Electronic Supplementary Information (ESI)

Lead-free Layered Dion-Jacobson Hybrid Double Perovskite Constructed by Aromatic Diammonium Cation

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Table of Content

Experimental section

Materials and Synthesis

All chemicals were purchased by Aladdin except as otherwise illustrated. For the preparation of [$(3AMPY)_2AgBiI_8 \cdot H_2O$] (3AMPY=3-(aminomethyl) pyridinium) **(1),** a reaction mixture contains stoichiometric 3AMPY (0.43 g, 4 mmol), Ag_2O (0.23 g, 1 mmol) and Bi_2O_3 (0.26 g, 1 mmol) in 20 mL HI (47%) solution was heated and stirred for a few minutes to get the clear solution, after that the clarified liquid was slowly cooled to room temperature. The red rectangular crystals of $(3AMPY)_2AgBiI_8 \cdot H_2O$ have been obtained by slow evaporation after several days.

Measurements

Powder X-Ray Diffraction Analysis and Thermogravimetric Analysis

MiniFlex 600 Powder X-Ray Diffractometer (PXRD) was used to check the phase purity of desired compounds. The experimental PXRD patterns were recorded in the 2 theta (2θ) range of 5°-50° with a step size of 3°/ min. The experimental PXRD patterns obtained at room temperature match well with the calculated data based on the single-crystal structure, which solidly confirm the purity of the as-grown crystals of $(3AMPY)_2AgBiI_8 \cdot H_2O$. Thermogravimetric (TG) measurement was implemented on a Netzsch STA 449C thermal analyser with an N_2 flow rate of 30 mL min^{-1} and a heating rate of 10 K min^{-1} from 300 K to 1000 K.

SCXRD Structure Determination

Single crystal X-ray diffraction (SCXRD) was performed on Bruker D8 diffractometer by using Mo Kα radiation (λ=0.71073 Å). Intensity data acquisition, data reduction and cell refinement were performed using the "multi-scan" program. The structures of all desired compounds were solved by direct methods and refinements were made by the least-squares program. Table S1 summarizes the detailed information of crystal parameters, structure refinement and data collection. The selected bond lengths and angles are shown in Table S2-S3.

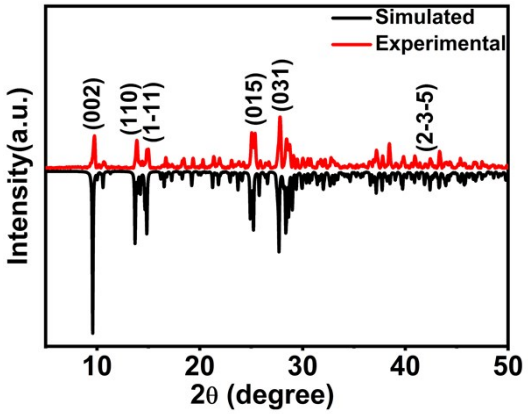
Ultraviolet-visible (UV-vis) Absorption Spectrum

UV-vis diffuse reflectance spectroscopy of $(3AMPY)_2AgBiI_8 \cdot H_2O$ was performed at room temperature on Perkin-Elmer Lambda 900 UV-Vis spectrophotometer in a variable wavelength range between 200 to 1000nm. The $BaSO_4$ was used as the 100% reflectance reference, and the powdered crystals were used for the measurements.

