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

Supporting Information for:

Water effect on effective Goldschmidt tolerance factor and photoelectric conversion efficiency of organic-inorganic perovskite: insight from first-principles calculations

Zhen-Kun Tang[1,2], Ya-Nan Zhu[2], Zhi-Feng Xu[1], Li-Min Liu[2]*

[1] College of Physics and Electronics Engineering & College of Chemistry and Materials Science, Hengyang Normal University, Hengyang 421008, China
[2] Beijing Computational Science Research Center, Beijing 100084, China

Email: limin.liu@csrc.ac.cn

S1. The geometrical configuration of interstitial H_2O molecule infiltrated into the $MAPbI_3$ supercells with different interstitial H_2O ratios

Figure S1 (a) shows the geometrical configuration of pure 2×2×1 $MAPbI_3$ supercell. When a single interstitial H_2O molecule infiltrate into the 2×2×1 $MAPbI_3$ supercell, the two hydrogen atoms of interstitial H_2O molecule will bonding with iodine anion by weak hydrogen-bonds, as shown in the Figure S1 (b). However, there are kinds of geometric constructions for two interstitial H_2O molecules in the 2×2×1 $MAPbI_3$ supercell. Considered the crystal structure and symmetry, 13 different configurations of two interstitial H_2O molecules in the $MAPbI_3$ supercell were chosen as the possible structures in our calculations, as shown in Figure S1 (c-o). Besides, the corresponding total energies and lattice parameters are listed on the Table S1. We note that the $2H_2O$-1 structure has the lowest total energy of 0.004-0.328 eV among other considered structures. In the $2H_2O$-1 structure, two H_2O molecules are located on the two sides of two nearby Pb-I6 octahedron. Symmetrical water molecule position results in the smallest total additional dipole moment and crystal lattice distortion. Thus, $2H_2O$-1 structure is the most stable configure with the lowest total energy. Besides, we note that the $2H_2O$-2 structure also has small crystal lattice distortion and total energy. Base on the $2H_2O$-1 and $2H_2O$-2 configure in the $MAPbI_3$ structure, we built the related configures of the 3, 4, 8, 12, and 16 interstitial H_2O molecule in the $MAPbI_3$ structure, shown in the Figure S1 (p-t), respectively.

Table S1 *The formation energies and lattice parameters of two interstitial H_2O molecules in the $MAPbI_3$ supercell.*

Structure	E (eV)	a (Å)	b (Å)	c (Å)	α(°)	β(°)	γ(°)	V (Å^3)
$2H_2O$-1	**0**	**17.472**	**17.438**	**12.888**	**88.744**	**90.484**	**89.897**	**3926.234**
$2H_2O$-2	0.004	17.458	17.452	12.893	88.877	90.468	89.824	3927.460
$2H_2O$-3	0.236	17.448	17.450	12.911	89.273	90.251	89.942	3931.096
$2H_2O$-4	0.207	17.435	17.473	12.907	88.970	90.268	89.899	3931.387
$2H_2O$-5	0.309	17.501	17.437	12.890	89.252	89.888	89.848	3933.535
$2H_2O$-6	0.241	17.474	17.419	12.905	88.908	90.610	89.824	3927.636
$2H_2O$-7	0.164	17.482	17.419	12.890	88.714	90.668	89.813	3924.269
$2H_2O$-8	0.194	17.484	17.432	12.901	89.247	90.251	89.860	3931.886
$2H_2O$-9	0.154	17.484	17.426	12.896	88.887	90.501	89.826	3928.858
$2H_2O$-10	0.328	17.481	17.441	12.904	88.910	90.146	89.924	3934.129
$2H_2O$-11	0.293	17.422	17.494	12.908	89.051	90.133	89.932	3933.693
$2H_2O$-12	0.304	17.404	17.514	12.898	88.971	90.258	89.813	3931.202
$2H_2O$-13	0.256	17.474	17.453	12.892	89.133	90.521	89.744	3931.453

