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

Supplementary Information (SI) for:

Ab initio study of the dynamics of electron trapping and detrapping processes in the $CH_3NH_3PbI_3$ perovskite

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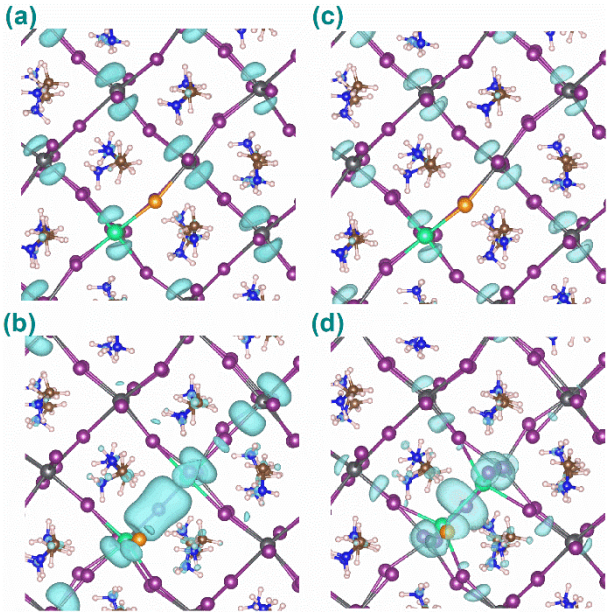

Figure SI1 (a) Charge density difference between the structure in Figure 2c (total charge = 0) and the same structure with one electron removed (total charge = +1). (b) Charge density difference between the structure in Figure 2d (total charge = 0) and the same structure with one electron removed (total charge = +1). (c) Charge density difference between the structure in Figure 2e (total charge = -1) and the same structure with one electron removed (total charge = 0). (d) Charge density difference between the structure in Figure 2f (total charge = -1) and the same structure with one electron removed (total charge = 0). The Pb ions originally bonded to the removed iodine are marked as green spheres. The color codes for the other atoms are the same as those in Figure 1. The charge densities are shown as the cyan contour surfaces.

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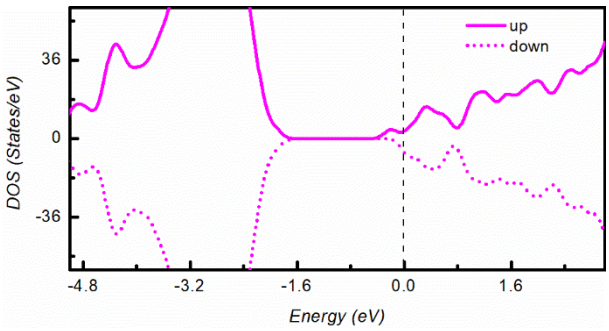

Figure SI2 The total density of states for the structure in Figure 2d with the Fermi level set at 0 eV.

