Supporting Information

Superhalogens as building blocks of two-dimensional organic-inorganic hybrid perovskites for optoelectronics applications

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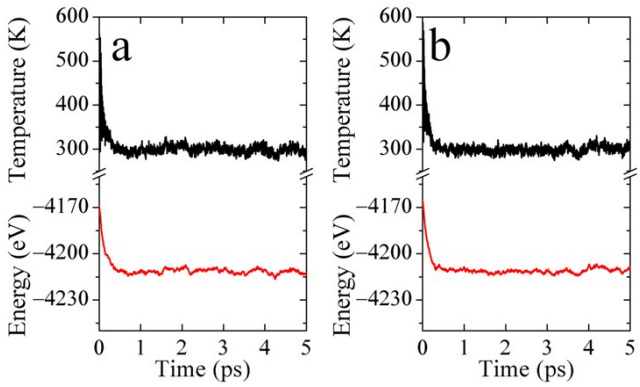


Figure S1. *Ab initio* MD simulated temperature and free energy of (a) $BA_2Sn(BH_4)_4$ and (b) $BA_2Ge(BH_4)_4$.

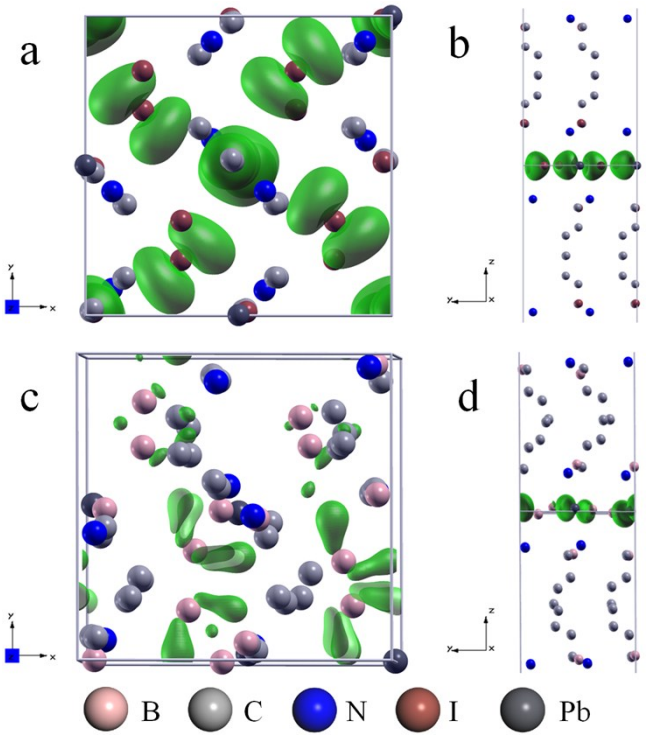
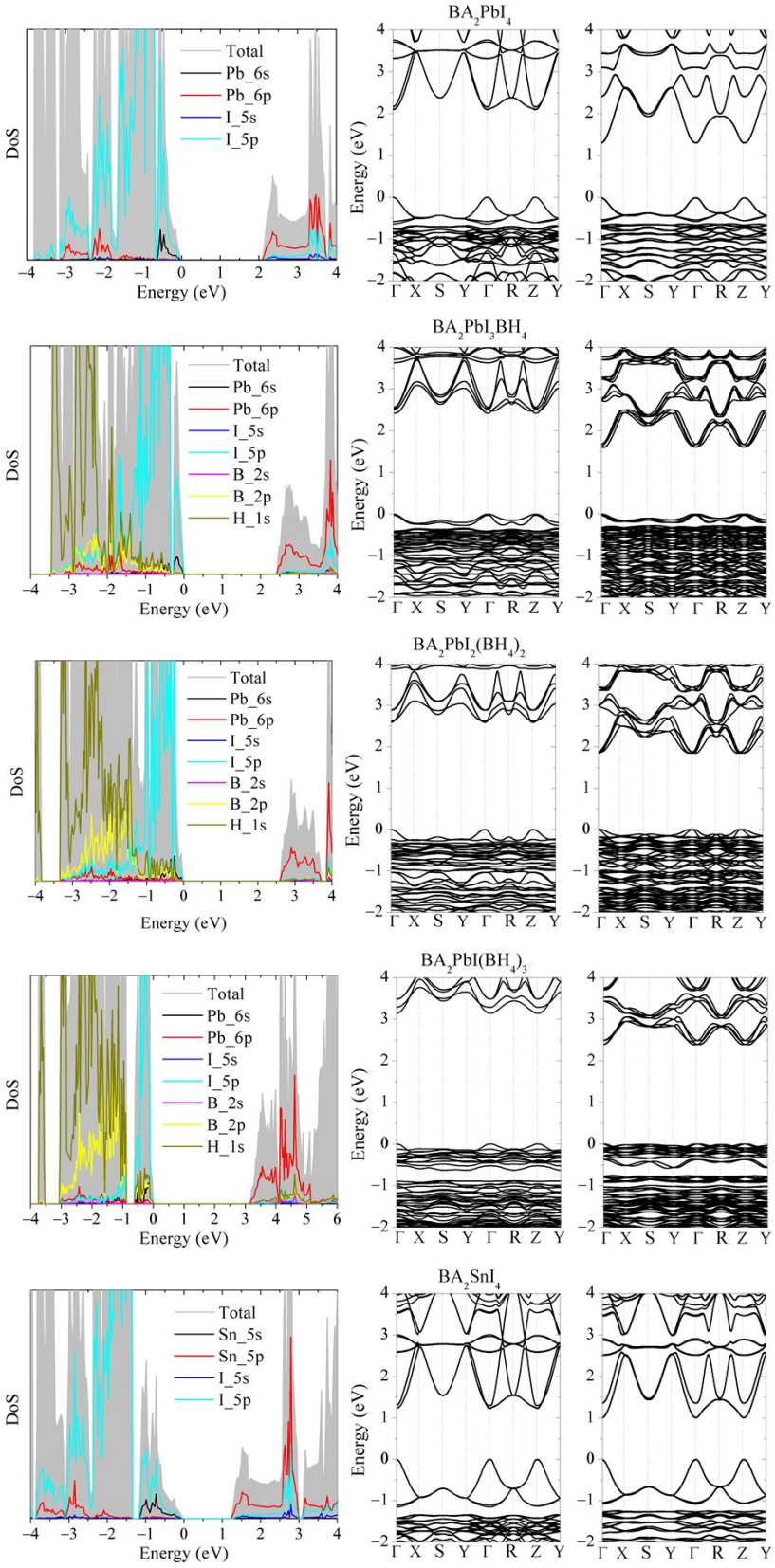
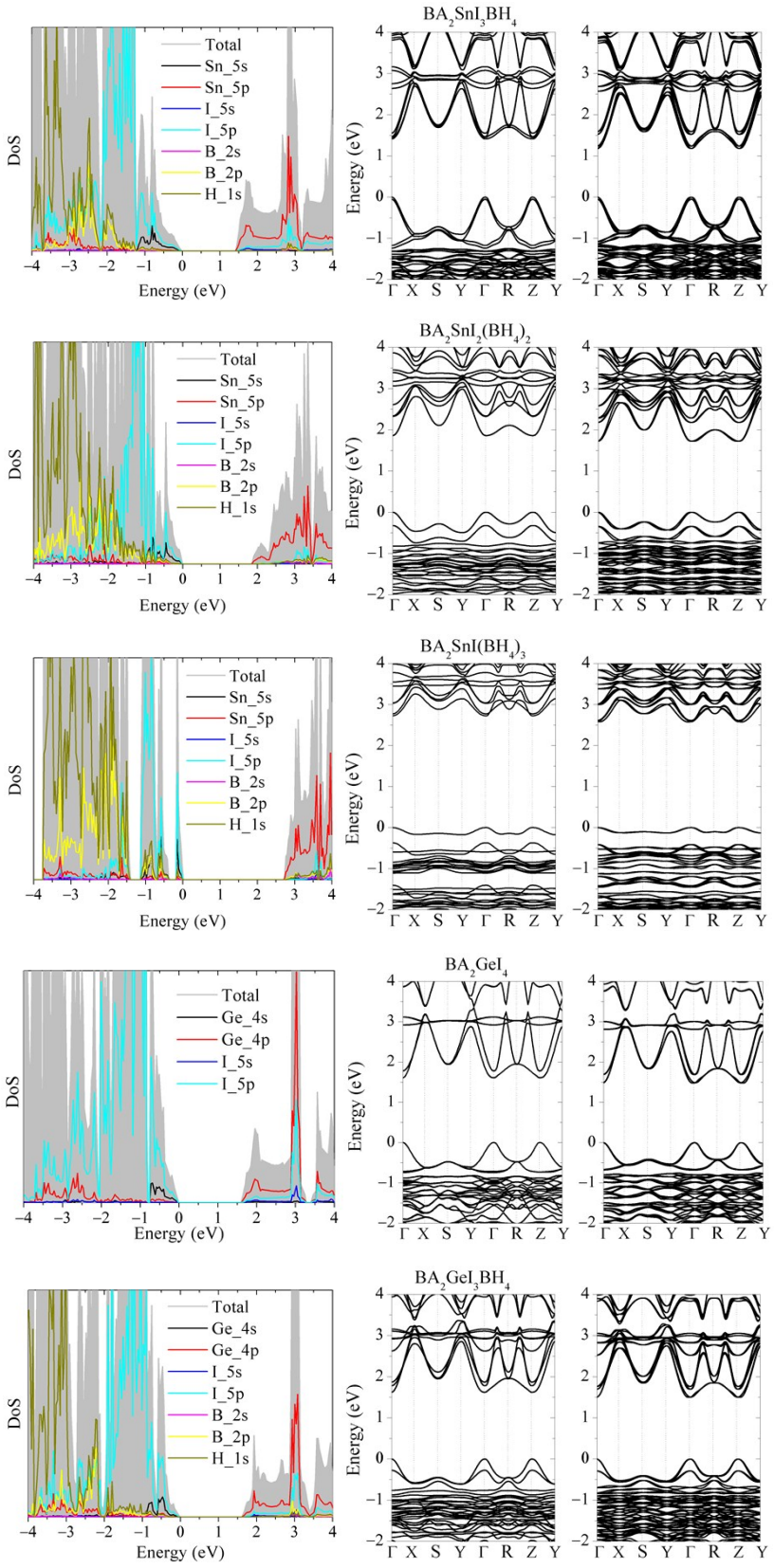


