Supporting Information

ABX_3-type lead-free perovskites using superatom ions with tunable photovoltaic performances

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Supplementary Tables and Figures

Table S1. Calculation for cubic $H_5O_2GeI_x(BH_4)_{3-x}$ perovskites. Herein, t, E_g, m_h^*, m_e^*, E_b, E_{M-X}, $\bar{E}_g$, V_{oc}, J_{sc}, FF and η are tolerance factor, hole effective masses (m_e), electron masses (m_e), exciton binding energy (meV), M-X bond average energy in MX_3 frame (eV/bond), average band gap (eV) for the cubic $H_5O_2SnI_x(BH_4)_{3-x}$ perovskites with the different orientations of superatoms, open circuit voltages (V), the maximum short circuit current density (mA/cm^2), fill factor and power conversion efficiency (%), respectively.

Perovskites	t	m_h^*	m_e^*	E_b	E_{M-X}	$\bar{E}_g$	V_{oc}	J_{sc}	FF	η
$H_5O_2GeI_3$	0.98	0.31	0.30	80.67	1.67	1.53	1.26	27.99	90.20	31.83
$H_5O_2GeI_2BH_4$	0.99	0.47	0.28	138.23	2.02	2.18	1.87	10.97	92.80	19.03
$H_5O_2GeI(BH_4)_2$	0.99	0.63	0.46	319.13	2.29	2.84	2.48	2.81	94.30	6.56
$H_5O_2Ge(BH_4)_3$	1.00	0.59	0.46	361.77	2.61	3.43	3.02	0.55	95.10	1.57

Table S2. Calculation for the band gaps (eV) of the cubic $H_5O_2MI_x(BH_4)_{3-x}$ perovskites with another orientation of superatoms.

Perovskites	$H_5O_2SnI_3$	$H_5O_2SnI_2(BH_4)$	$H_5O_2SnI(BH_4)_2$	$H_5O_2Sn(BH_4)_3$
Band gaps	1.04	1.67	2.23	3.36
Perovskites	$H_5O_2GeI_3$	$H_5O_2GeI_2(BH_4)$	$H_5O_2GeI(BH_4)_2$	$H_5O_2Ge(BH_4)_3$