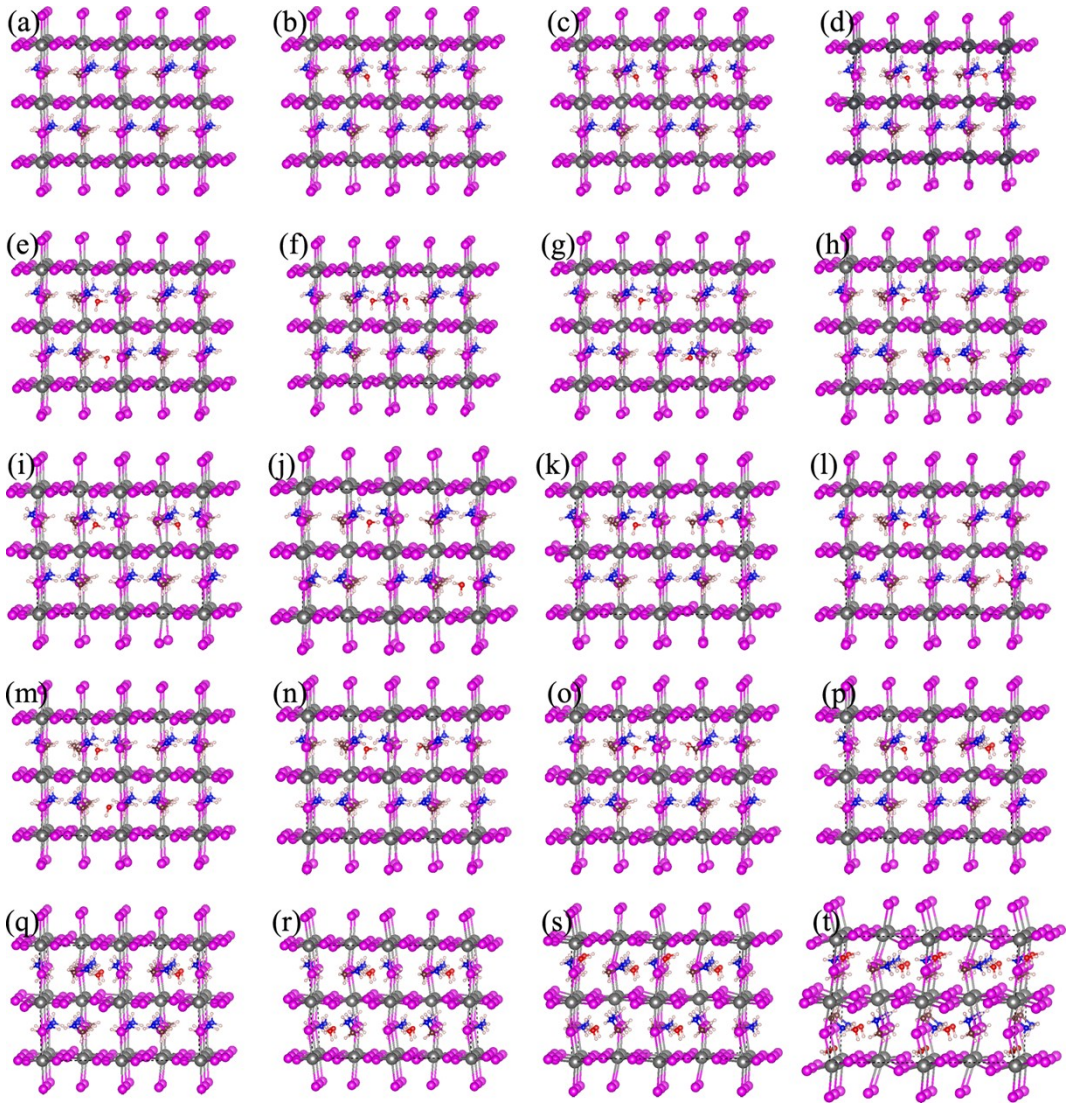

Figure S1 *Snapshots of Li-ion transfer in the LiBOB-DEC (a-c), LiBOB-MPN (d-f) and LiBOB-GLN (g-i) system. The yellow, red, pink, light green, blue, and white balls represent Li, O, B, C, N, and H atoms, respectively.*

S2. The ground state electronic structure of interstitial H_2O molecule infiltrated $MAPbI_3$ supercells with different ratios of $MAPbI_3$ and H_2O

It is well known that primitive $MAPbI_3$ structure is a direct band gap semiconductor with a value of 1.50 eV, as shown in the Figure S2 (a). Thus, it is necessary to know whether the $MAPbI_3$ structures with interstitial H_2O molecules own unique electronic structures. In order to study the detail electronic structures of the interstitial H_2O molecule infiltrated $MAPbI_3$ structures, the ground state band structures for the $MA(H_2O)_xPbI_3$ with seven different interstitial H_2O ratios are investigated, and the calculated results are shown in Figure S2 (b-h). The band structures show that the $MA(H_2O)_xPbI_3$ structures are semiconductors with direct band gaps at the Gamma point. Besides, the band structures of $MA(H_2O)_xPbI_3$ structures are similar with that of the pure $MAPbI_3$ structure, which are also semiconductors with direct band gaps. However, the band gaps of $MA(H_2O)_xPbI_3$ structures will increase with the increasing

interstitial H_2O ratio x. That is to say, all $MA(H_2O)_xPbI_3$ structures exhibit different kinds of optical absorption properties.

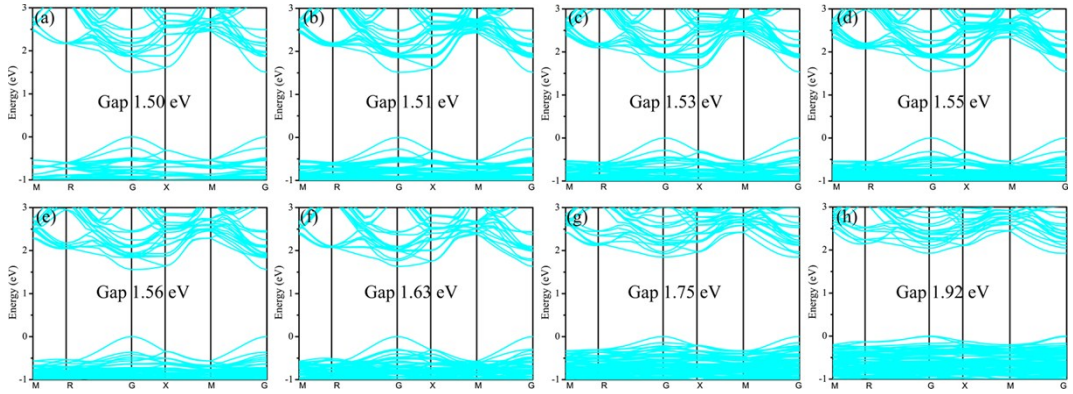

Figure S2 *The calculated band structures of the H_2O molecular insert $MAPbI_3$ with different H_2O:$MAPbI_3$ ratios. The (a-h) represent the band structure of the H_2O molecular insert $MAPbI_3$ with H_2O:$MAPbI_3$ ratio of 0, 1/16, 1/8, 3/16, 1/4, 1/2, 3/4, and 1, respectively.*