

Supporting Information

A 3D lead iodide hybrid based on a 2D perovskite subnetwork

Maroua Ben Haj Salah ¹, Justine Tessier ¹, Nicolas Mercier ^{1,*}, Magali Allain,¹ Antonin Leblanc ¹, Xiaoyang Che², Claudine Katan² and Mikael Kepenekian ^{2,*}

¹ MOLTECH-Anjou, UMR-CNRS 6200, Université d'Angers, 2 Bd Lavoisier, 49045 Angers

² Univ Rennes, ENSCR, INSA Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes), UMR 6226, Rennes F-35000, France

Synthesis of HO-(CH₂)₃-NH₃⁺I⁻: The 3-Amino-1-propanol iodide salt is synthesized from 3-amino-1-propanol and a 57% solution of hydriodic acid (HI). First, the 3-Amino-1-propanol (500 mg) was dissolved in absolute ethanol and cooled to 0 °C. Then, upon stirring, HI (851mg) was slowly added (3-amino-1-propanol and HI in 1:1 stoichiometric amounts). The solution was stirred for 2 h. Then, rotary evaporation was applied to evaporate the solvent with a pressure of 0.1 MPa at 45 °C, giving a white solid. The precipitate was washed three times with diethyl ether and dried under vacuum (60 °C, 5 h).

(HPA)₆(MA)Pb₅I₁₇: Crystals of (HPA)₆(MA)Pb₅I₁₇ (HPA⁺= hydroxypropylammonium or 3-ammonium-1-propanol), were synthesized by liquid-gas slow diffusion method. Lead iodide (300 mg) was first dissolved into hydroiodic acid (1.5mL), in which both methylamine iodide (20.70 mg) and 3-Amino-1-propanol iodide (158 mg) were added in a second step which finally contained the following 3-Amino-1-propanol iodide /methylamine iodide /lead iodide stoichiometry of 6/1/5. The solution was stirred during 20 minutes at room temperature until complete dissolution. This saturated solution was placed into a saturated ethanol vapor atmosphere. After 2 days, crystals were obtained and washed 3 times by ethyl acetate and heated at 40°C during 1 hour. This method gave pure phase of (HPA)₆(MA)Pb₅I₁₇.

Single-crystal X-ray diffraction.

X-ray single-crystal diffraction data of $(\text{HPA})_6(\text{MA})\text{Pb}_5\text{I}_{17}$ were collected at 149K on a Rigaku Oxford Diffraction SuperNova diffractometer equipped with an Atlas CCD detector and micro-focus Cu-K α radiation ($\lambda = 1.54184 \text{ \AA}$). The structure was solved by direct methods, expanded and refined on F^2 by full matrix least-squares techniques using SHELX programs (G. M. Sheldrick 2013, SHELXS 2013/1 and SHELXL 2013/4). All non-H atoms were refined anisotropically and multiscan empirical absorption was corrected using CrysAlisPro program (CrysAlisPro, Agilent Technologies, V1.171.38.41r, 2015). The H atoms were placed at calculated positions and refined using a riding model. The methylammonium cation is positioned on an inversion centre and it has been modeled with two half atoms of nitrogen and carbon positioned at the same place. CCDC-2122380 contains the supplementary crystallographic data for this paper. A summary of crystallographic data and refinement results for this structure is listed in Table 1.

Table S1. Summary of crystal data and structure refinement for $(\text{HPA})_6(\text{MA})\text{Pb}_5\text{I}_{17}$

Empirical formula	C19 H66 I17 N7 O6 Pb5
Formula weight	3682.03
Temperature	149.3(5) K
Wavelength	1.54184 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 8.8709(4) Å alpha = 111.196(5)°. b = 13.8776(8) Å beta = 90.710(4)°. c = 15.8097(7) Å gamma = 105.477(5)°.
Volume	1735.93(16) Å ³
Z, Calculated density	1, 3.522 Mg/m ³
Absorption coefficient	82.704 mm ⁻¹
F(000)	1588
Crystal size	0.130 x 0.041 x 0.016 mm
Theta range for data collection	3.020 to 72.588°
Limiting indices	-10 < h < 10, -17 < k < 15, -19 < l < 18
Reflections collected / unique	11564 / 6633 [R(int) = 0.0423]
Completeness to theta = 71.000	97.80%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.30162
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6633 / 0 / 253
Goodness-of-fit on F ²	1.023
Final R indices [I > 2sigma(I)]	R1 = 0.0387, wR2 = 0.0992 [5625 Fo]
R indices (all data)	R1 = 0.0474, wR2 = 0.1052
Largest diff. peak and hole	1.655 and -2.618 e.Å ⁻³