Band gaps	1.55	2.18	2.88	3.58

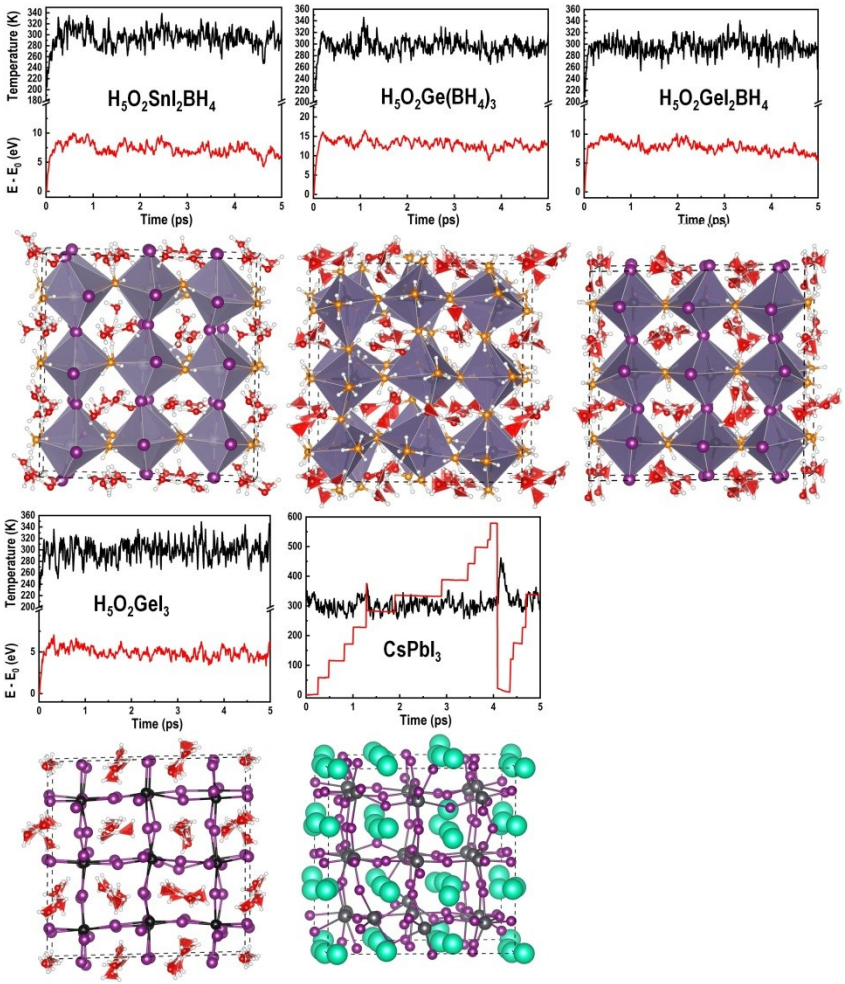

Fig. S1. Ab initio molecular dynamics simulation of the energy, temperature and structures for the perovskites with a 3×3×2 supercell (3×3×3 supercell for cubic $CsPbI_3$ perovskite) after 300 K and 105 Pa. The initial energies (E_0) of these perovskites are set to zero. Atomic colors: H (white), O (red), B(orange), Ge (black), Sn (grey), Pb (dark grey), Cs (cyan), and I (violet).

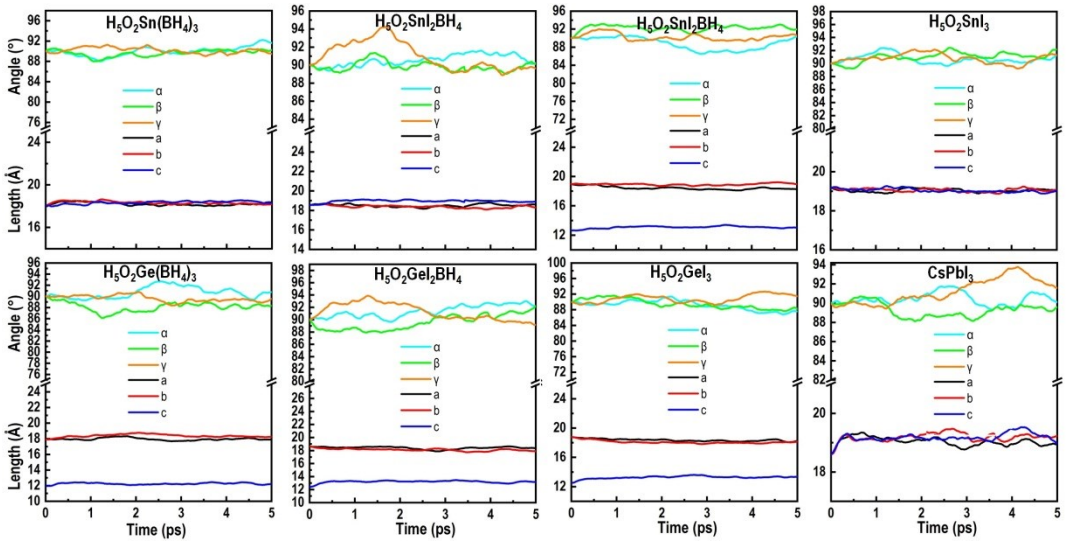

Fig. S2. Ab initio molecular dynamics simulation of the lattice parameters for the cubic perovskites

under 300 K and 10^5 Pa.