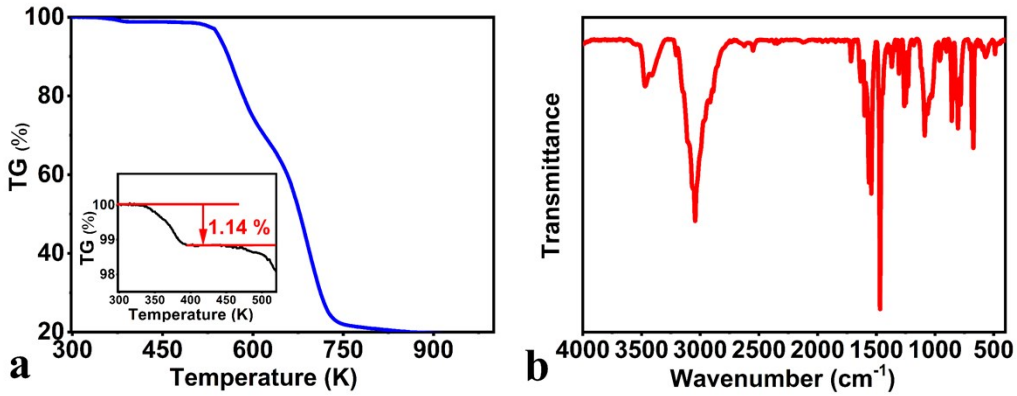
Near the cut-off of the optical transmission, the band gap, the absorption value and the wave frequency obey the equation: $(hv*F(R_\infty))^{1/n} = A\,(hv-E_g)$ where h, v, $F(R_\infty)$, A, and E_g are the Planck's constant, the frequency of vibration, the Kubelka-Munk equation, the proportional constant and the band gap, respectively. In the equation, n decides the characteristics of the transition in a semiconductor (n=1/2, direct absorption; n=2, indirect absorption). The values of n and E_g were determined by the following steps: first, plot ln(αhv) vs ln (hv - E_g) using the approximate E_g value, and then determine the value of n with the slope of the straight line near the band edge; second, plot (αhv)1/n vs hv and then obtain the band gap E_g by extrapolating the straight line to the hv axis intercept.

Computational Details

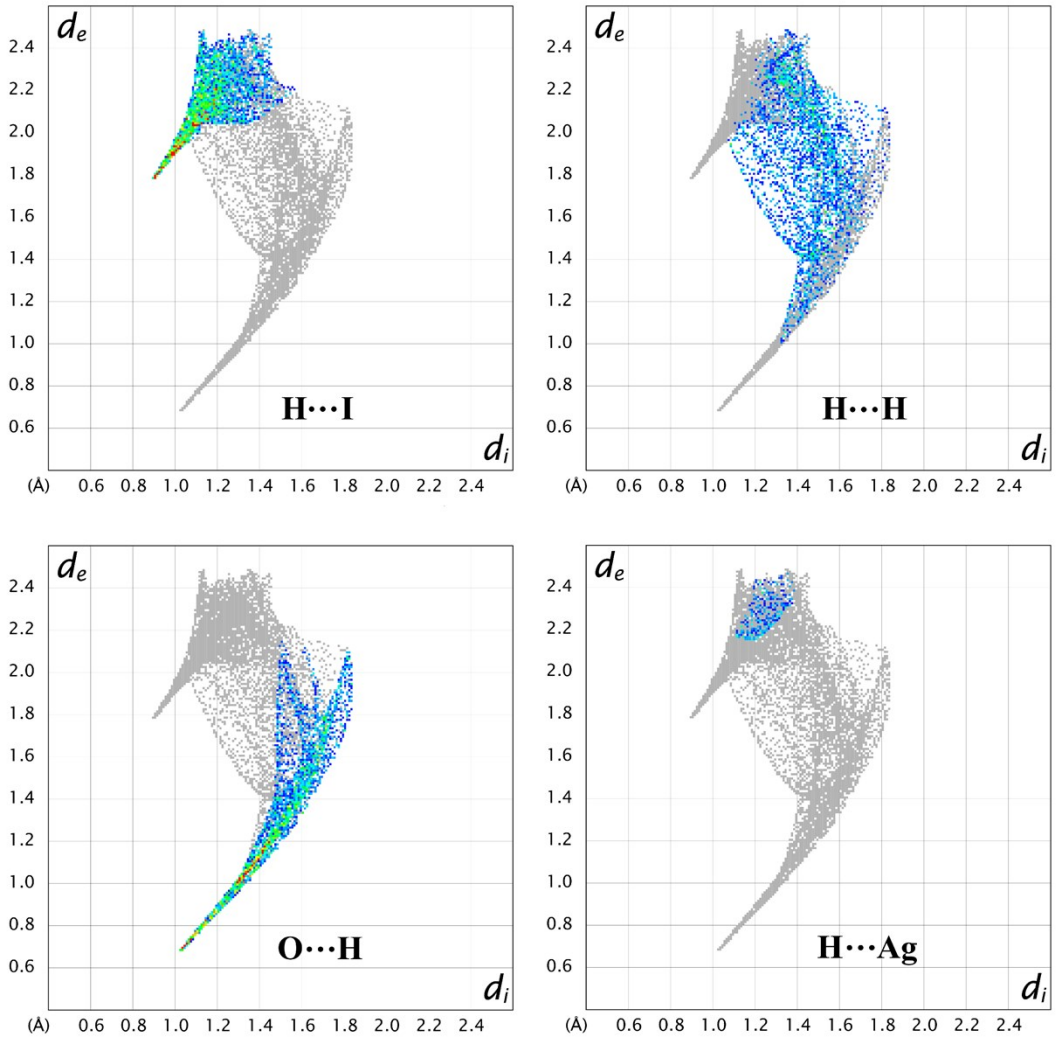
First-principles density function theory (DFT) calculations were performed with the Cambridge Sequential Total Energy Package (CASTEP). The exchange-correlation functional was described by a generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof functional for solids (PBEsol) scheme. The interactions between the ionic cores and the electrons were described by the norm-conserving pseudopotential.[4] The following orbital electrons were treated as valence electrons: Bi $6s^2$ $6p^3$; Ag $4d^{10}$ $5s^2$ $5p^3$; I $5s^2$ $5p^5$; C $2s^2$ $2p^2$; N $2s^22p^3$ and H $1s^1$. The numbers of plane waves included in the basis sets were determined by a cutoff energy 765 eV. To achieve the accurate density of the electronic states, the *k*-space integrations were done with Monkhorst-Pack grids with a 6 × 6 × 3 *k*-point for compound **1**. The other parameters and convergent criteria were the default values of CASTEP code.



