# **Supporting information**

# Shedding Light on the Stability and Structure-Property Relationships of 2D Hybrid Lead Bromide Perovskites

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### 1. <u>Methods</u>

#### Single Crystal X-ray Diffraction:

Single crystal diffraction experiments were performed:

(1) Using a four-circle Rigaku XtaLAB Synergy system equipped with a PhotonJet (Mo,  $\lambda$ = 0.71073 Å) micro-focus sealed X-ray tube and Hybrid Pixel Array Detector at 273 K, 293 K and 323 K.

(2) Using either a Bruker Molly or Duo instrument with MoK $\alpha$  IµS microfocus source ( $\lambda$ = 0.71073 Å) with MX Optics at 293 K.

The collected data were integrated and applied with multiscan absorption correction using the APEX3 software. The structure was solved by charge flipping and refined by full-matrix least squares on  $F^2$  with the Jana2006 package.<sup>1</sup>

The parameters of bond angle variance and bond length distortion were determined by using the VESTA software.<sup>2</sup>

#### **Powder X-ray Diffraction:**

Powder X-ray diffraction patterns were collected on a Rigaku Miniflex system (CuK $\alpha$  radiation) operated at 40 kV and 15 mA. A typical scan rate was 15 sec/step with a step size of 0.02 deg. Rietveld analysis was performed with the Jana2006 package.<sup>1</sup> The preferred orientation of the calculated PXRD patterns of the examined materials was determined based on the March–Dollase approach.<sup>3</sup>

#### Variable Temperature Powder X-ray Diffraction:

Variable Temperature Powder X-ray diffraction measurements were performed on a STOE-STADI-MP powder diffractometer equipped with an asymmetric curved Germanium monochromator (MoK $\alpha$ 1 radiation,  $\lambda = 0.70930$  Å) and one-dimensional silicon strip detector (MYTHEN2 1K from DECTRIS). The line focused Mo X-ray tube was operated at 50 kV and 40 mA. Powder sample was packed in a glass capillary and sealed under vacuum. Temperature stability is typically 0.1 C. Instrument was calibrated against a NIST Silicon standard (640d) prior to the measurement.

#### **Optical Absorption Spectroscopy:**

Optical diffuse reflectance measurements were performed using a Shimadzu UV-3600 UV–VIS NIR spectrometer operating in the 200–2500 nm region at room temperature. BaSO<sub>4</sub> was used as a non-absorbing reflectance reference for all measurements. The bandgap was estimated by diffuse reflectance spectroscopy on powder samples of the studied materials, where the Kubelka-Munk model was used to derive absorption values.

#### **Steady-State and Time-Resolved Photoluminescence:**

The samples were measured using a time-correlated single-photon spectrometer (FS5 – Edinburgh instruments). For steady state photoluminescence (PL) the samples were excited at 405 nm and the emission was collected between 450 nm to 900 nm. A 455 nm long pass filter was used to remove scattered excitation light. For time-resolved PL (TRPL) the samples were excited by a 405 nm pulsed diode laser (repetition rate – 1 MHz / time frame of 1  $\mu$ s) and the time-resolved emission was collected at the peak of the PL. The measured TRPL decay ( $I_{(t)}$ ) of each sample was fitted by a three exponent function, convoluted with the instrument response function.

$$I_{(t)} = \sum_{i=1}^{3} a_i \times e^{-\frac{t}{\tau_i}} + b$$

 $\tau_i$  and  $a_i$  are the lifetime and amplitude of the different decay components and *b* is the background level. The ratio of photons emitted by each component  $(Ph_i)$  can be calculated by

$$Ph_i = (a_i \times \tau_i)/(a_1 \times \tau_1 + a_2 \times \tau_2 + a_3 \times \tau_3), (i = 1, 2, 3)$$

The average lifetime of each sample  $\tau_{avg}$  is defined by

$$\tau_{avg} = \sum_{i=1}^{3} Ph_i \times \tau_i$$

#### **TGA/DSC Measurements:**

The Thermogravimetric Analysis (TGA) measurements were performed on a Netzsch's Simultaneous Thermal Analysis (STA) system. An amount of ~15 mg of sample was placed inside an alumina cap and heated up to 600°C under He flow (211.0 mL/min) with a heating rate of 10 °C/min. DSC measurements were performed on the same instrument, at a scan rate of 5 °C/min in sealed aluminum pans under He (211.0 mL/min).