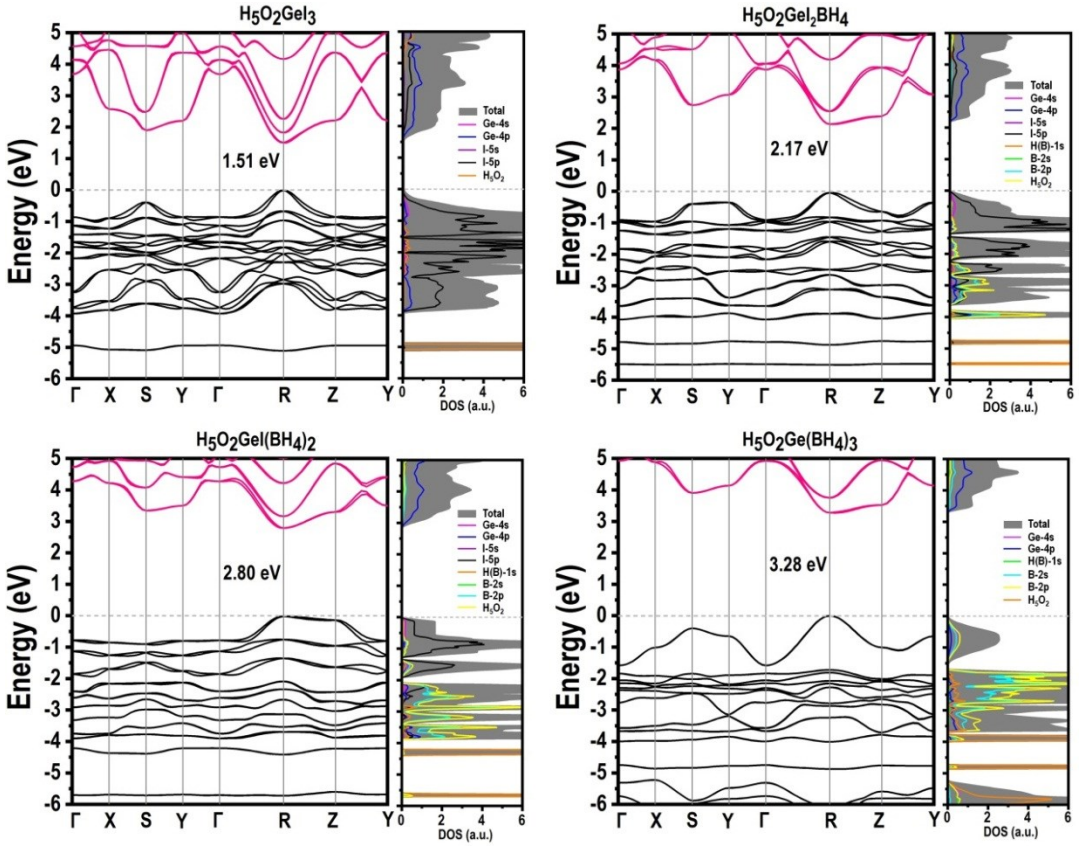

Fig. S3 The calculated band structures and density of states for the cubic $H_5O_2GeI_x(BH_4)_{3-x}$ perovskites by using the standard HSE06 functional with 43% exact Hartree-Fock exchange including SOC effect and vdW correction, respectively. Fermi level is set to zero.

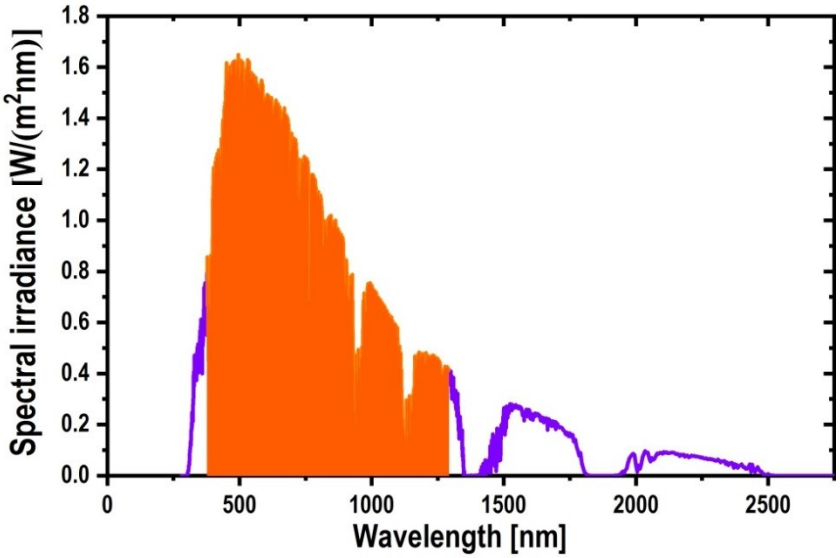

Fig. S4. Schematic representation for the spectral irradiance of AM 1.5G. The absorption region of the cubic $H_5O_2GeI_x(BH_4)_{3-x}$ perovskites is marked in yellow.

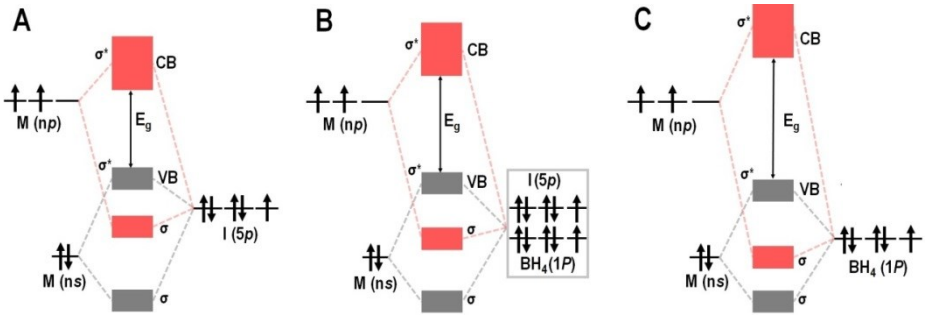

Fig. S5. Schematic representation for the bonding (σ) and antibonding (σ*) orbitals of the (A) $H_5O_2MI_3$, (B) $H_5O_2MI_y(BH_4)_{3-y}$ and (C) $H_5O_2M(BH_4)_3$ perovskites and the formation of their valence and conduction bands, respectively. (M = Ge and Sn, y = 1, 2).