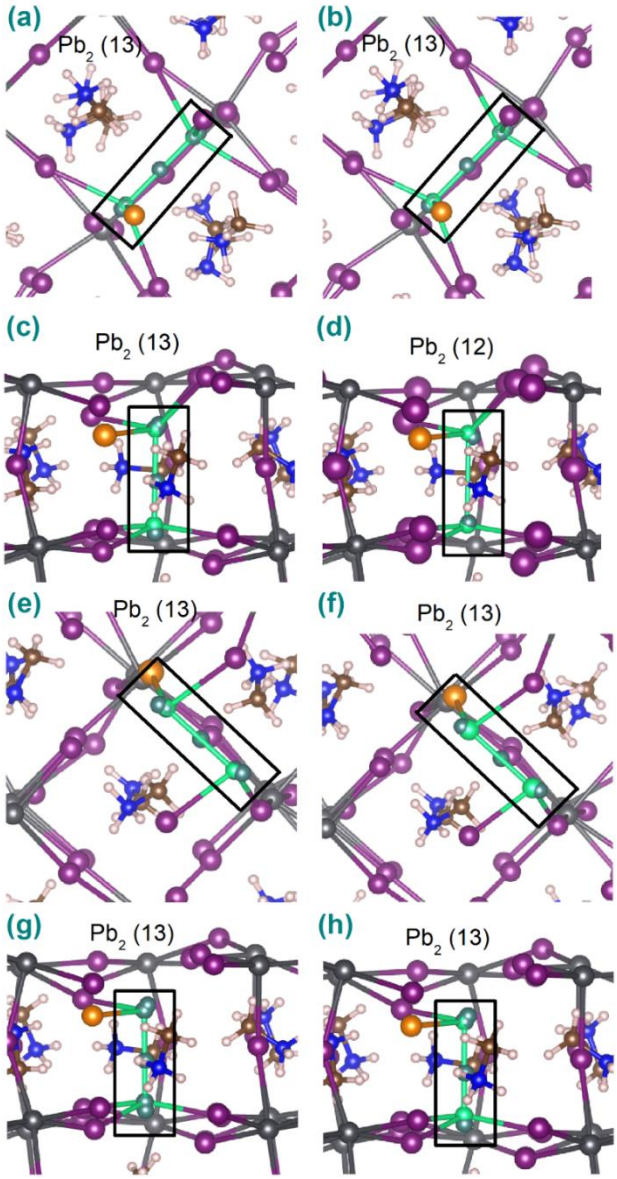

Figure SI3 (a) Spin-up and (b) spin-down Wannier centers (WCs) (shown as dark green spheres) assigned to the Pb_2 species (shown as green spheres) in the structure in Figure 2f. The charge state of the Pb_2 species is +2. (c) Spin-up and (d) spin-down WCs (shown as dark green spheres) assigned to the Pb_2 species (shown as green spheres) in the structure in Figure 3d. The charge state of Pb_2 species is +3. (e) Spin-up and (f) spin-down WCs (shown as dark green spheres) assigned to the Pb_2 species (shown as green spheres) in the structure in Figure 3e. The charge state of Pb_2 species is +2. (g) Spin-up and (h) spin-down WCs (shown as dark green spheres) assigned to the Pb_2 species (shown as green spheres) in the structure in Figure 3f. The charge state of Pb_2 species is +2. The parentheses show the number of the WCs for the Pb_2 species. The excess electrons were strongly trapped by the Pb_2 species. The color codes for the atoms

are the same as those in Figure 1.

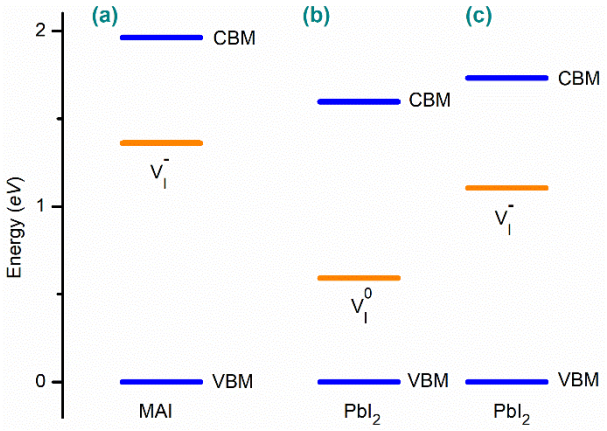

Figure SI4 The defect levels (i.e. the Kohn−Sham orbital levels for the excess electrons), the valence band maximum (VBM) and the conduction band minimum (CBM) of (a) the structure in Figure 2f, (b) the structure in Figure 3d, and (c) the structure in Figure 3f calculated by the HSE functional with SOC. The VBM of each system is set at 0 eV. The Kohn−Sham orbital levels are the orange horizontal lines. Since there is no spin in the systems in Figure 2f and 3f, the orange horizontal line in Figure SI2a and SI2c represents the Kohn−Sham states for two electrons. As there is an unpaired electron in the structure in Figure 2d, the orange horizontal line in Figure SI2b represents the Kohn−Sham state for one electron.

