Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

First-principles study of Lead-free Ge-based 2D Ruddlesden–Popper hybrid perovskites for solar cells applications

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I. Formation energy (eV)

Using DFT calculation, we obtain the formation energy of the proposed perovskites to understand the stability of 2D and 3D structures.

For 3D and 2D perovskites, the formation energies (E_f) are defined as:[1, 2]

3D perovskite:

$$E_f(MAPbI_3) = E_{MAPbI_3} - E_{MAI} - E_{PbI_2} \quad (1)$$

2D perovskite:

$$E_f\left(BA_2MA_{n-1}Pb_nI_{3n+1}\right) = \frac{E_{BA_2MA_{n-1}Pb_nI_{3n+1}} - nE_{PbI_2} - (n-1)E_{MAI} - 2E_{BAI}}{n} \quad (2)$$

Here where E_{MAPbI_3}, E_{MAI}, E_{PbI_2}, E_{BAI}, represent the optimized crystal energy. For formation energy calculation of Ge-based perovskites, Ge is used instead of Pb in the above equations. If the formation energy of a compound is negative, it indicates that the material is thermodynamically stable, while a more negative value means more stability.[1] The calculated formation energy of the proposed compounds is listed in Table S1.

Table S1. Calculated formation energy of 2D RP perovskites $(BA)_2(MA)_{n-1}M_nI_{3n+1}$ (M=Pb, Ge; n = 1-5, and ∞)

Compounds	n	(eV)	Compounds	n	(eV)
BA_2PbI_4	1	- 0.541	BA_2GeI_4	1	-0.433
$BA_2MA\ Pb_2I_7$	2	-0.380	$BA_2MA\ Ge_2I_7$	2	-0.301
$BA_2(MA)_2Pb_3I_{10}$	3	-0.276	$BA_2(MA)_2Ge_3I_{10}$	3	-0.235
$BA_2(MA)_3Pb_4I_{13}$	4	-0.238	$BA_2(MA)_3Ge_4I_{13}$	4	0.169
$BA_2(MA)_4Pb_5I_{16}$	5	-0.184	$BA_2(MA)_4Ge_5I_{16}$	5	-0.116
$MAPbI_3$	∞	-0.082	$MAGeI_3$	∞	-0.071

