Electronic supporting information for paper

Pyrrolidinium lead iodide from crystallography: a new perovskite with low bandgap and good water resistance

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1. Thin film synthesis

1m Mol of pyrrolidinium hydroiodide (98%, TCI) and 1m Mol of lead iodide (99.999%, Sigma) were dissolved in 1ml DMF (99.99%, Sigma), respectively. Drop casting method and spin coating were adopted to fabricate the perovskite films. After annealing at 120°C for 1-hour, polycrystalline films were obtained from both methods. We then extracted yellow needle-like single crystal from the drop casting film.

2. Powder X-ray diffraction study

X-ray powder diffraction (XRD) patterns of polycrystalline material were collected using a Bruker-AXS D8 DISCOVER X-ray diffractometer with CuKα1 radiation (λ = 1.79026 Å) in the range of 8–78° (2θ) with a step size of 0.002° and a time setting of 0.1 s per step.

3. Single crystal X-ray diffraction study

Data-sets of hexagonal PyPbI3 were collected using a Bruker APEX-II diffractometer equipped with a CCD detector (graphite-monochromatized Mo-Kα radiation, λ = 0.71073 Å) at 297K. Data integration and cell refinement were performed using the Olex2 software.[1] The structure was analyzed by direct methods and refined using the XL (Sheldrick, 2008) software package.[2] All nonhydrogen atoms of the structure were refined with anisotropic thermal parameters, and the refinements converged for $Fo^2 > 2\sigma(Fo^2)$. All the calculations were performed using SHELXTL crystallographic software package. Symmetry analysis on the model using PLATON revealed that no obvious space group change was needed. In the refinement, the commands EDAP and EXYZ were used to restrain some of the related bond lengths and bond angles. CCDC-1886890 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The experimental data and are given in table S1.

4. Optical properties tests

UV-vis spectra were acquired from thin film samples at room temperature using a DU 800 Spectrophotometer. The Tauc plot was used to estimate the bandgap of the material.

The photoluminescence test is conducted by Ar-ion laser (excitation wavelength=514.5 nm) at room temperature from Melles Griot (35LAP431208) at a power of 130mW with a repetition rate of 50 Hz. The PL signals were collected using a liquid N_2-cooled silicon CCD.

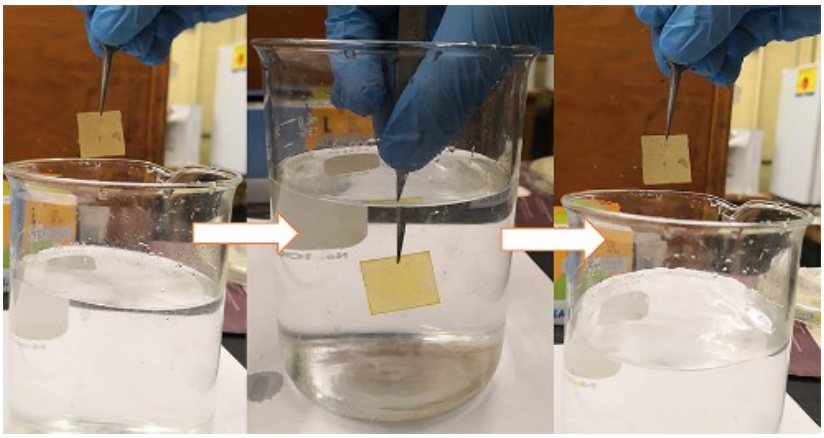

Figure S1. Photographs of $PyPbI_3$ before (left) and after (right) dipping in water

Table S1. Crystal data and structure refinement for $(C_4H_8NH)PbI_3$

compound	$(C_4H_8NH)PbI_3$
empirical formula	$C_4H_{10}NPbI_3$
formula weight	660.00
temperature	297K
wavelength	0.71073 Å
crystal system	hexagonal
space group	P63/mmc (No. 194)
unit cell dimensions	a= 9.3117(5) Å c= 8.1080(4) Å
volume	608.84(7) $Å^3$
Z	1.99992
density (calculated)	3.600 $g \cdot cm^{-3}$
absorption coefficient	21.405 mm^{-1}
Absorption (exp) Tmin, Tmax	2.53, 23.57
F(000)	564
crystal size	0.37*0.05*0.03 mm^3
θ range for data collection	2.526 to 30.433 °
index ranges	-13<h<9 -8<k<13 -11<l<11
reflections collected	6688
independent reflections	384 (Rint = 0.0406)
refinement method	Full-matrix least-squares on F^2
data / restraints / parameters	384/0/21
goodness-of-fit on F^2	1.042
final R indices [I>2σ(I)]	0.0235
R indices (all data)	0.0589

Reference

1 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, , DOI:10.1107/S0021889808042726.

2 G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.*, , DOI:10.1107/S2053229614024218.