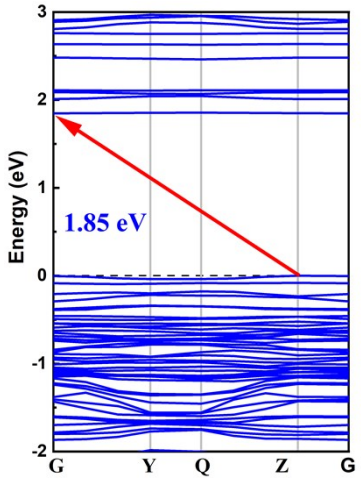
SFig.1 Experimental and simulated powder x-ray diffractions patterns (PXRD) spectra of **1**.



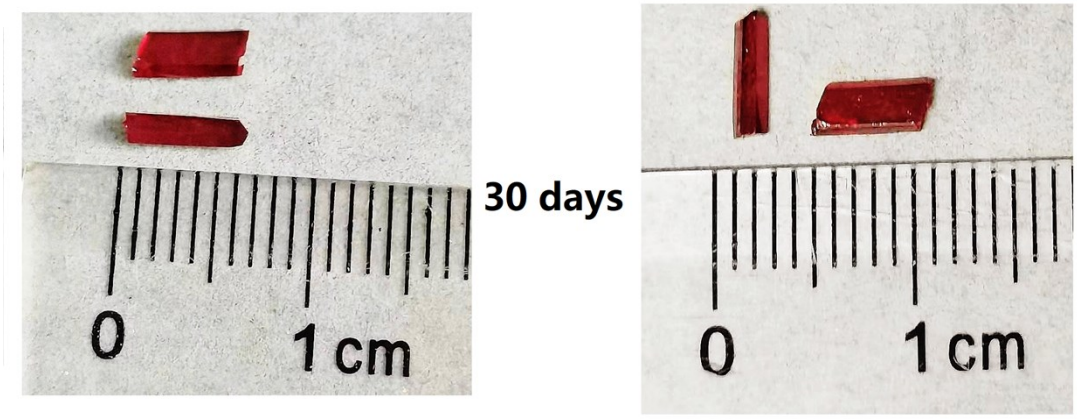
SFig.2 (a) The TGA of the compound **1**, (b) Infrared spectrum of **1** obtained at room temperature.