II. Electronic properties

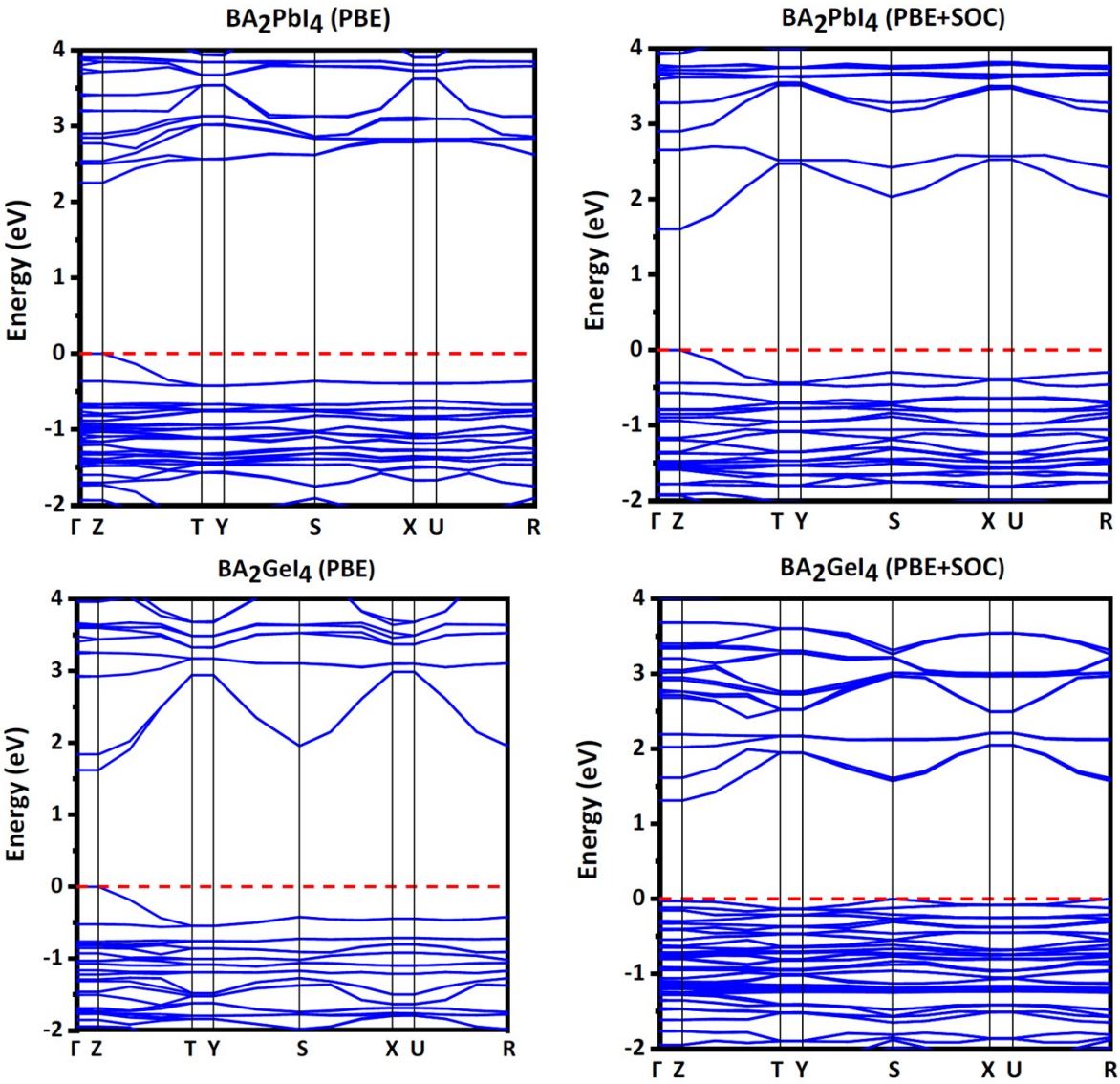


Figure S1. Band structures of 2D RP perovskites $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ (n=1), and $(BA)_2(MA)_{n-1}Ge_nI_{3n+1}$ (n=1) calculated with PBE (left panel), and PBE+SOC (right panel).