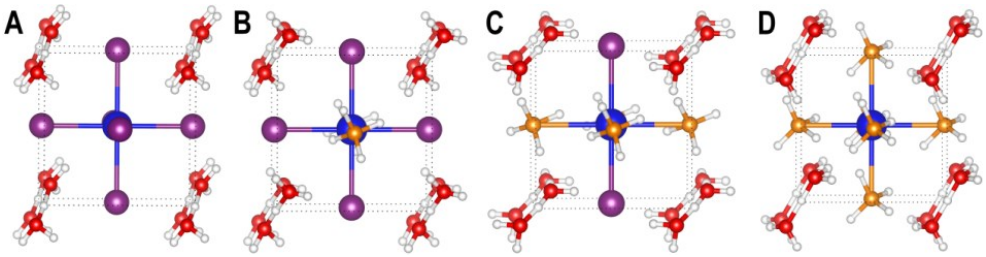

Fig. S6. (A-D) The models of the cubic $H_5O_2MI_3$, $H_5O_2MI_2BH_4$, $H_5O_2MI(BH_4)_2$, and $H_5O_2M(BH_4)_3$ perovskites with another orientation of superatoms (M = Ge, Sn), respectively.

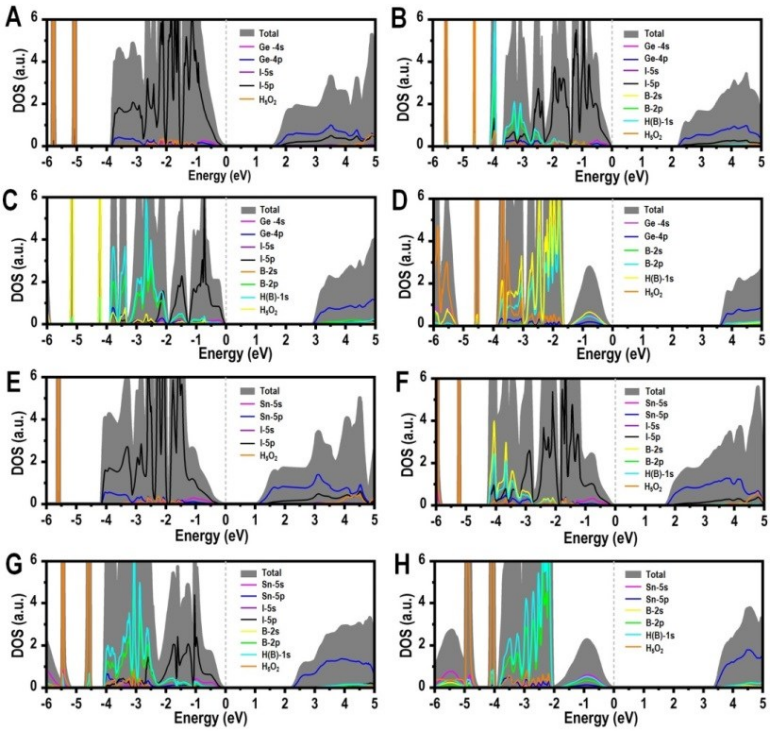

Fig. S7. The calculated density of states for (A $H_5O_2GeI_3$, (B) $H_5O_2GeI_2BH_4$, (C) $H_5O_2GeI(BH_4)_2$, (D) $H_5O_2Ge(BH_4)_3$, (E) $H_5O_2SnI_3$, (F) $H_5O_2SnI_2BH_4$, (G) $H_5O_2SnI(BH_4)_2$ and (H) $H_5O_2Sn(BH_4)_3$ perovskites with another orientation of superatoms by using the standard HSE06 functional with

43% exact Hartree-Fock exchange including SOC effect and vdW correction, respectively. The dash line represents Fermi level set to zero.