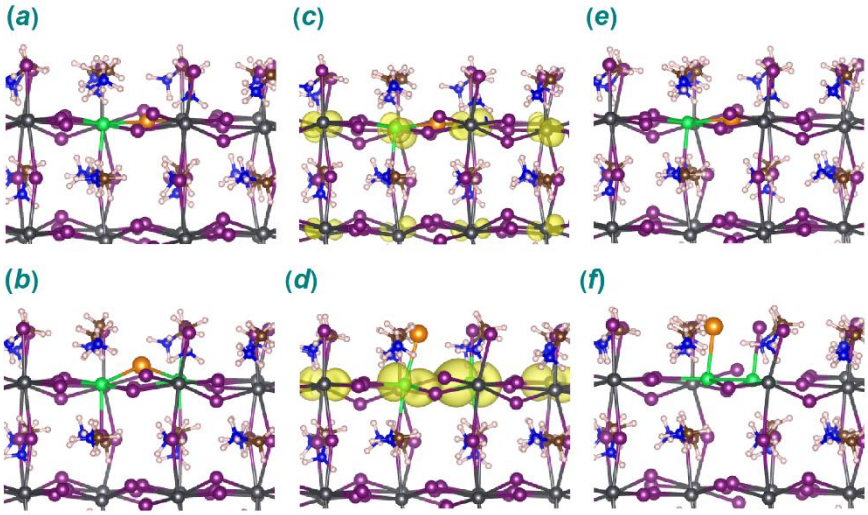

Figure SI5 (a) The side view of the structure in Figure 2a; (b) the side view of the structure in Figure 2b; (c) The side view of the structure in Figure 2c; (d) the side view of the structure in Figure 2d; (e) the side view of the structure in Figure 2e; (f) the side view of the structure in Figure 2f. The Pb ions originally bonded to the removed iodine are marked as green spheres. The color codes for the other atoms are the same as those in Figure 1. The spin densities are shown as the yellow contour surfaces.

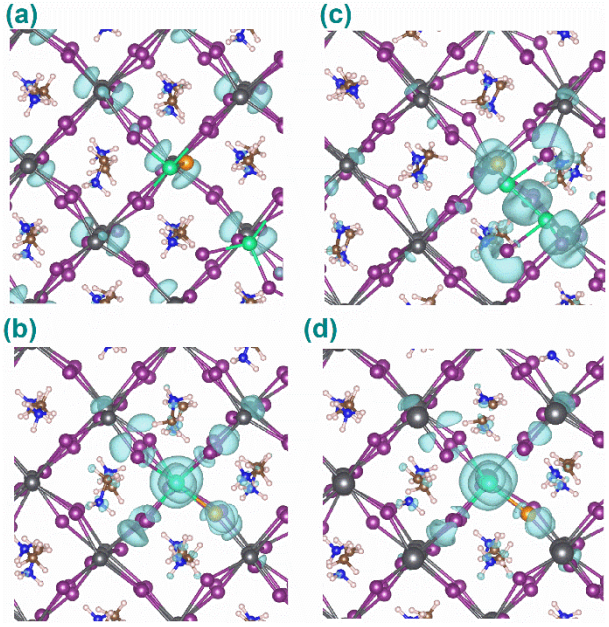

Figure SI6 (a) Charge density difference between the structure in Figure 3c (total charge = 0) and the same structure with one electron removed (total charge = +1). (b) Charge density

difference between the structure in Figure 3d (total charge = 0) and the same structure with one electron removed (total charge = +1). (c) Charge density difference between the structure in Figure 3e (total charge = -1) and the same structure with one electron removed (total charge = 0). (d) Charge density difference between the structure in Figure 3f (total charge = -1) and the same structure with one electron removed (total charge = 0). The Pb ions originally bonded to the removed iodine are marked as green spheres. The color codes for the other atoms are the same as those in Figure 1. The charge densities are shown as the cyan contour surfaces.

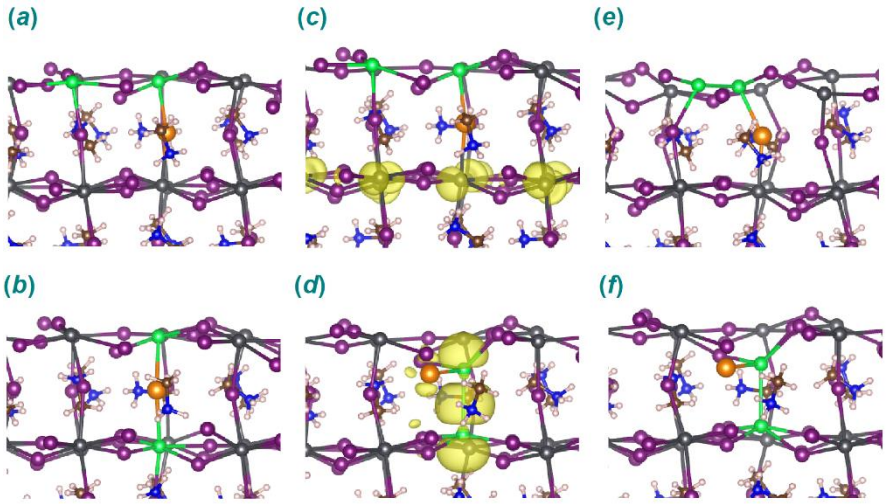

Figure SI7 (a) The side view of the structure in Figure 3a; (b) the side view of the structure in Figure 3b; (c) The side view of the structure in Figure 3c; (d) the side view of the structure in Figure 3d; (e) the side view of the structure in Figure 3e; (f) the side view of the structure in Figure 3f. The Pb ions originally bonded to the removed iodine are marked as green spheres. The color codes for the other atoms are the same as those in Figure 1. The spin densities are shown as the yellow contour surfaces.