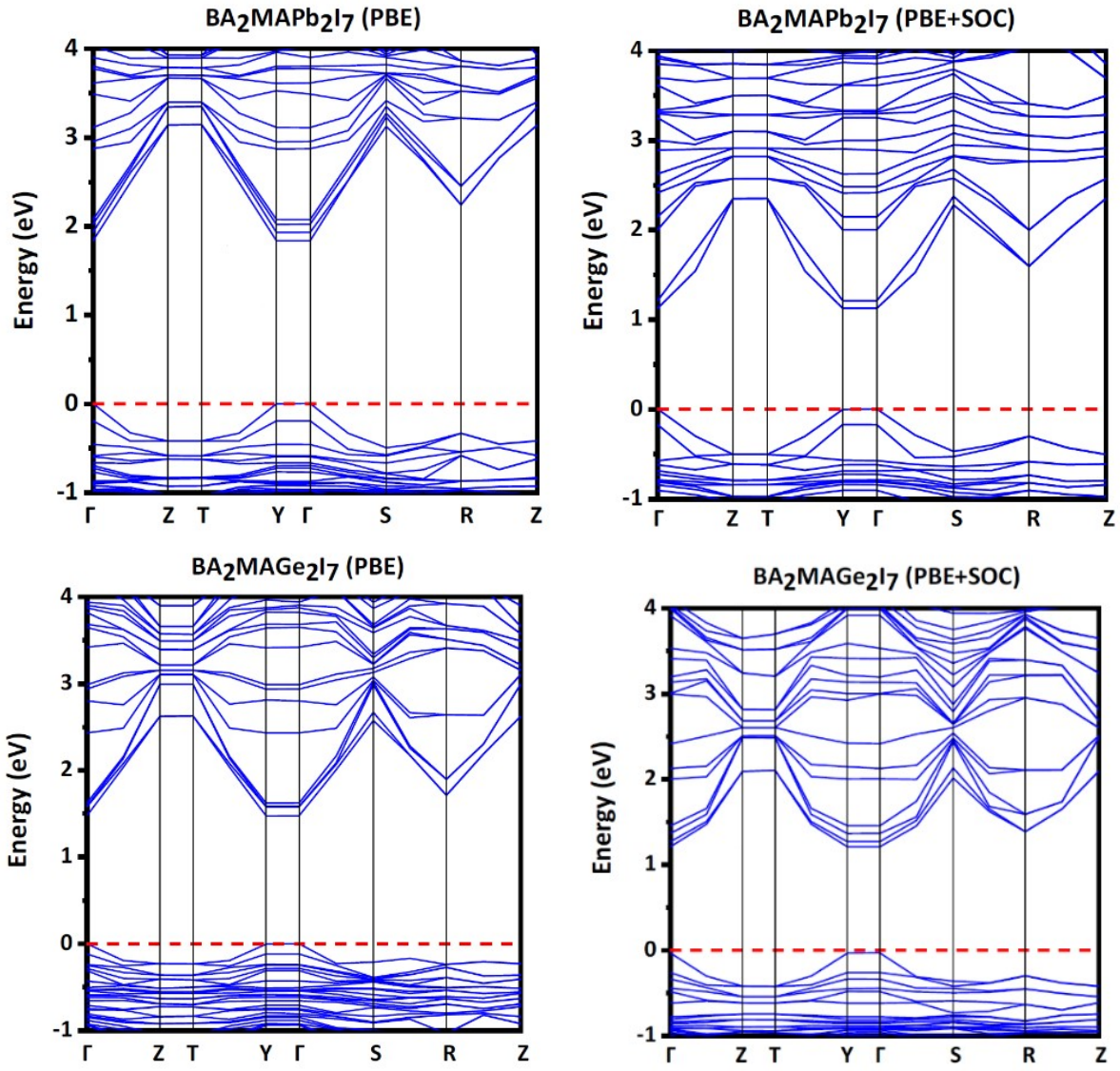
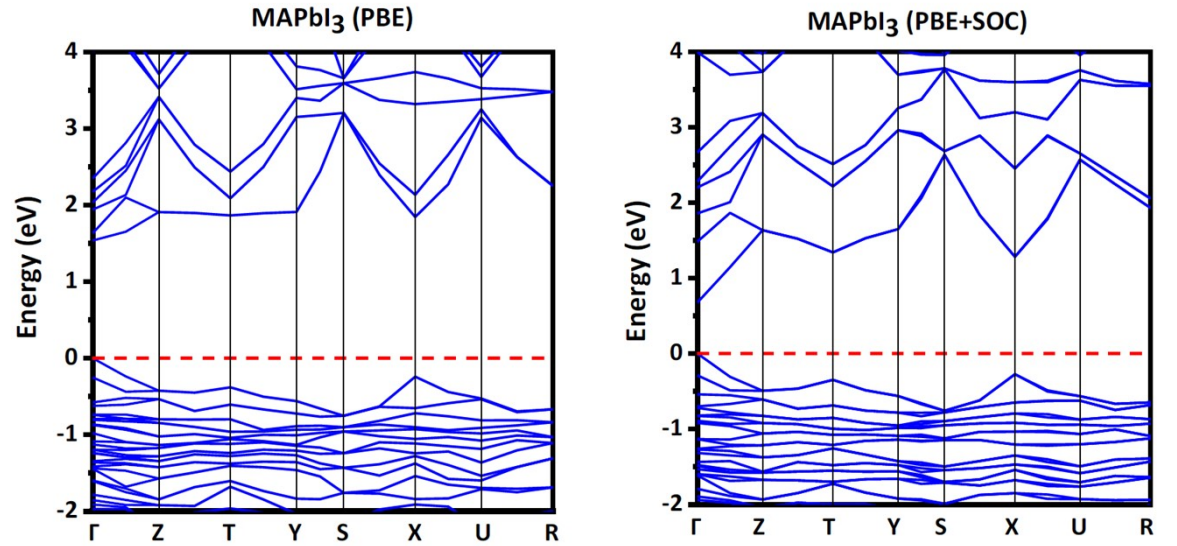


Figure S2. Band structures of 2D RP perovskites $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ (n=2), and $(BA)_2(MA)_{n-1}Ge_nI_{3n+1}$ (n=2) calculated with PBE (left panel) and with PBE+SOC (right panel).