Figure S2. (a) VBM and (b) CBM associated charge density of BA_2PbI_4. (c) VBM and (d) CBM associated charge density of $BA_2Pb(BH_4)_4$


BA2PbI4
BA2PbI3BH4
BA2PbI2(BH4)2
BA2PbI(BH4)3
BA2SnI4
DoS
Energy (eV)
Total
Pb_6s
Pb_6p
I_5s
I_5p
B_2s
B_2p
H_1s
Sn_5s
Sn_5p
Γ X S Y Γ R Z Y


BA2SnI3BH4
BA2SnI2(BH4)2
BA2SnI(BH4)3
BA2GeI4
BA2GeI3BH4
DoS
Energy (eV)
Total
Sn_5s
Sn_5p
Ge_4s
Ge_4p
I_5s
I_5p
B_2s
B_2p
H_1s
Γ X S Y Γ R Z Y

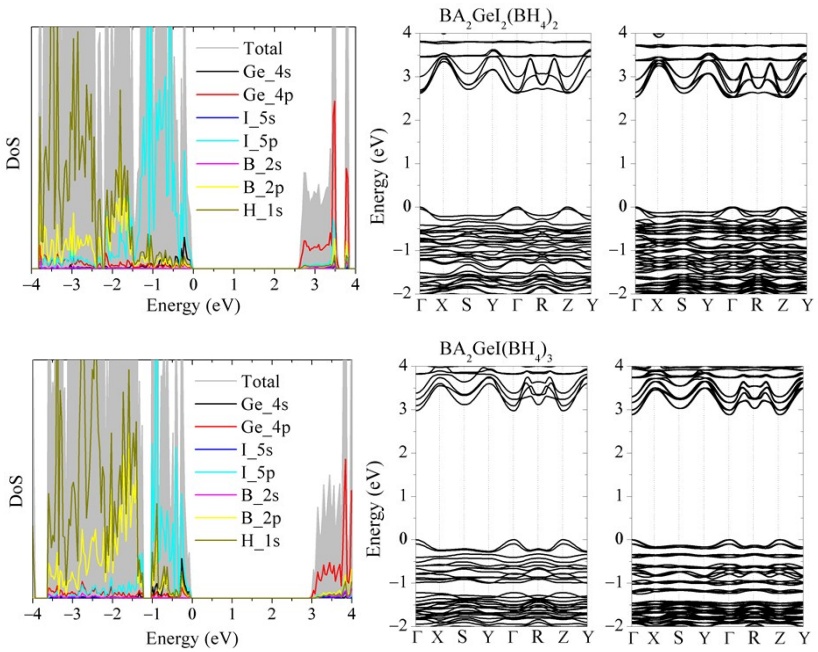


Figure S3. DOS without SOC and band structures without (left panel) and with (right panel) SOC of $BA_2MI_{4-x}(BH_4)_x$ (M = Pb, Sn, Ge; x = 0–3).