Powder X-Ray diffraction

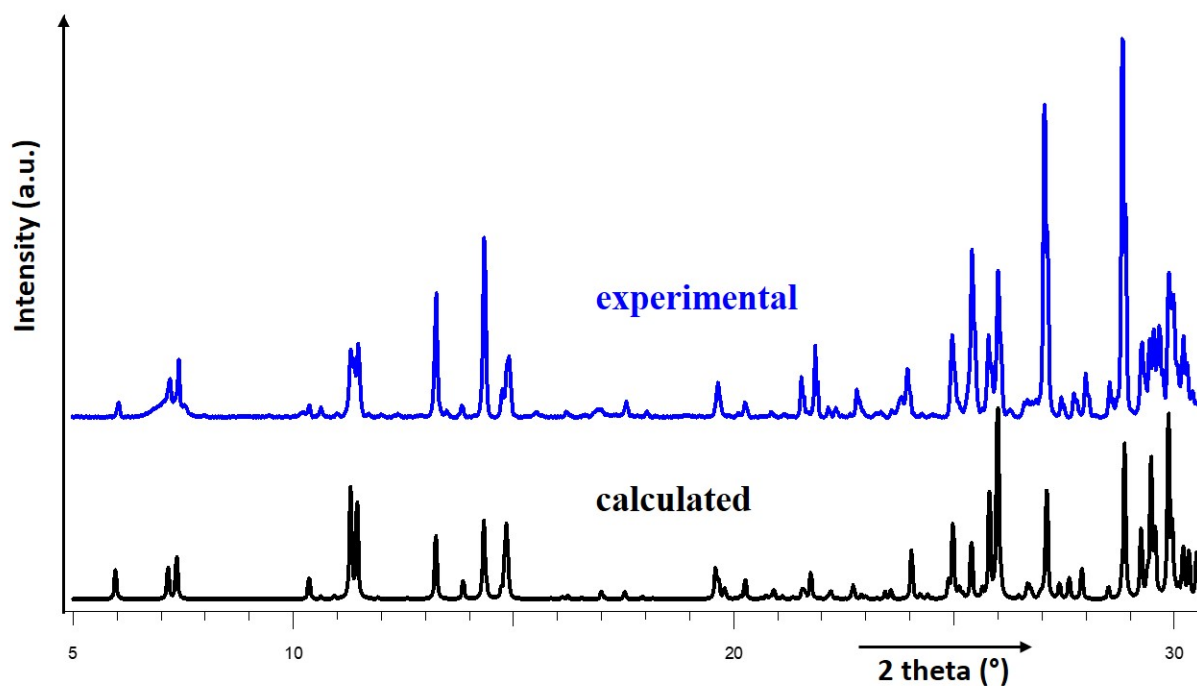


Figure S1. Calculated PXRD from single crystal data of the studied crystal of $(\text{HPA})_6(\text{MA})\text{Pb}_5\text{I}_{17}$ (black -taking the room temperature unit cell: $a = 8.948 \text{ \AA}$, $b = 13.913 \text{ \AA}$, $c = 16.016 \text{ \AA}$, $\alpha = 111.15^\circ$, $\beta = 90.37^\circ$, $\gamma = 106.49^\circ$) and the experimental PXRD of the same phase (blue).

