Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

First-Principles Characterization of Two-Dimensional $(CH_3(CH_2)_3NH_3)_2(CH_3NH_3)_{n-1}Ge_nI_{3n+1}$ Perovskite

Liyuan Wu[a,b], Pengfei Lu[a], Yuheng Li[b], Yan Sun[b], Joseph Wong[b], and Kesong Yang[*b]

[a]*State Key Laboratory of Information Photonics and Optical Communications, Beijing University of Posts and Telecommunications, Beijing 100876, China*

[b]*Department of NanoEngineering, University of California San Diego, 9500 Gilman Drive, Mail Code 0448, La Jolla, California 92093-0448, United States*

* Correspondence: kesong@ucsd.edu

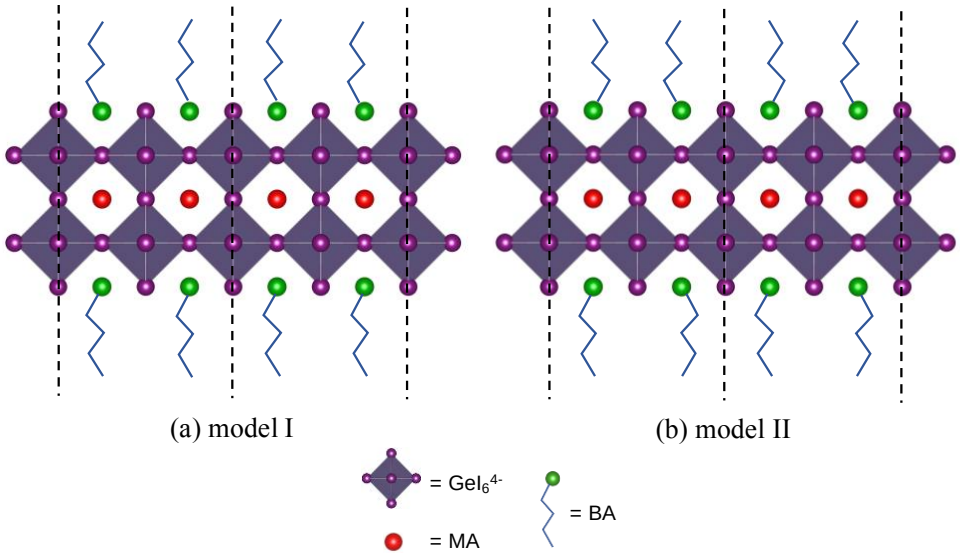

Figure S1 Schematic crystal structures of 2D perovskites. (a) Model I: all the ammonium heads of BA cations are along the same direction, and (b) Model II: the ammonium heads exhibit an alternative order.

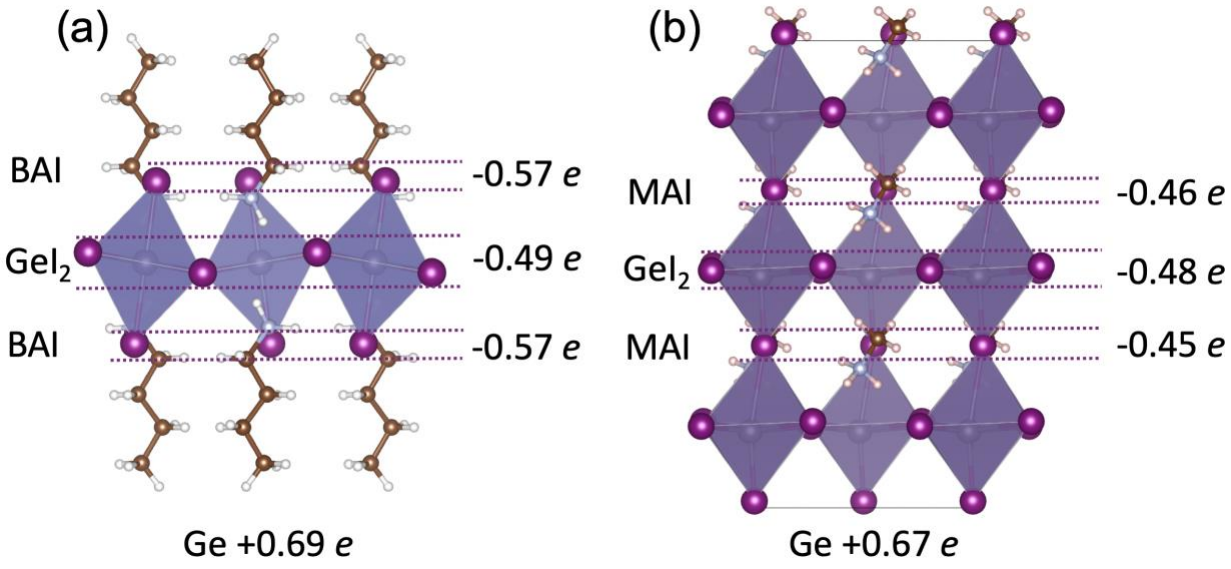

Figure S2 Bader charge analysis of Ge cation and I anions for (a) 2D perovskite $(BA)_2GeI_4$ and (b) 3D perovskite $MAGeI_3$.