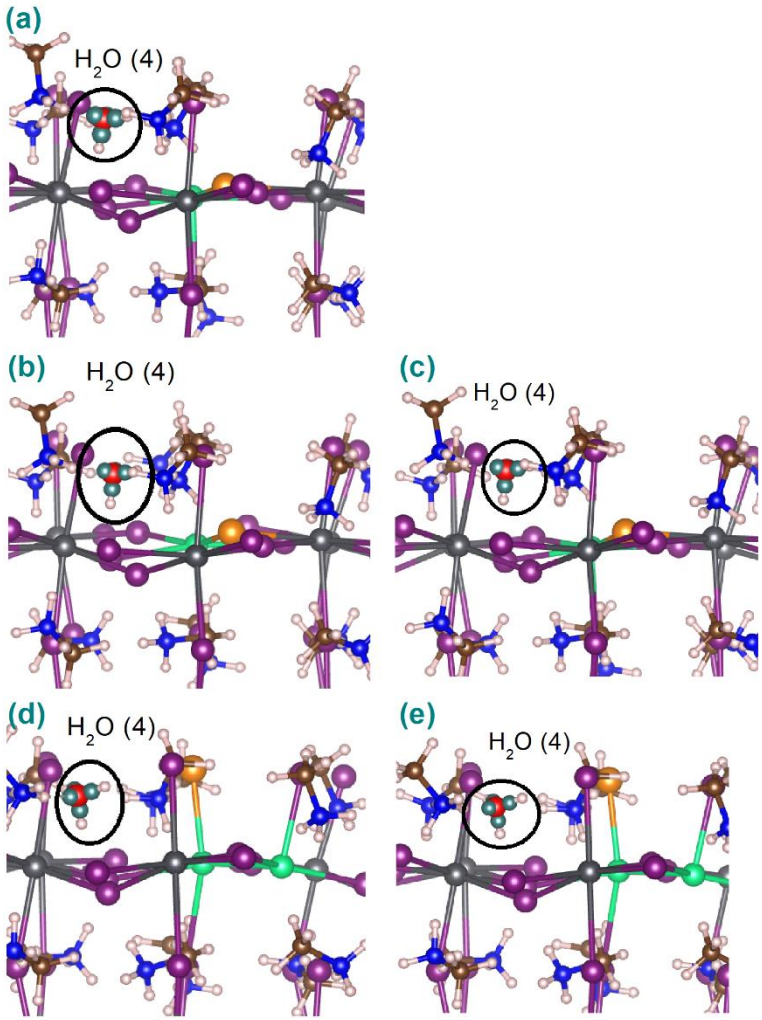

Figure SI8 (a) Spin-unpolarized WCs (shown as dark green spheres) assigned to the H_2O species adsorbed on the structure in Figure 2a. (b) Spin-up and (c) spin-down WCs (shown as dark green spheres) assigned to the H_2O species absorbed on the structure in Figure 2c. (d) Spin-up and (e) spin-down WCs (shown as dark green spheres) assigned to the H_2O species absorbed on the structure in Figure 2f. The parentheses show the number of WCs for the H_2O species. The charge states of the H_2O molecule in all three cases are zero. There is no electron transfer between the H_2O and the MAI-terminated $MAPbI_3$ surfaces. The Pb ions originally bonded to the removed iodine are marked as green spheres. The color codes for the other atoms are the same as those in Figure 1.