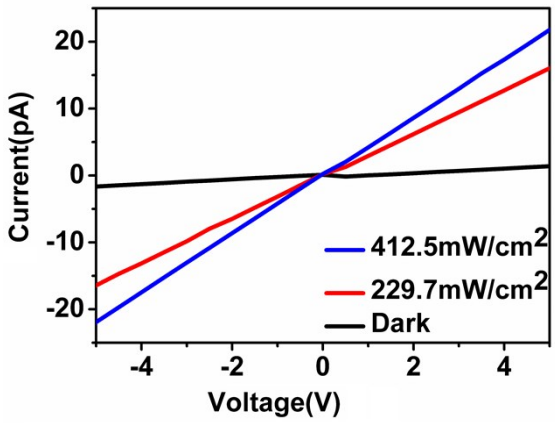
SFig.3 The 2D fingerprint plot of H_2O molecule.



SFig.4 The electronic energy band structure of **1**.



SFig.5 Crystal stability test of **1**.



SFig.6 The I-V curves of 1 under the 637 nm light illumination.

Table S1. Crystal Data and Structure Refinement for **$(3AMPY)_2AgBiI_8 \cdot H_2O$**.

Formula	$(3AMP)_2AgBiI_8 \cdot H_2O$
Formula weight (g/mol)	1570.38
Temperature (K)	200.02 K
Crystal system	triclinic
Space group	P-1
a (Å)	8.5258(4)
b (Å)	9.7136(5)
c (Å)	18.5101(10)
α (deg)	86.146(2)

β (deg)	88.192(2)
γ (deg)	88.857(2)
Volume (Å^3)	1528.46(13)
Z	2
D_{calcd} (g/cm3)	3.412
F(000)	1368.0
limiting indices	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -24 ≤ l ≤ 24
reflns collected	55189
completeness (%)	99.8
data / restraints / param	7023/0/249
final R indices [I>2σ(I)]	R_1 = 0.0302, wR_2 = 0.0644
R indices (all data)	R_1 = 0.0367, wR_2 = 0.0675

Table S2. Selected bond lengths (Å) for **$(3AMPY)_2AgBiI_8 \cdot H_2O$** .

Bond	(Å)	Bond	(Å)
Bi1– I8	3.0652(4)	I8– Ag1[1]	3.7719(9)
Bi1– I6	2.9722(4)	I1– Ag1	2.6995(8)
Bi1– I7	3.1183(5)	I5– Ag12	3.2672(9)
Bi1– I5	3.0839(4)	I2– Ag1	2.6923(7)
Bi1– I4	3.0456(5)	I3– Ag1	3.0470(8)

[1]1-X,+Y,+Z; [2]+X,1+Y,+Z; [3]1-X,1-Y,-1/2+Z; [4]1-X,1-Y,1/2+Z; [5]+X,2-Y,1/2+Z; [6]+X,1-Y,1/2+Z; [7]+X,2-Y,-1/2+Z; [8]+X,1-Y,-1/2+Z; [9]+X,-1+Y,+Z; [10]1-X,-Y,-1/2+Z; [11]1-X,-Y,1/2+Z

Table S3. Selected bond angles (°) for **$(3AMPY)_2AgBiI_8 \cdot H_2O$**.

Bond	(°)	Bond	(°)
I8–Bi1–I7	87.595(13)	I1–Ag1–I63	73.556(19)
I8–Bi1–I5	177.948(14)	I2–Ag1–I63	80.298(19)
I6–Bi1–I8	90.958(12)	I2–Ag1–I1	152.85(3)
I6–Bi1–I7	89.557(12)	I3–Ag1–I63	171.75(2)
I7–Bi1–I3	92.661(13)	Ag1–I3–Bi1	155.34(2)
I5–Bi1–I7	90.761(13)	Bi1–I8–Ag11	161.980(18)
I4–Bi1–I8	91.007(13)	Bi1–I5–Ag12	169.68(2)

[1]+X,1-Y,1-Z; [2]+X,1/2-Y,1/2+Z; [3]+X,1/2+Y,1/2-Z; [4]1-X,-Y,1-Z; [5]1-X,+Y,+Z; [6]+X,-Y,1-Z; [7]1-X,1/2-Y,1/2+Z; [8]+X,-1+Y,+Z; [9]1-X,1/2-Y,-1/2+Z; [10]+X,1-Y,-Z