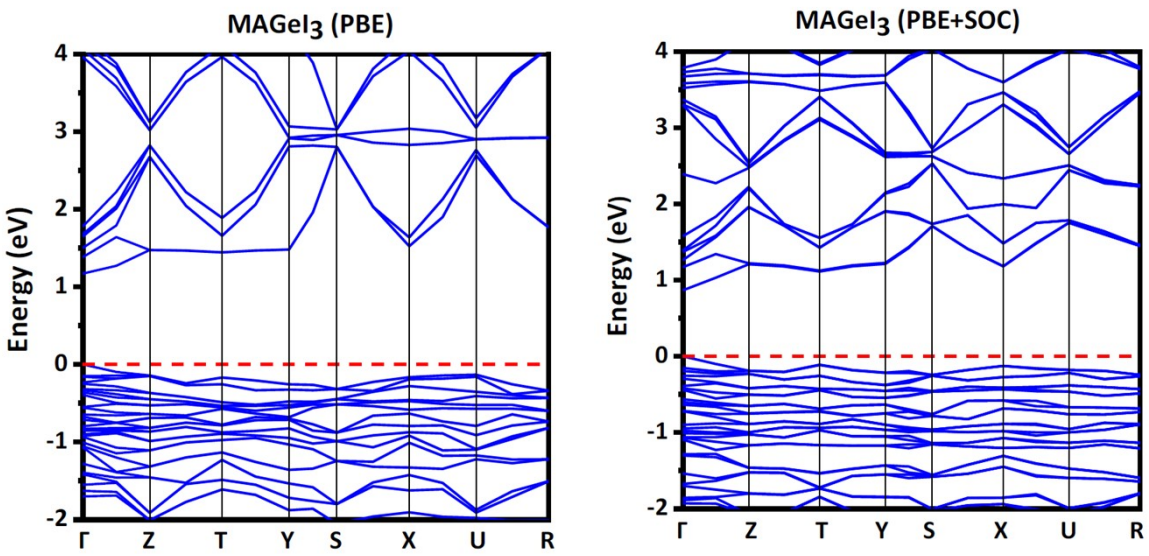


Figure S3. Band structures of 3D perovskites $MAPbI_3$, and $MAGeI_3$ calculated with PBE (left panel), and with PBE+SOC (right panel).

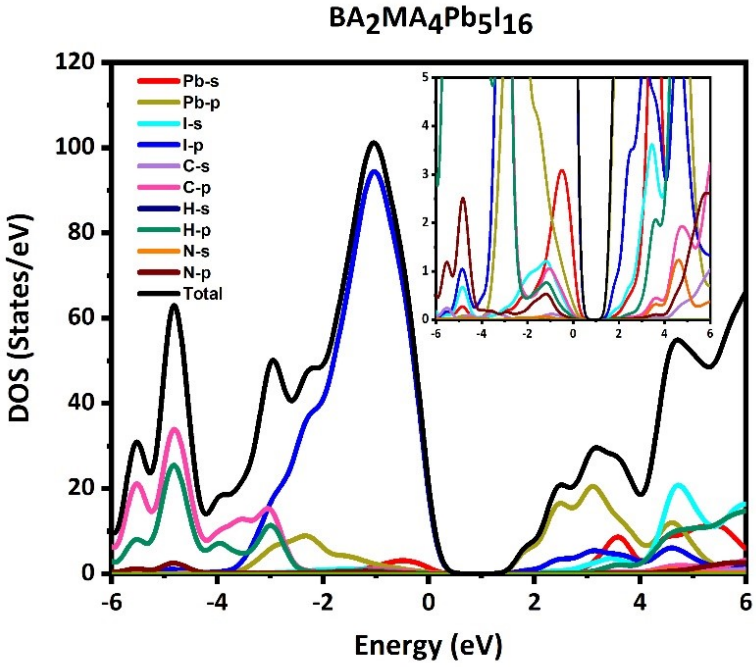


Figure S4. The total DOS and PDOS for the Pb-based 2D perovskite $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ (n= 5).