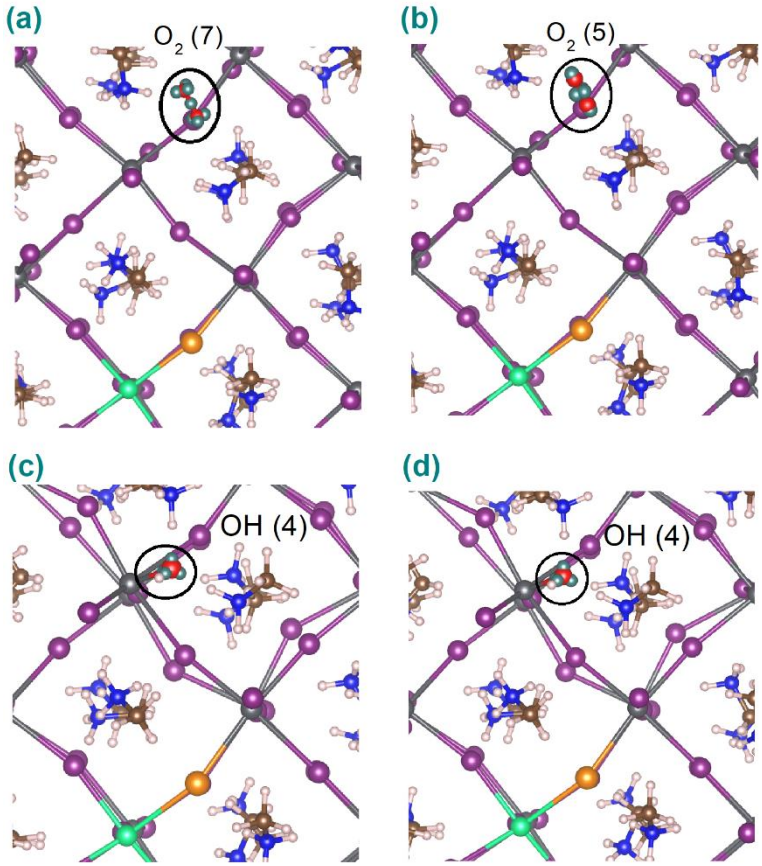

Figure SI9 (a) Spin-up and (b) spin-down WCs (shown as dark green spheres) assigned to the O_2 species in the structure in Figure 4a. (c) Spin-up and (d) spin-down WCs (shown as dark green spheres) assigned to the OH species in the structure in Figure 4b. The parentheses show the number of WCs for different species. There are two unpaired electrons in the O_2 species. The charge state of the O_2 species is zero. However, the charge state of the OH species is -1. Although there is no excess electron in the perovskite surface, an electron in the $MAPbI_3$ surface was abstracted by the OH species. The Pb ions originally bonded to the removed iodine are marked as green spheres. The color codes for the other atoms are the same as those in Figure 1.

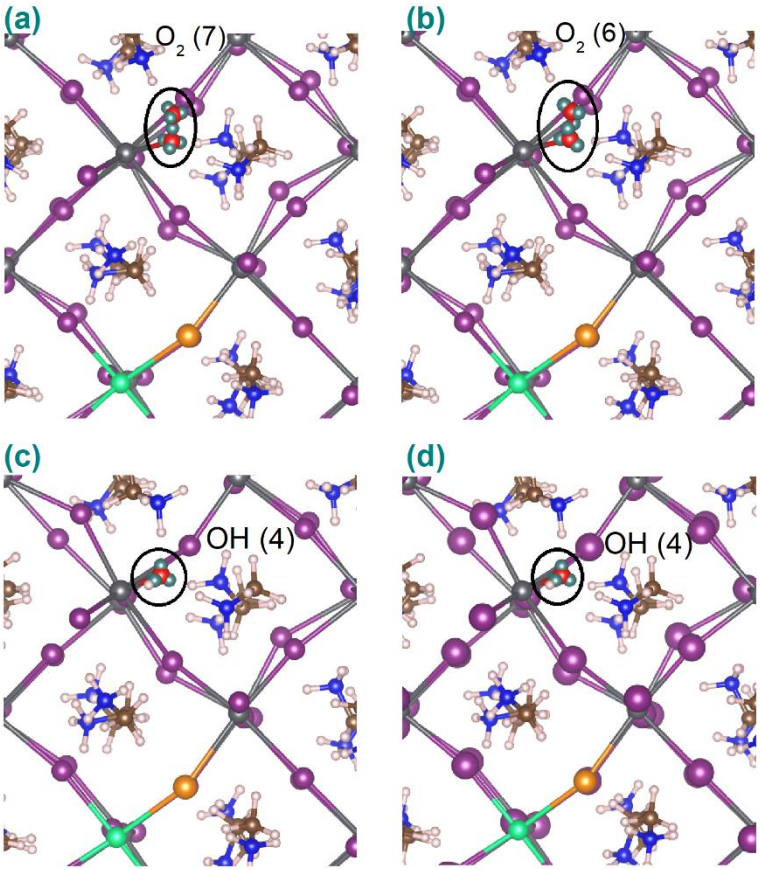

Figure SI10 (a) Spin-up and (b) spin-down WCs (shown as dark green spheres) assigned to the O_2 species in the structure in Figure 4c. (c) Spin-up and (d) spin-down WCs (shown as dark green spheres) assigned to the OH species in the structure in Figure 4d. The parentheses show the number of WCs for different species. There is an unpaired electron in the O_2 species, and the charge state of the O_2 species is -1. The charge state of the OH species is -1. An excess electron in the $MAPbI_3$ surface was abstracted by the O_2 and OH species, respectively. The Pb ions originally bonded to the removed iodine are marked as green spheres. The color codes for the other atoms are the same as those in Figure 1.

