Supporting information for

Zero-Dimensional Lead-Free Bismuth-Based Metal Halide: $[C_6H_5(CH_2)_2CH(NH_3)CH_3]_2BiCl_5$

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Methods

Synthesis

All chemicals and solvents were of reagent grade and used as received. Single crystals of $C_6H_5(CH_2)_2CH(NH_3)CH_3$ (**MPA$_2$-BiCl$_5$**) are synthesized as follow: $BiCl_3$ (1 mmol) was dissolved in 4 mL concentrated hydrochloric acid HCl solution in a beaker. Then add 1-Methyl-3-phenylpropylaminium (2 mmol) to 2 mL H_2O in another beaker. Whereafter, the latter was slowly dripped into the former along the wall.

Thermal measurements

Thermogravimetric analysis (TGA) measurements of **MPA_2-$BiCl_5$** were performed on a TA-Instruments STD2960 system from 293 to 1050 K.

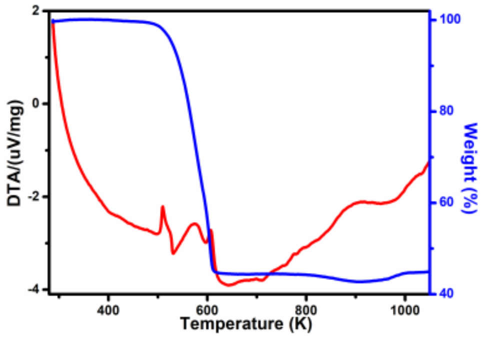

Figure S1. TG and DTA curves of **MPA_2-$BiCl_5$** between 300 and 1050 K.

Single crystal X-ray diffraction

Single crystal X-ray diffractions were carried out with graphite monochromated Mo radiation (λ = 0.71073 Å) on an Oxford Diffraction Gemini E Ultra diffractometer. Data sets were collected by using *CrysAlis^{Pro}* software. The program Olex2-1.2 was employed as an interface to invoke program SHELXS97 and SHELXL97 executables.[1] The crystal structures were solved by direct methods with SHELXS97 and refined by full-matrix least squares on F^2 with anisotropic atomic displacement parameters for all non-hydrogen atoms using SHELXL97.[2,3] All H atoms were located from molecular geometric calculations and refined with isotropic temperature parameters. The crystallographic information of **MPA_2-$BiCl_5$** determined at 100 K and 293 K are listed in the Table 1. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif (CCDC 2219486 and 2217399).

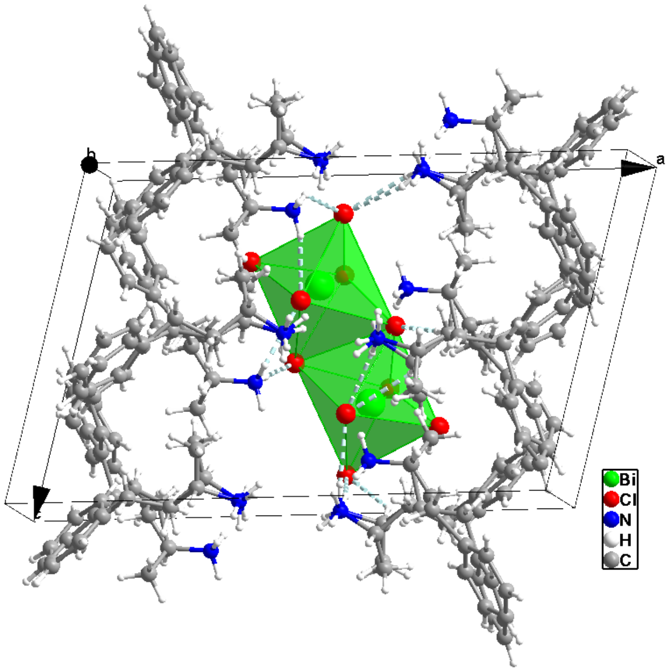

Figure S2. Asymmetric unit and the atom labeling scheme of **MPA$_2$-BiCl$_5$** at 100 K.

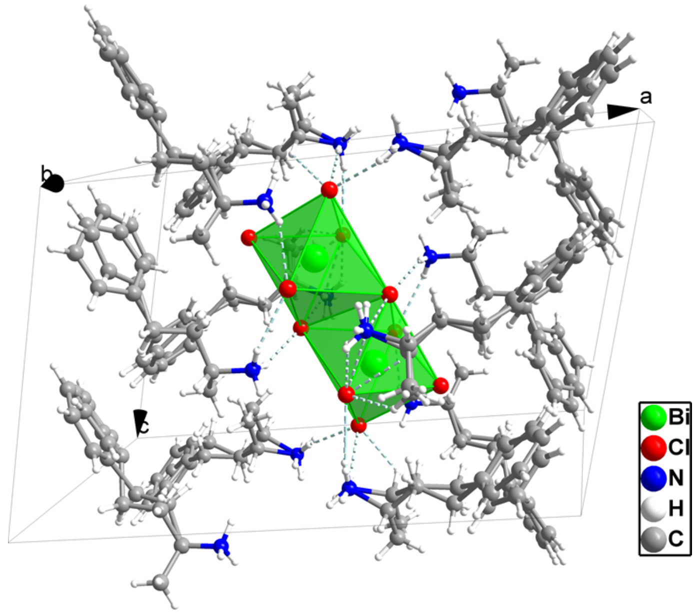

Figure S3. Asymmetric unit and the atom labeling scheme of **MPA$_2$-BiCl$_5$** at 293 K.

UV-vis absorption spectra

UV-vis absorption spectra were obtained using a Shimadzu (Tokyo, Japan) UV-2550 spectrophotometer in a range of 200~800 nm. The powder crystals of three compositions were used for the measurement. The optical band gap was determined by a variant of the *Tauc* equation:[4]

$$[h\nu \cdot F(R_\infty)]^{1/n}=A(h\nu-E_g)$$

where h is the Planck's constant, ν represents the frequency of vibration, A is the proportional constant, E_g is the bandgap and $F(R_\infty)$ is Kubelka-Munk equation:[5] $F(R_\infty) = (1-R_\infty)^2/2R_\infty$. In addition, n=1/2 stands for direct band gap, while n=2 is indirect band gap.

Density functional theory (DFT) calculations

The first-principles calculations were performed using the CASTEP code,[6] a total energy package based on pseudopotentail density functional theory (DFT).[7,8] The correlation and exchange terms in the Hamiltonian were described by the functionals developped by Perdew, Burke and Ernzerhof (PBE)[9] in the generalized gradient approximation (GGA)[10] form. The optimized fine pseudopotential was adopted to model the effective interactions between the valence electrons and atomic cores, which allow us to choose a relatively small plane-wave basis set without compromising the computational accuracy. Kinetic energy cutoff 240 eV and dense Monkhorst-Pack[11] with medium *k*-point meshes interval in the Brillouin zones were chosen.

Reference

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