^1H NMR

DMSO : 2.53 ppm

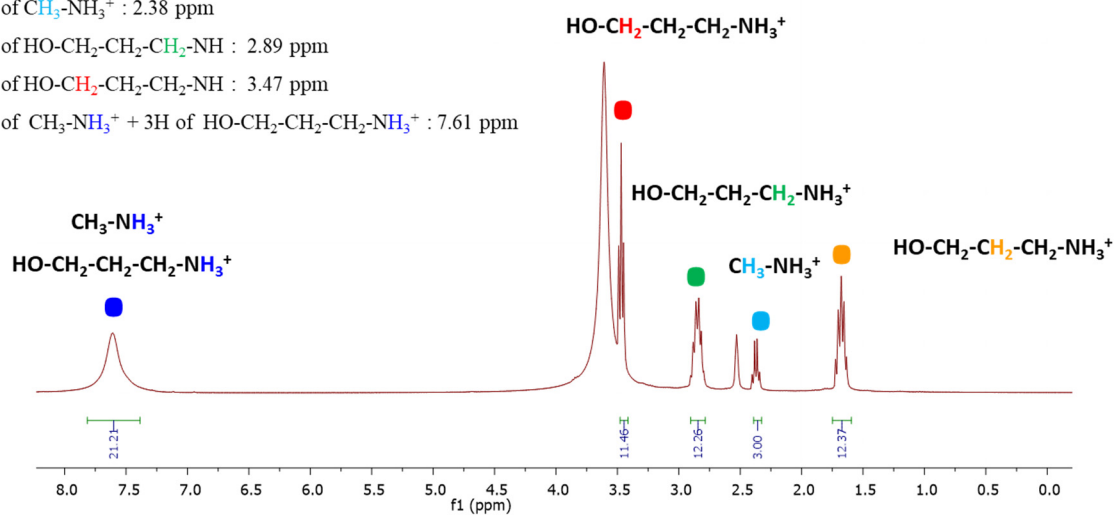
 H_2O : 3.55 ppm2 H of $\text{HO-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}^+$: 1.69 ppm3 H of $\text{CH}_3\text{-NH}_3^+$: 2.38 ppm2 H of $\text{HO-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}$: 2.89 ppm2 H of $\text{HO-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}$: 3.47 ppm3 H of $\text{CH}_3\text{-NH}_3^+$ + 3H of $\text{HO-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_3^+$: 7.61 ppm

Figure S2. ^1H NMR of $(\text{HPA})_6(\text{MA})\text{Pb}_5\text{I}_{17}$ in deuterated DMSO solution giving the expected $\text{HO}(\text{CH}_2)_3\text{NH}_3 / \text{MA}$ ratio of 6.

TGA

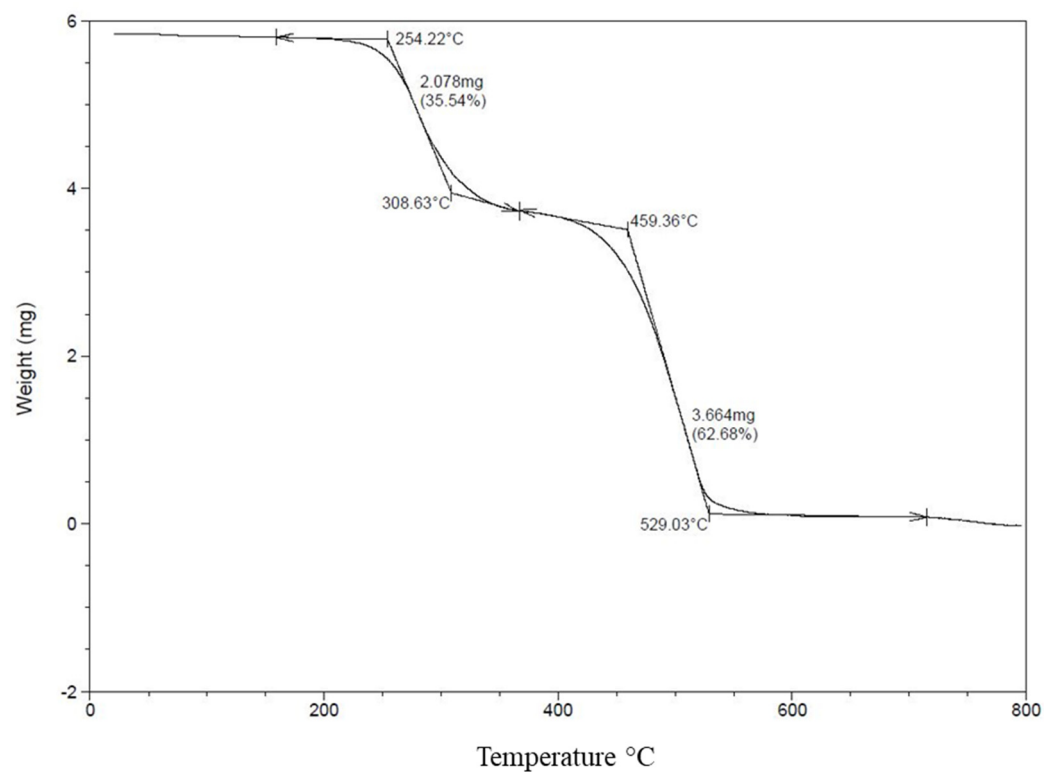


Figure S3. TGA curve of (HPA)₆(MA)Pb₅I₁₇ showing a two steps weight loss from 200 °C, the last one corresponding to the loss of PbI₂ (exp: 62.68 %, calculated : 62.60%).