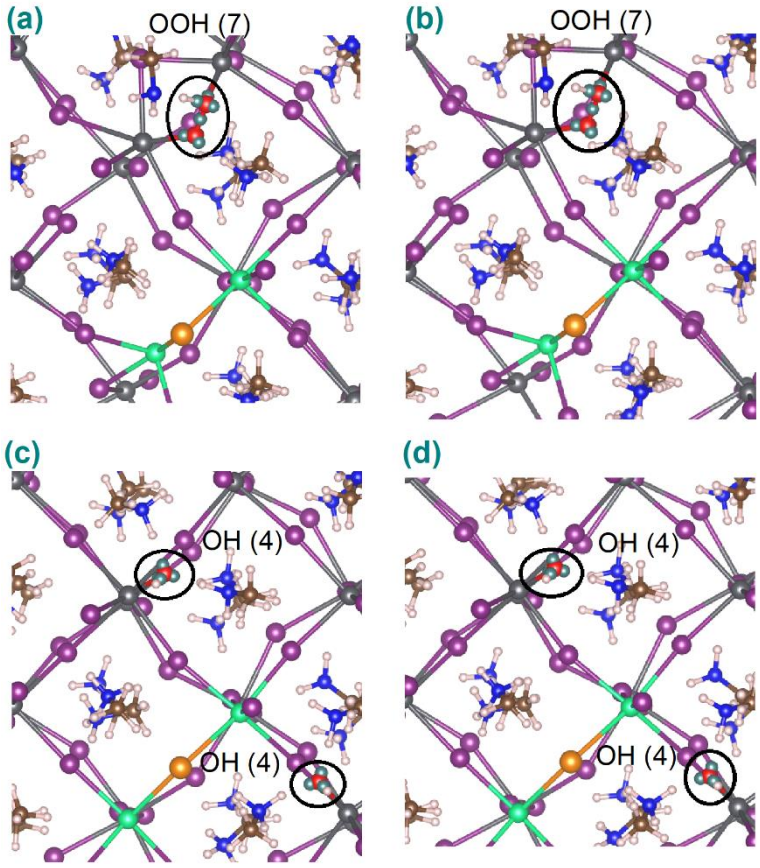

Figure SI11 (a) Spin-up and (b) spin-down WCs (shown as dark green spheres) assigned to the O_2 species in the structure in Figure 4e. (c) Spin-up and (d) spin-down WCs (shown as dark green spheres) assigned to the OH species in the structure in Figure 4i. The parentheses show the number of WCs for different species. There is no unpaired electron in the resulting OOH, and the charge state of the OOH is -1. Two excess electrons in the $MAPbI_3$ surface were abstracted by the OOH. The charge state of the OH species is -1. Two excess electrons in the $MAPbI_3$ surface were abstracted by the two OH species. The color codes for the atoms are the same as those in Figure 1. The Pb ions originally bonded to the removed iodine are marked as green spheres.