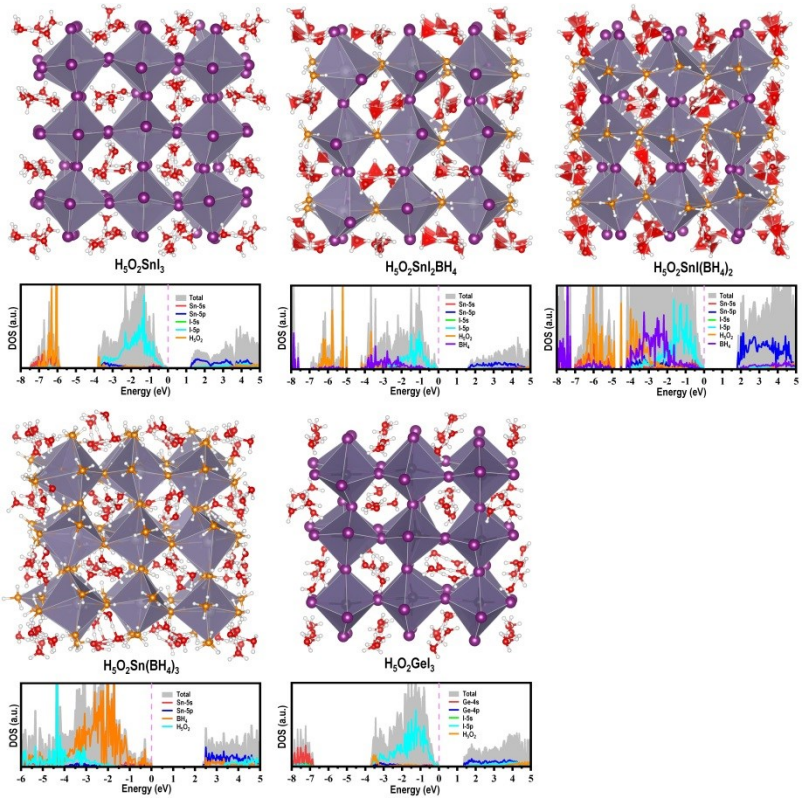

Fig. S8 After AIMD simulation of 5 ps, the calculated density of states for the perovskites with a 3×3×2 or 3×3×3 supercell by using PBE-GGA including vdW correction, respectively. The dash line represents Fermi level set to zero.

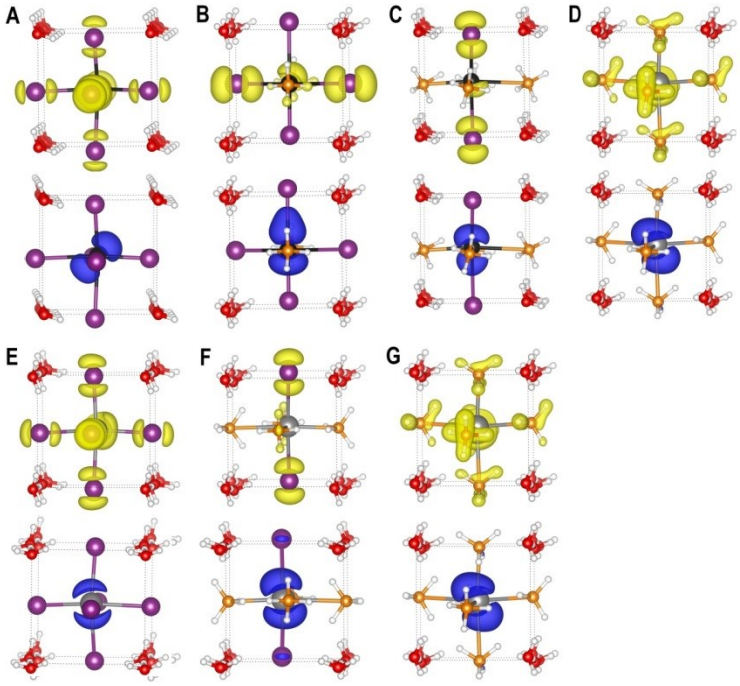

Fig. S9. Partial charge densities of VBM (yellow) and CBM (blue) states for the cubic (A)

$H_5O_2GeI_3$, (B) $H_5O_2GeI_2BH_4$, (C) $H_5O_2GeI(BH_4)_2$, (D) $H_5O_2GeI(BH_4)_3$, (E) $H_5O_2SnI_3$, (F) $H_5O_2GeI(BH_4)_2$ and (G) $H_5O_2Ge(BH_4)_3$ perovskites (isovalue = 0.002 e/Å^3), respectively. Atomic colors: H (white), B (orange), O (red), I (violet), Ge (black) and Sn (grey), respectively.