#### **SEM studies:**

Scanning Electron Microscopy (SEM) measurements were recorded on EPIC SEM Hitachi S-3400, working conditions voltage, distance.

#### **Ferroelectric Characterizations:**

Ferroelectric characterizations were conducted with a cypher AFM (Asylum Research, Oxford Instrument, Santa Barbara, CA) on 2D HOIP thin films prepared by hot casting on FTO substrate. Pt/Ir coated conductive AFM cantilevers (SCM-PIV-V2, Bruker Probes) were used in all studies. Tapping mode AFM images were first captured and switching spectroscopy piezoresponse force microscopy (SS-PFM) were then conducted on random locations. More than 3 samples for each 2D HOIPs were tested. During SS-PFM, a DC bias is applied to the tip to polarize the sample and an AC field is used to measure the magnitude and direction of the spontaneous polarization in the sample, as reflected by the amplitude and phase of the AFM cantilever vibration, respectively.

#### **Density Functional Theory Calculations (DFT)**

First-principles calculations are based on density functional theory (DFT) as implemented in the SIESTA package. <sup>4-5</sup> The nonlocal van der Waals density functional of Dion *et al.* corrected by Cooper (C09) is used for geometry optimizations.<sup>6-7</sup> Spin-orbit coupling is taken into account through the on-site approximation as proposed by Fernández-Seivane *et al.*.<sup>8</sup> To prevent conflicts between the on-site treatment and the nonlocality of C09, single point calculations are conducted with the revPBE functional on which C09 is based.<sup>9</sup> Core electrons are described with Troullier-Martins pseudopotentials <sup>10</sup>, while valence wavefunctions are developed over double- $\zeta$  polarized basis set of finite-range numerical pseudoatomic orbitals <sup>11</sup>. In all cases, an energy cutoff of 150 Ry for real-space mesh size has been used. Experimental structures are used for the inorganic skeleton, well characterized by X-ray diffraction. As this is not the case for light atoms, the positions of organic cations have been optimized. The macroscopic polarization is computed using the geometric Berry phase approach.<sup>12</sup> Starting from the *C*2/c centrosymmetric structure of C6Br, we perform a linear deformation up to the non-centrosymmetric *C* c structure.

### **Profilometry Measurements**

The film thickness was determined using a high resolution Dektak 150 Stylus Profilometer, where the average height of all films was between 230 nm-350 nm.

#### Atomic Force Microscopy (AFM)

Bruker Dimension FastScan Atomic Force Microscope (AFM) was used to map the sample topography of prepared films.

### 2. Characterization:



**Figure S1:** Representative microscope images of (A)  $(C_6H_{16}N)_2(MA)Pb_2Br_7$ , (B)  $(C_7H_{18}N)_2(MA)Pb_2Br_7$  and (C)  $(C_8H_{20}N)_2(MA)Pb_2Br_7$ .

### 2.1 X-ray Diffraction Measurements



**Figure S2.** Comparison of the experimental PXRD pattern from crystals with the calculated PXRD pattern from the solved single crystal structure of  $(C_6H_{16}N)_2(MA)Pb_2Br_7$  from in-house instrument ( $\lambda = 1.5406$  Å).



**Figure S3.** Comparison of the experimental PXRD pattern from crystals with the calculated PXRD pattern from the solved single crystal structure of  $(C_7H_{18}N)_2(MA)Pb_2Br_7$  from in-house instrument ( $\lambda = 1.5406$  Å).



**Figure S4.** Comparison of the experimental PXRD pattern from crystals with the calculated PXRD pattern from the solved single crystal structure of  $(C_8H_{20}N)_2(MA)Pb_2Br_7$  from in-house instrument ( $\lambda = 1.5406$  Å).



**Figure S5.** Comparison of the experimental PXRD pattern from crystals with the calculated PXRD pattern from the reported single crystal structure<sup>13</sup> of  $(C_4H_{12}N)_2(MA)Pb_2Br_7$ .



**Figure S6.** Comparison of the experimental PXRD pattern from thin films (one-step method) with the calculated PXRD pattern from the solved single crystal structure of  $(C_6H_{16}N)_2(MA)Pb_2Br_7$  from in-house instrument ( $\lambda = 1.5406$  Å).