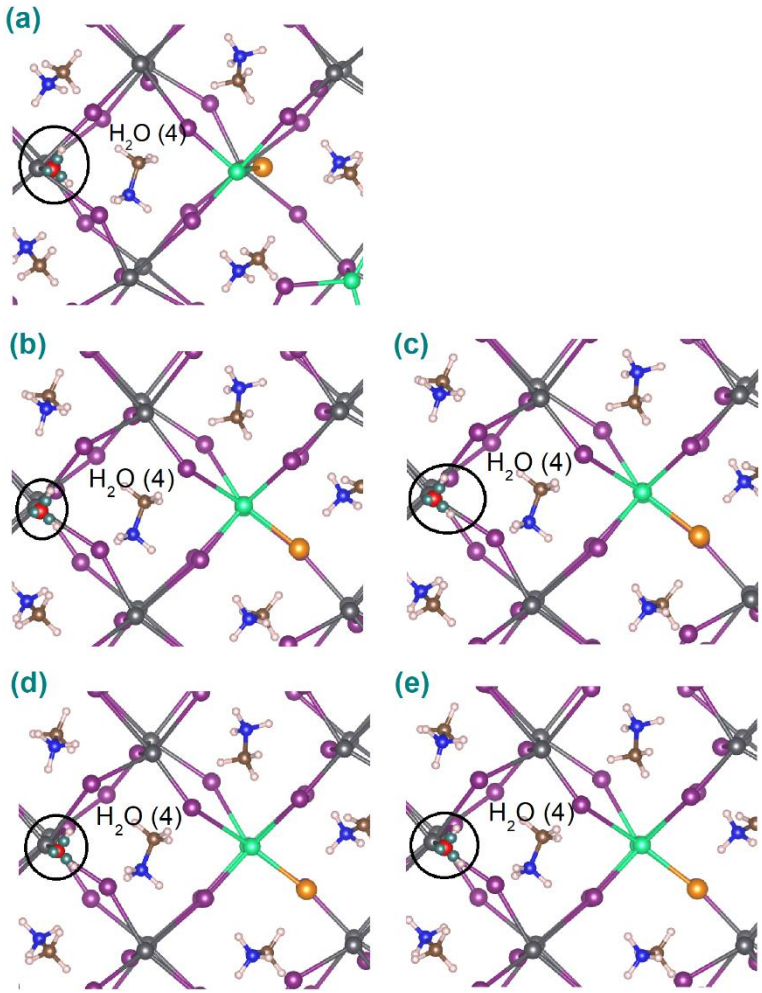

Figure SI12 (a) Spin-unpolarized WCs (shown as dark green spheres) assigned to the H_2O species absorbed in the structure in Figure 3a. (b) Spin-up and (c) spin-down WCs (shown as dark green spheres) assigned to the H_2O species adsorbed in the structure in Figure 3d. (d) Spin-up and (e) spin-down WCs (shown as dark green spheres) assigned to the H_2O species adsorbed in the structure in Figure 3f. The parentheses show the number of WCs for the H_2O species. The charge states of the three H_2O molecules are zero, respectively. There is no electron transfer between the H_2O and PbI_2-terminated $MAPbI_3$ surfaces. The Pb ions originally bonded to the removed iodine are marked as green spheres. The color codes for the other atoms are the same as those in Figure 1.

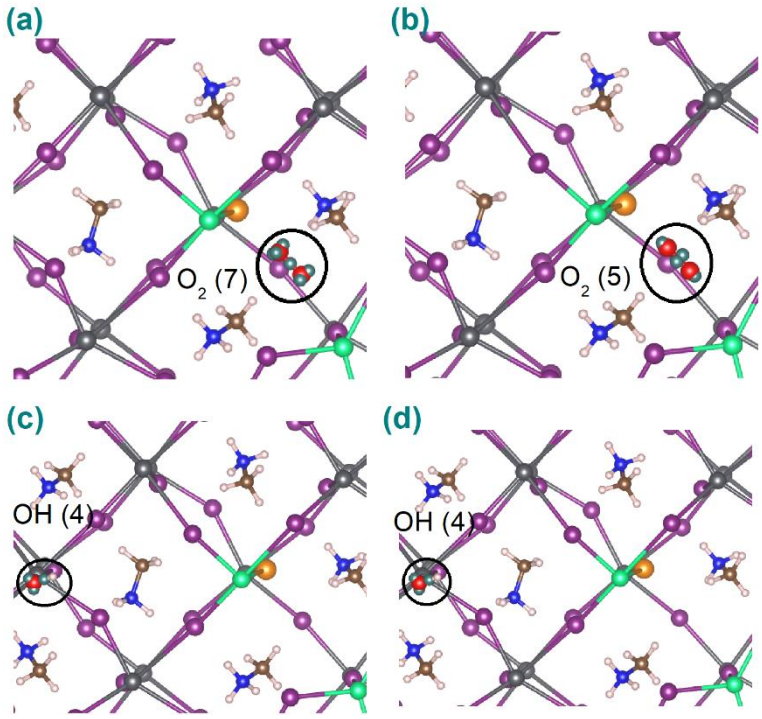

Figure SI13 (a) Spin-up and (b) spin-down WCs (shown as dark green spheres) assigned to the O_2 species in the structure in Figure 5a. (c) Spin-up and (d) spin-down WCs (shown as dark green spheres) assigned to the OH species in the structure in Figure 5b. The parentheses show the number of WCs for different species. There are two unpaired electrons in the O_2 species. The charge state of the O_2 species is zero. However, the charge state of the OH species is -1. Although there is no excess electron in the perovskite surface, an electron in the $MAPbI_3$ surface was abstracted by the OH species. The Pb ions originally bonded to the removed iodine are marked as green spheres. The color codes for the other atoms are the same as those in Figure 1.