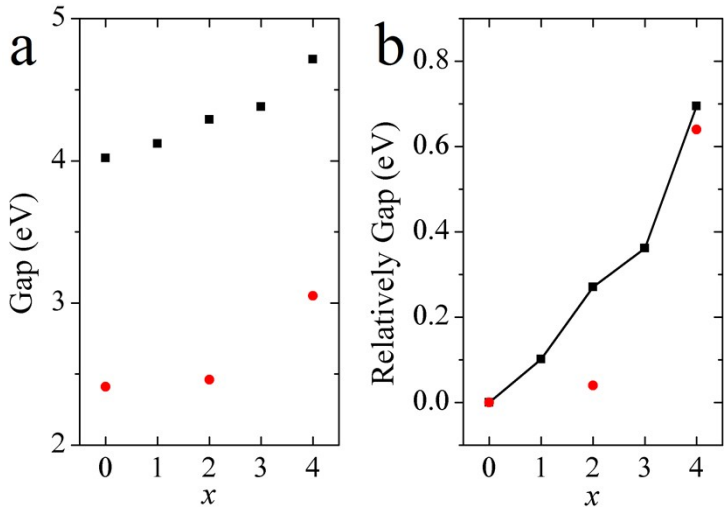


Figure S4. (a) Calculated HOMO-LUMO gap using DFT-B3LYP (in black square) compared to the experimental value (in red circle) [1] of $BA_2PbI_{4-x}Br_x$. (b) Relative gap change obtained by normalizing the B3LYP value to the experiment at $x = 0$.

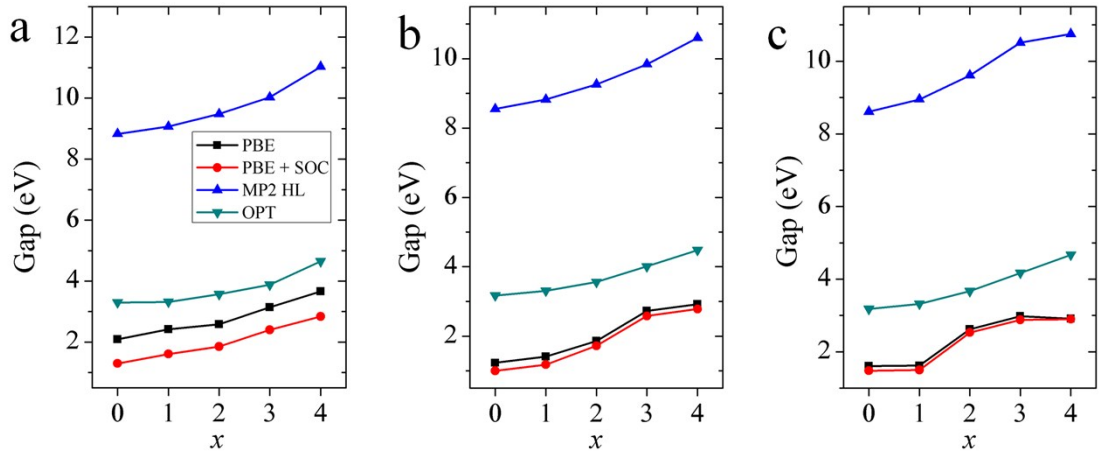


Figure S5. (a), (b) and (c) PBE and PBE + SOC gaps of bulk $BA_2MI_{4-x}(BH_4)_x$ (M = Pb, Sn, Ge; x = 0–4). HOMO-LUMO and optical gaps of corresponding cluster models.

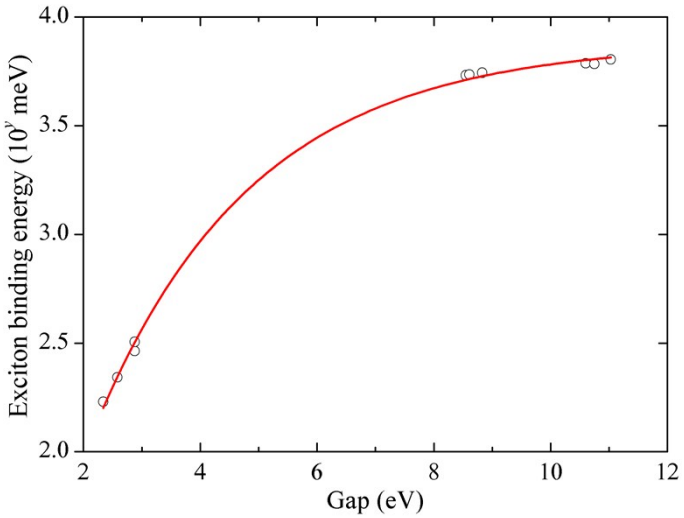


Figure S6. Least-square fitting to collected data (open circles) of some 2D hybrid perovskites and studied clusters (Table S2) using Eq. (1) in the paper. The y-axis is in the power of ten.