**Figure S7.** Comparison of the experimental PXRD pattern from thin films (one-step method) with the calculated PXRD pattern from the solved single crystal structure of  $(C_7H_{18}N)_2(MA)Pb_2Br_7$  from in-house instrument ( $\lambda = 1.5406$  Å).



**Figure S8.** Comparison of the experimental PXRD pattern from thin films (one-step method) with the calculated PXRD pattern from the solved single crystal structure of  $(C_8H_{20}N)_2(MA)Pb_2Br_7$  from in-house instrument ( $\lambda = 1.5406$  Å).



**Figure S9.** Comparison of the experimental PXRD pattern from thin films (one-step method) with the calculated PXRD pattern from the reported single crystal structure<sup>13</sup> of  $(C_4H_{12}N)_2(MA)Pb_2Br_7$ .

# 2.2 Additional Structural Analysis

**Table S1.** Comparison of dimensions of 2D lattice in studied bilayer lead bromide and lead iodide perovskites.

	C4BrN2	C4IN2	C6BrN2	C6IN2	C8BrN2	C8IN2
V (Å <sup>3</sup> )	2672.04	3118.7	3180.0	3526.6	3668.0	3965.4
d (g/cm <sup>3</sup> )	2.869	3.159	2.5277	2.899	2.293	2.6722
a (Å)	39.136	8.947	46.069	45.355	52.952	50.432
<b>b</b> (Å)	8.346	39.347	8.2722	8.9209	8.3232	8.972
<b>c</b> (Å)	8.180	8.8589	8.3454	8.8062	8.3225	8.8421

Table S2. Pb-Br bond distances (Å) and Pb-Br-Pb angles (°) for (C6)<sub>2</sub>(MA)Pb<sub>2</sub>Br<sub>7</sub>.

Label	Distances	Label	Angles (°)
Pb(1)-Br(1)	3.03(6)	Pb(1)-Br(1)-Pb(2)	178.8(2)
Pb(1)-Br(2)#1	2.96(6)	Pb(1)-Br(5)-Pb(1)#4	158.6(2)
Pb(1)-Br(5)	2.960(5)	Pb(2)-Br(6)-Pb(2)#5	166.3(5)
Pb(1)-Br(5)#2	3.015(6)	Pb(1)-Br(7)-Pb(1)#5	158.3(2)
Pb(1)-Br(7)	3.006(6)	Pb(2)-Br(9)-Pb(2)#4	164.0(3)
Pb(1)-Br(7)#3	2.980(4)		
Pb(2)-Br(1)	3.11(6)		

Pb(2)-Br(4)	2.91(6)
Pb(2)-Br(6)	2.957(5)
Pb(2)-Br(6)#3	2.957(6)
Pb(2)-Br(9)	2.954(5)

Table S3. Pb-Br bond distances (Å) and Pb-Br-Pb angles (°) for (C7)<sub>2</sub>(MA)Pb<sub>2</sub>Br<sub>7</sub>.

Label	Distances	Label	Angles (°)
Pb(1)-Br(6)	3.03(7)	Pb(1)-Br(1)-Pb(1)#4	166.3(13)
Pb(1)-Br(1)	2.936(7)	Pb(1)-Br(2)-Pb(1)#5	168.5(3)
Pb(1)-Br(1)#1	2.999(7)	Pb(1)-Br(6)-Pb(2)#4	178.68(3)
Pb(1)-Br(2)	2.931(4)	Pb(2)-Br(3)-Pb(2)#4	166.62(17)
Pb(1)-Br(2)#2	2.981(4)	Pb(2)-Br(7)-Pb(2)#5	163.4(5)
Pb(1)-Br(4)	2.88(7)		
Pb(2)-Br(3)	2.938(4)		
Pb(2)-Br(3)#1	3.001(4)		
Pb(2)-Br(5)	2.86(7)		
Pb(2)-Br(7)	2.919(5)		
Pb(2)-Br(7)#2	3.020(5)		

Table S4. Pb-Br bond distances (Å) and Pb-Br-Pb angles (°) for (C8)<sub>2</sub>(MA)Pb<sub>2</sub>Br<sub>7</sub>.

