonal	Trigonal	Trigonal	Trigonal
Space group	$P\bar{3}m1$ (No. 164)	$P\bar{3}m1$ (No. 164)	$P\bar{3}$ (No. 147)	$P\bar{3}$ (No. 147)
a/ Å	7.7021(11)	7.7414(5)	7.6399(2)	7.6324(4)
c/ Å	7.0724(14)	7.0841(7)	7.0651(2)	7.0554(6)
V/ Å^3	363.34(13)	367.67(6)	357.126(14)	355.94(5)
Z	1	1	1	1
ρ_0/gcm^{-3}	3.681	3.641	3.563	3.575
μ/ mm^{-1}	19.681	0.8930 + 1.098λ	19.730	0.911 + 1.124λ
θ range/°	2.880 - 26.271	7.387 - 78.264	2.883 - 27.316	7.385 - 78.437
No. of reflections	445	2695	541	1241
No. of parameters	26	85	24	42
R_{int}	0.072	0.131	0.076	0.050
GOF	1.270	1.041	1.199	1.105
R(F)[a]	0.0237	0.0545	0.0246	0.0352
$R_w(F_0^2)$[b]	0.0569	0.1144	0.0576	0.0662

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

D*—H···*A	***D*—H (Å)**	**H···*A* (Å)**	***D*···*A* (Å)**	***D*—H···*A* (°)**
N1—H1···Br1	1.011(3)	2.805(4)	3.6468(5)	141.0(2)
N1—H1···Br1	1.011(3)	2.760(3)	3.5142(9)	131.7(3)

D*—H···*A	***D*—H (Å)**	**H···*A* (Å)**	***D*···*A* (Å)**	***D*—H···*A* (°)**
N1—H11···Br1	1.01(7)	2.81(7)	3.76(8)	156(5)
N1—H12···Br1	1.03(6)	2.75(5)	3.72(3)	156(7)
N1—H13···Br1	1.01(8)	2.76(5)	3.43(5)	125(4)

References

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(2) Zikovsky, J.; Peterson, P. F.; Wang, X.-P. P.; Frost, M.; Hoffmann, C. *J. Appl. Crystallogr.* **2011**, *44*, 418.
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