Stability

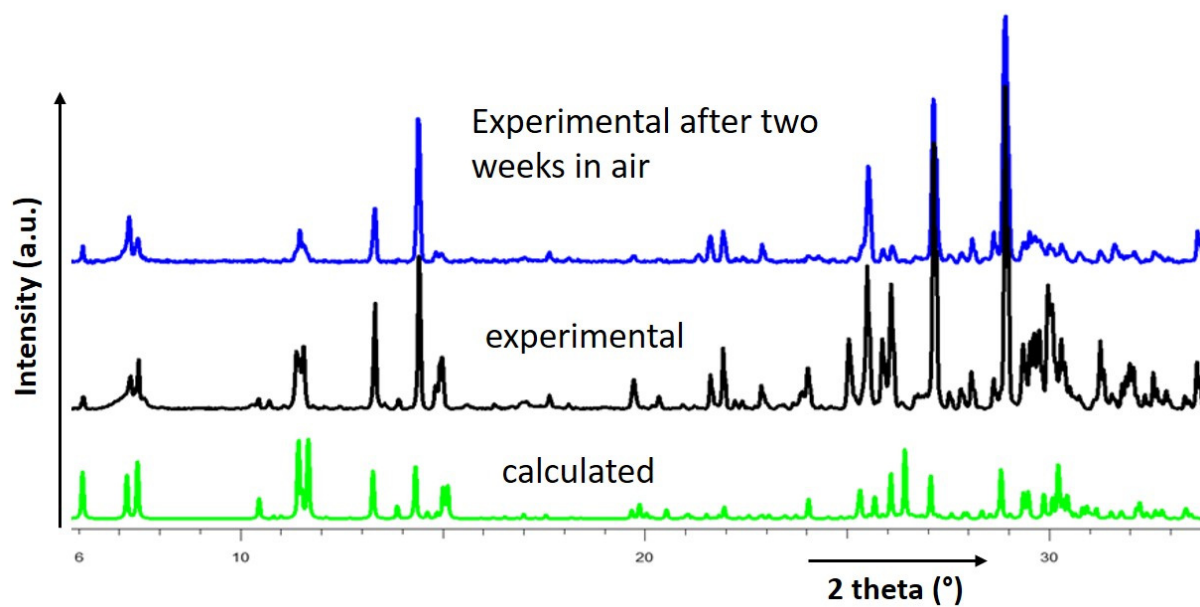


Figure S4. PXRD patterns of a fresh prepared crystallized powder of $(\text{HPA})_6(\text{MA})\text{Pb}_5\text{I}_{17}$ and after two weeks left in the air (green: calculated PXRD).