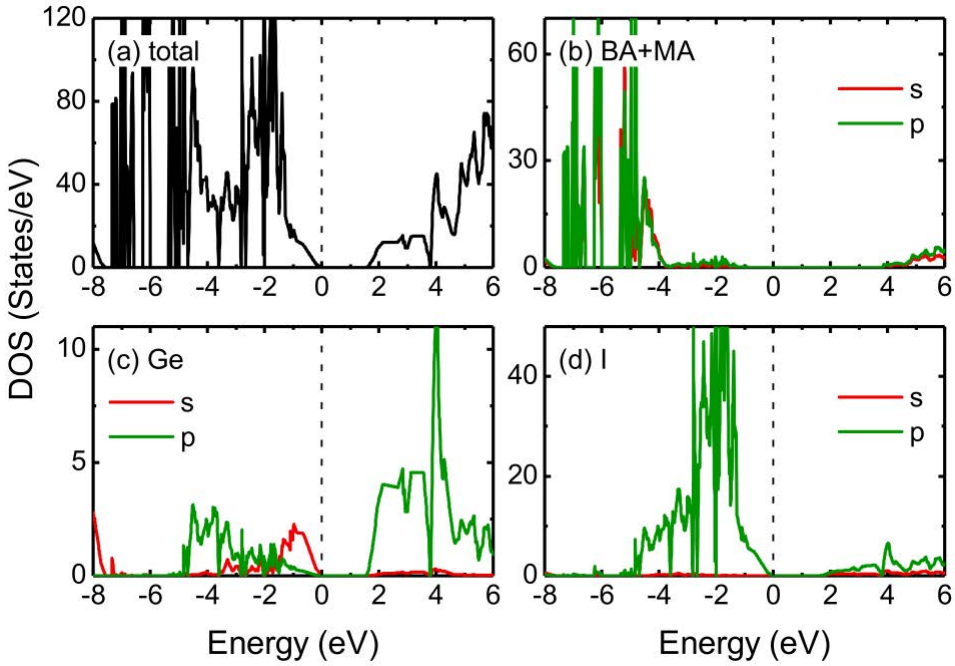

Figure S3 Density of states (DOS) of $(BA)_2(MA)Ge_2I_7$. (a) Total DOS, and partial DOS of (b) BA and MA molecules, (c) Ge, and (d) I. Red and green lines donate the *s* and *p* contribution, respectively. The Fermi level is indicated by the black vertical dash line.

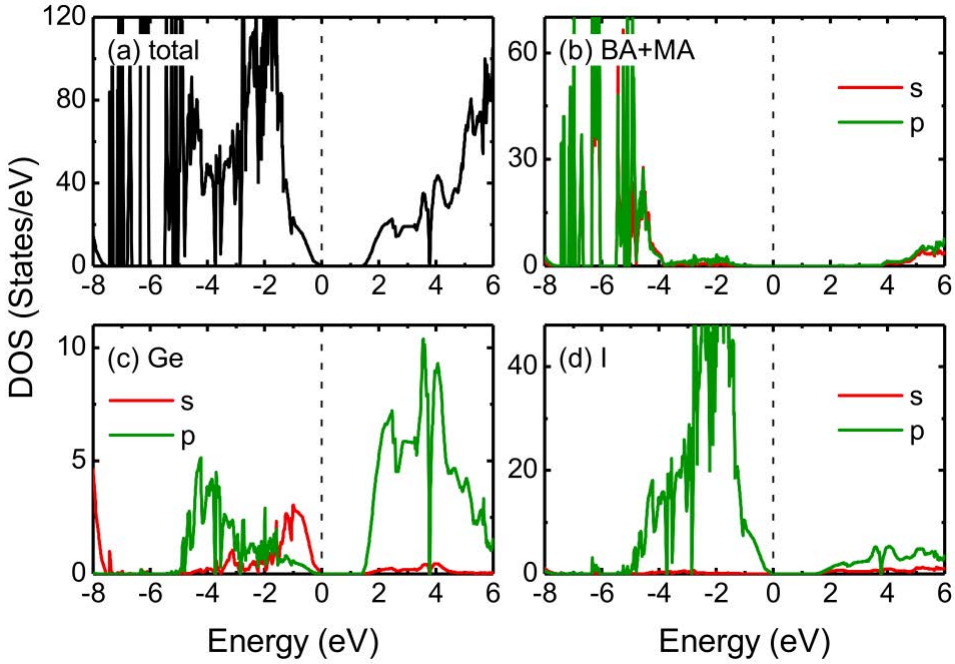

Figure S4 Density of states (DOS) of $(BA)_2(MA)_2Ge_3I_{10}$. (a) Total DOS, and partial DOS of (b) BA and MA molecules, (c) Ge, and (d) I. Red and green lines donate the *s* and *p* contribution, respectively. The Fermi level is indicated by the black vertical dash line.