Label	Distances	Label	Angles (°)
Pb(1)-Br(3)	3.089(7)	Pb(2)-Br(3)-Pb(1)	179.6(3)
Pb(1)-Br(4)	2.978(4)	Pb(1)#4-Br(4)-Pb(1)	165.4(2)
Pb(1)-Br(4)#1	2.956(5)	Pb(2)-Br(5)-Pb(2)#2	165.5(3)
Pb(1)-Br(10)#2	2.953(4)	Pb(2)-Br(6)-Pb(2)#1	166.2(2)
Pb(1)-Br(10)	2.976(5)	Pb(1)#3-Br(10)-Pb(1)	165.8(2)
Pb(1)-Br(14)	2.781(7)		
Pb(2)-Br(3)	3.048(7)		
Pb(2)-Br(5)#3	2.982(5)		

Pb(2)-Br(5)	2.950(5)
Pb(2)-Br(6)	2.959(4)
Pb(2)-Br(6)#4	2.970(4)
Pb(2)-Br(15)	2.930(4)



Figure S10. Bond length distortion of  $(C_mH_{2m+1}N)_2(MA)Pb_2Br_7$  (m=4, 6 and 8) versus  $(C_mH_{2m+1}N)_2(MA)Pb_2I_7$  (m=4, 6 and 8).



**Figure S11.** Comparison of average equatorial Pb–Br–Pb angles of  $(C_mH_{2m+1}N)_2(MA)Pb_2Br_7$  (m=4, 6 and 8) versus  $(C_mH_{2m+1}N)_2(MA)Pb_2I_7$  (m=4, 6 and 8).

**Table S6:** Single crystal X-ray diffraction data of  $(C_6H_{16}N)_2(MA)Pb_2Br_7$  from its above room-<br/>temperature phase, collected at 323K.

Empirical formula	C13 H46 Br7 N3 Pb2		
Formula weight	1171.9		
Temperature	322.99 К		
Wavelength	0.71073 Å		
Crystal system	monoclinic		
Space group	C 1 2/c 1		
Unit cell dimensions	$ \begin{array}{l} a = 48.559(2) \ \mbox{\AA}, \ \alpha = 90^{\circ} \\ b = 8.3282(3) \ \mbox{\AA}, \ \beta = 90.049(3)^{\circ} \\ c = 8.3246(3) \ \mbox{\AA}, \ \gamma = 90^{\circ} \end{array} $		
Volume	3366.5(2) Å <sup>3</sup>		
Ζ	4		
Density (calculated)	2.3121 g/cm <sup>3</sup>		
Absorption coefficient	18.299 mm <sup>-1</sup>		
F(000)	2032		
$\theta$ range for data collection	2.48 to 30.73°		
Index ranges	-62<=h<=61, -11<=k<=11, -9<=l<=11		
Reflections collected	10572		
Independent reflections	2945 $[R_{int} = 0.0542]$		
Completeness to $\theta = 24.24^{\circ}$	98%		
Refinement method	Full-matrix least-squares on F <sup>2</sup>		
Data / restraints / parameters	2945 / 11 / 71		
Goodness-of-fit	2.62		
Final R indices [I>3 $\sigma$ (I)]	$R_{obs} = 0.0866, wR_{obs} = 0.1788$		
R indices [all data]	$R_{all} = 0.1153, wR_{all} = 0.1836$		

### 2.3 Variable-Temperature Powder X-ray Diffraction



**Figure S12.** (A) Variable temperature PXRD patterns of  $(C_6H_{16}N)_2(MA)Pb_2Br_7$  from reversible heating cycle measurement in the temperature range of from 20°C to 80°C. (B) The reversible cooling cycle measurement in the temperature range of from 20°C to -100°C.



**Figure S13.** Variable temperature PXRD patterns of  $(C_6H_{16}N)_2(MA)Pb_2Br_7$  from heating cycle (20°C to 80°C), before and after measurement.

# 2.4 Thermal analysis

## 2.4.1 Differential Scanning Calorimetry



**Figure S14.** DSC scans of (A)  $(C_6H_{16}N)_2(MA)Pb_2Br_7$ , (B)  $(C_7H_{18}N)_2(MA)Pb_2Br_7$  and (C)  $(C_8H_{20}N)_2(MA)Pb_2Br_7$  with scan rate of 5K/min.

### 2.4.2 Thermogravimetric analysis



**Figure S15.** TGA curve for the  $(C_6H_{16}N)_2(MA)Pb_2Br_7$  compound, recorded under helium flow with a heating rate of 10 deg/min.