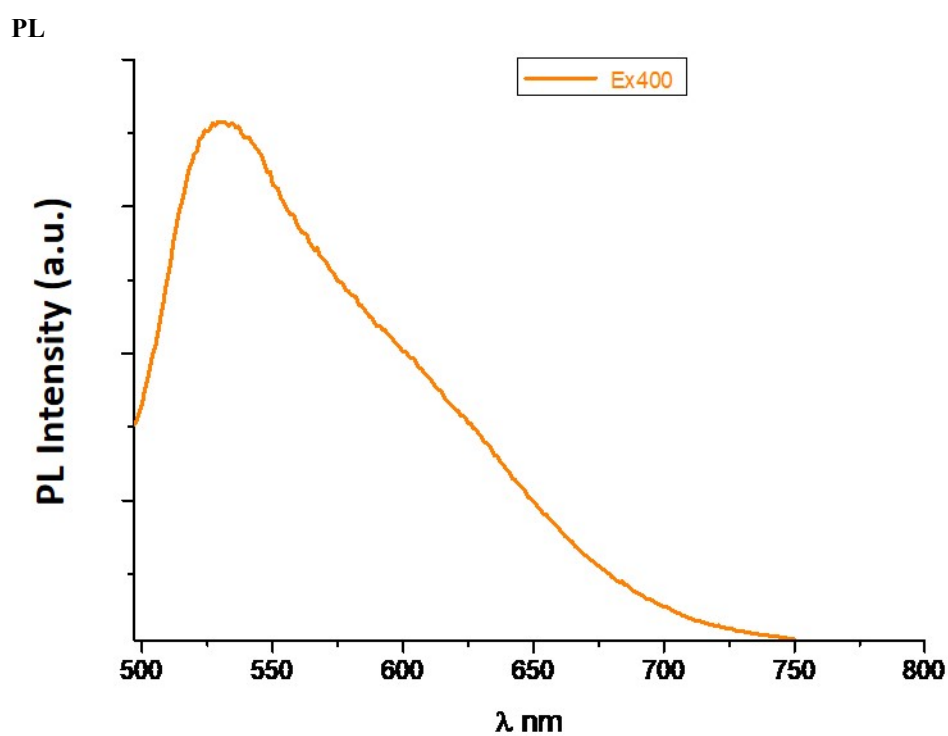


Figure S5. Photoluminescence emission of crystallized powder of $(\text{HPA})_6(\text{MA})\text{Pb}_5\text{I}_{17}$ (exc: 400 nm).

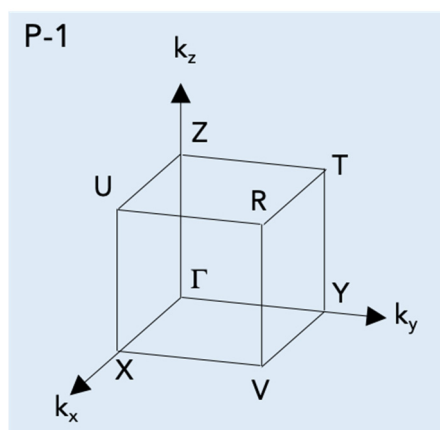


Figure S6. Brillouin zone for the P-1 crystal group.

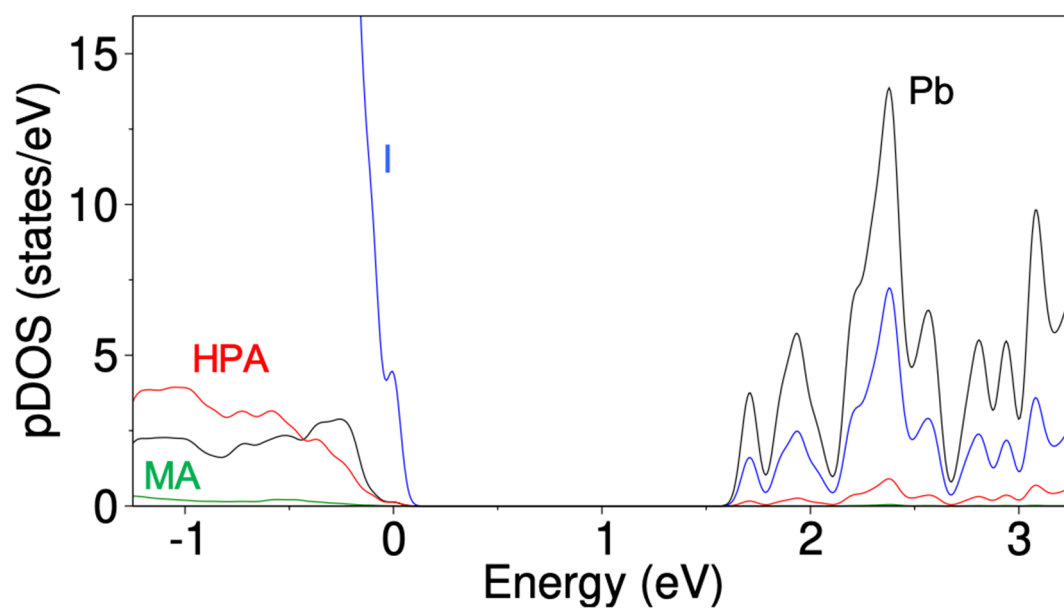


Figure S7. Density of states projected on Pb (black line), I (blue line), HPA (red line) and MA (green line).