Table S1. Effective masses (relative to the electron mass m_0) of $BA_2SnI_{4-x}(BH_4)_x$ and $BA_2GeI_{4-x}(BH_4)_x$ for holes and electrons along Γ−X, Γ−Y, and Γ−Z.

$BA_2SnI_{4-x}(BH_4)_x$	**hole**			**electron**		
x	Γ−X	Γ−Y	Γ−Z	Γ−X	Γ−Y	Γ−Z
0	0.14	0.14	∞	0.24	0.12	∞
1	0.17	0.16	∞	0.25	0.18	∞
2	0.3	0.31	∞	0.2	0.21	∞
3	1.09	1.07	∞	0.52	0.65	∞
4	0.46	0.41	∞	0.48	1.12	∞

$BA_2GeI_{4-x}(BH_4)_x$	**hole**			**electron**		
x	Γ−X	Γ−Y	Γ−Z	Γ−X	Γ−Y	Γ−Z
0	0.21	0.28	∞	0.14	0.63	∞
1	0.2	0.26	∞	0.14	0.54	∞
2	0.53	0.77	∞	0.33	0.76	∞
3	0.83	0.76	∞	0.43	0.36	∞
4	0.41	0.5	∞	0.54	0.62	∞

Table S2 The estimated bandgaps (eV) from the cluster model compare to the experimental values in 3D hybrid perovskites

admixture	E_g (x=0, exp.)	E_g (x=3, calc.)	E_g (x=3, exp.)
$CsSnI_{3-x}Br_x$	1.3[a]	1.78	1.8[a]
$MAPbI_{3-x}Br_x$	1.57[b]	2.45	2.29[b]
$MASnI_{3-x}Br_x$	1.3[c]	1.96	2.15[c]
$MASnBr_{3-x}Cl_x$	2.15[c]	2.78	3.69[d]
$MAPbI_{3-x}Cl_x$	1.57[b]	3.08	3.1[e]
$MAPbBr_{3-x}Cl_x$	2.29[b]/2.35[e]	2.97/3.03	3.1[e]
$FAPbI_{3-x}Br_x$	1.48[f]	2.29	2.23[f]

[a]Experimental value in Ref. S2
[b]Experimental value in Ref. S3
[c]Experimental value in Ref. S4
[d]Experimental value in Ref. S5
[e]Experimental value in Ref. S6
[f]Experimental value in Ref. S7

Table S3. Experimental and calculated fundamental gaps and exciton binding energies of some 2D hybrid perovskites. These data are used in Figure S6. It should be noted that exciton binding energy of cluster is much larger than that of 2D exciton binding energy.

Perovskite	Gap (eV)	Exciton binding energy (meV)
BA_2PbI_4	8.83 [a]	5530 [b]
BA_2SnI_4	8.55 [a]	5380 [b]
BA_2GeI_4	8.61 [a]	5430 [b]
$BA_2Pb(BH_4)_4$	11.03 [a]	6380 [b]
$BA_2Sn(BH_4)_4$	10.60 [a]	6120 [b]
$BA_2Ge(BH_4)_4$	10.75 [a]	6080 [b]
BA_2PbI_4	2.88 [c]	290 [c]
$(C_9H_{19}NH_3)_2PbI_4$	2.88 [c]	320 [d]
$(C_{10}H_{21}NH_3)_2PbI_4$	2.88 [c]	320 [d]
$(C_6H_5C_2H_4NH_3)_2PbI_4$	2.58 [e]	220 [e]
$(C_6H_5C_2H_4NH_3)_2CH_3NH_3Pb_2I_7$	2.34 [e]	170 [e]

[a]MP2 calculated HOMO-LUMO gap of the studied cluster models.

[b]Exciton binding energy calculated by HOMO-LUMO gap minus optical gap.

[c]Experimental value in Ref. S8

[d]Experimental value in Ref. S9

[e]Experimental value in Ref. S10

References

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