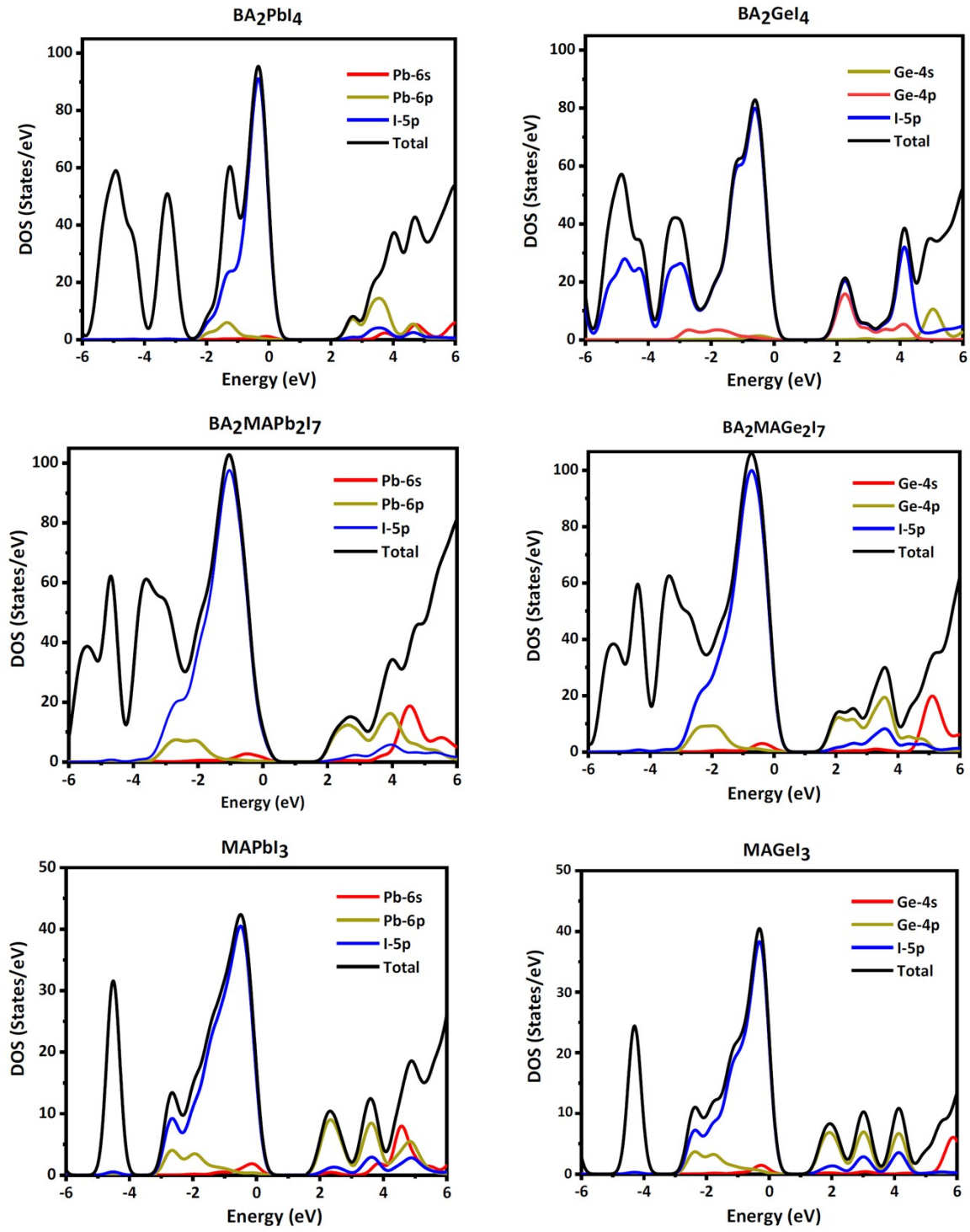


Figure S5. The total DOS and PDOS for the 2D RP perovskites $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ for n= 1, 2, and ∞ (left panel), and 2D perovskites $(BA)_2(MA)_{n-1}Ge_nI_{3n+1}$ for n= 1, 2, and ∞ (right panel).

Reference

1. Y. Yang, F. Gao, S. Gao and S.-H. Wei, *Journal of Materials Chemistry A*, 2018, **6**, 14949-14955.
2. L. N. Quan, M. Yuan, R. Comin, O. Voznyy, E. M. Beauregard, S. Hoogland, A. Buin, A. R. Kirmani, K. Zhao and A. Amassian, *Journal of the American Chemical Society*, 2016, **138**, 2649-2655.