**Figure S16.** TGA curve for the  $(C_7H_{18}N)_2(MA)Pb_2Br_7$  compound, recorded under helium flow with a heating rate of 10 deg/min.



**Figure S17.** TGA curve for the  $(C_8H_{20}N)_2(MA)Pb_2Br_7$  compound, recorded under helium flow with a heating rate of 10 deg/min.



#### **2.5 DFT Calculations**

**Figure S18.** Permanent dipole per unit cell computed using the geometric Berry phase approach along the three lattice vectors for  $(C_6H_{16}N)_2(MA)Pb_2Br_7$  as a function of distortion from the high symmetry non-polar *C*2/c structure (x=0) to the polar *C*c structure (x=1). The dipole per unit cell is set equal to zero for the non-polar phase *C*2/c. The lines are a guide to the eye. Polarization

appears in the (a,c) plane with the polarization along the stacking axis a, 3 orders of magnitude larger than along the in-plane lattice vector c.



**Figure S19.** DFT calculations of band structures for  $(C_6H_{16}N)_2(MA)Pb_2Br_7$  solved in *C2/c* versus *Cc* at 273 K.



**Figure S20.** DFT calculations of band structures for  $(C_6H_{16}N)_2(MA)Pb_2Br_7$  at 323 K (above-room temperature phase transition), solved in *C*2/c space group.

### 2.6 Stability Tests



**Figure S21.** (A) X-ray diffraction patterns of thin-films of  $(C_mH_{2m+1}NH_3)_2(CH_3NH_3)Pb_2Br_7$  (m = 4, 6–8) from air stability testing after 5 months. (B) Absorption spectra of thin-films of  $(C_mH_{2m+1}NH_3)_2(CH_3NH_3)Pb_2Br_7$  (m = 4, 6–8) from air stability testing after 5 months.



**Figure S22:** Absorption spectra of thin-films of  $(C_mH_{2m+1}NH_3)_2(CH_3NH_3)Pb_2Br_7$  (m = 4, 6–8) from light stability testing (**A**) 4hrs in total and (**B**) 8hrs in total.



**Figure S23:** X-ray diffraction patterns of thin-films of  $(C_mH_{2m+1}NH_3)_2(CH_3NH_3)Pb_2Br_7$  (m = 4, 6–8) from light stability testing (A) 4hrs in total and (B) 8hrs in total.



**Figure S24:** Absorption spectra of thin-films of  $(C_mH_{2m+1}NH_3)_2(CH_3NH_3)Pb_2Br_7$  (m = 4, 6–8) from heat stability testing (**A**) 4hrs in total and (**B**) 7 hrs in total.



**Figure S25:** X-ray diffraction patterns of thin-films of  $(C_mH_{2m+1}NH_3)_2(CH_3NH_3)Pb_2Br_7$  (m = 4, 6–8) from heat stability testing (A) 4hrs in total, (B) 5hrs in total and (C) 7 hrs in total.

### 2.7 Switching Spectroscopy-Piezoresponse Force Microscopy (SS-PFM)



**Figure S26.** (A) Surface morphology of the resulting thin film samples of  $(C_8H_{16}NH_3)_2(CH_3NH_3)Pb_2I_7$  (B) Local response of the phase and (C) Amplitude to the applied DC electrical field, respectively.



**Figure S27.** (A) Surface morphology of the resulting thin film samples of high-temperature phase of  $(C_6H_{12}NH_3)_2(CH_3NH_3)Pb_2Br_7$  (B) Local response of the phase and (C) Amplitude to the applied DC electrical field, respectively.

### 2.8 Time-resolved photoluminescence under liquid nitrogen



**Figure S28.** Time-resolved PL decays and fitting of  $(C_mH_{2m+1}NH_3)_2(CH_3NH_3)Pb_2Br_7$  (m = 4, 6–8) collected under liquid nitrogen.



2.9 Atomic Force Microscopy (AFM)

**Figure S29.** AFM of films (**A**) C6BrN2 prepared inside the glovebox with root mean square (rms) roughness 32.3 rms, (**B**) C6BrN2 prepared outside the glovebox with 60.3 nm (**C**) C4BrN2 prepared inside the glovebox with 11.9 nm, (**D**) C4BrN2 prepared outside the glovebox with 17.5 nm.

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