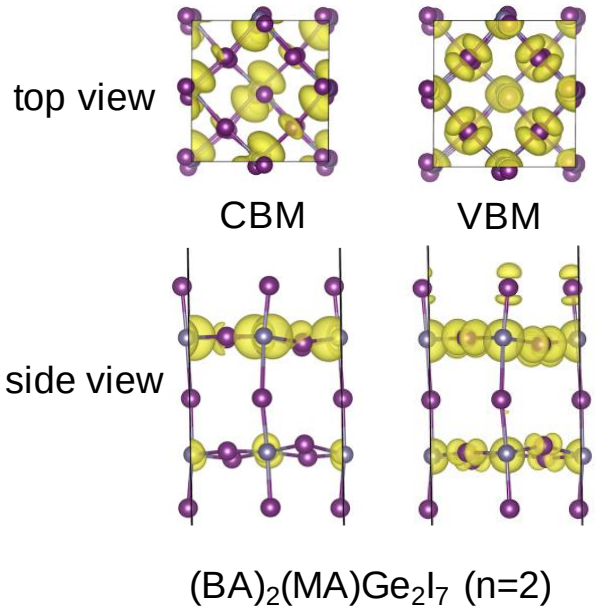

Figure S5 Top and partial side views of decomposed charge densities of CBM and VBM of $(BA)_2(MA)Ge_2I_7$. The isosurface level is 0.0015 e/Bohr^3. The organic molecules are hidden for a clear display of charge density.

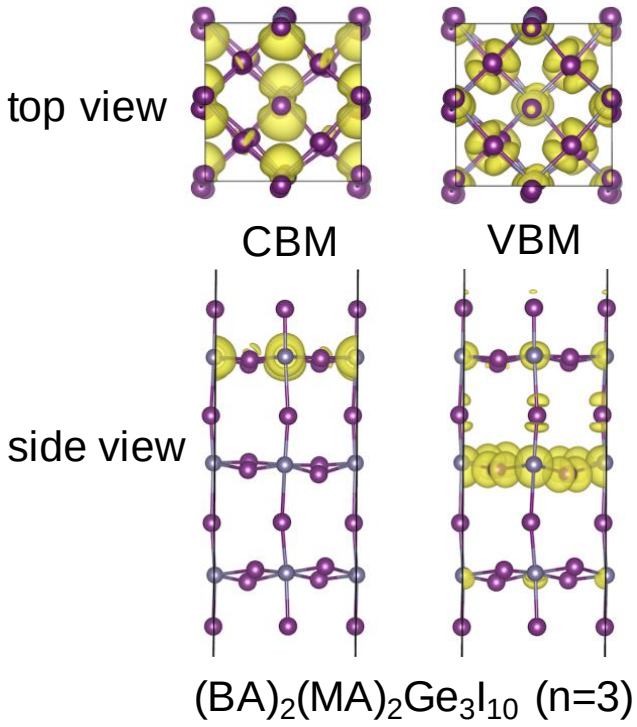

Figure S6 Top and partial side views of decomposed charge densities of CBM and VBM of $(BA)_2(MA)_2Ge_3I_{10}$.

Table S1. Calculated lattice constants of 2D perovskites $(BA)_2(MA)_{n-1}GenI_{3n+1}$ for Mode I and Model II within the PBE functional.

System	Structure	a (Å)	b (Å)	c (Å)
n=1	Model I	8.399	8.648	30.183
	Model II	8.164	8.547	29.109
	Exp.[1]	8.272	8.722	28.014
n=2	Model I	8.443	8.506	42.127
	Model II	8.454	8.777	41.183
n=3	Model I	8.506	8.785	54.793
	Model II	8.393	8.714	54.192

[1] D. B. Mitzi, Chem. Mater., 1996, 8, 791–800.

Table S2. The total number of unit cell atoms m, and the energy difference between model I and model II $\Delta E = (E_{\text{model I}} - E_{\text{model II}})/m$.

System	m	ΔE (meV/atom)
n=1	156	0.744
n=2	204	1.470
n=3	252	1.611