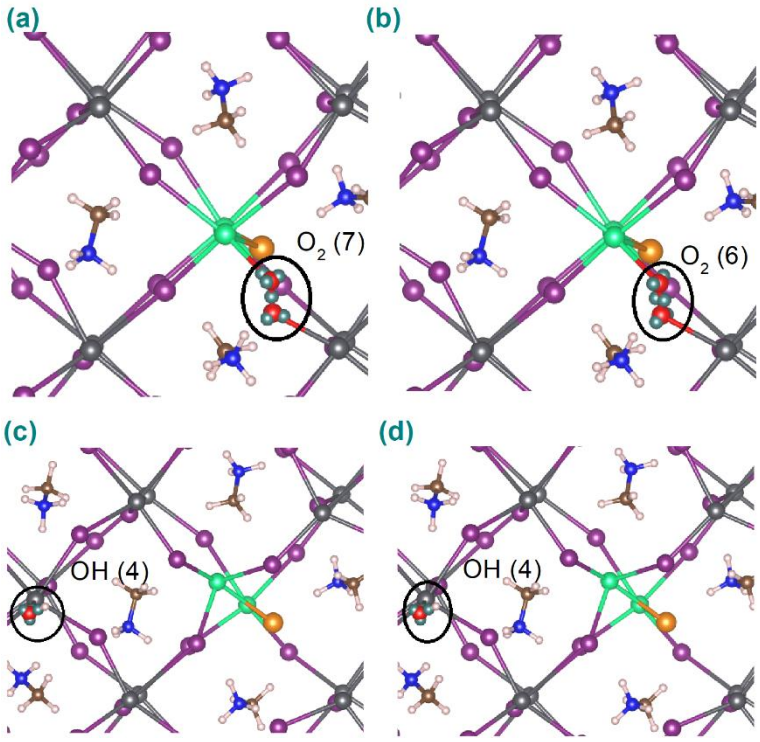

Figure SI14 (a) Spin-up and (b) spin-down WCs (shown as dark green spheres) assigned to the O_2 species in the structure in Figure 5c. (c) Spin-up and (d) spin-down WCs (shown as dark green spheres) assigned to the OH species in the structure in Figure 5d. The parentheses show the number of WCs for different species. There is an unpaired electron in the O_2 species, and the charge states of the O_2 species is -1. The charge states of the OH species is -1. An excess electron in the $MAPbI_3$ surface was abstracted by the O_2 and OH species, respectively. The color codes for the atoms are the same as those in Figure 1. The Pb ions originally bonded to the removed iodine are marked as green spheres.

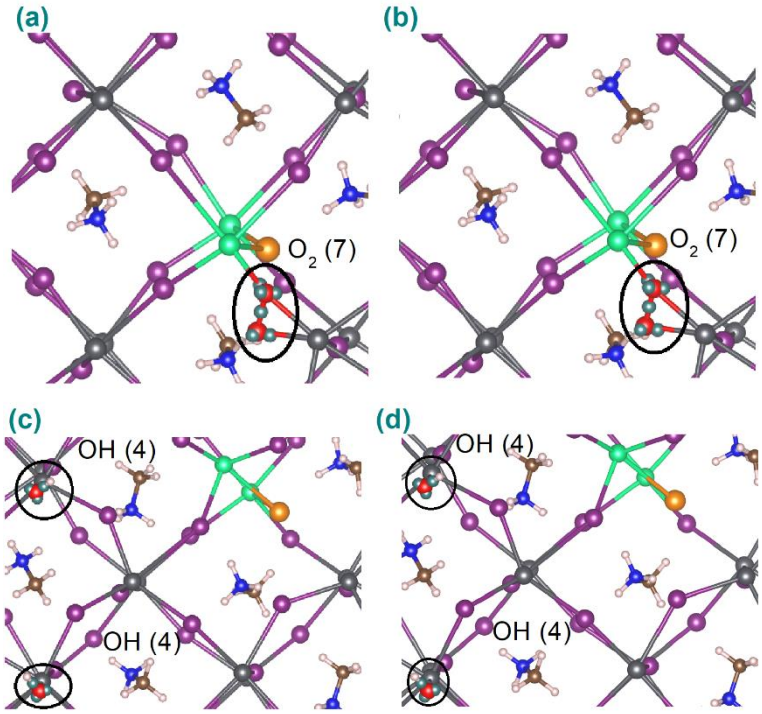

Figure SI15 (a) Spin-up and (b) spin-down WCs (shown as dark green spheres) assigned to the O_2 species in the structure in Figure 5f. (c) Spin-up and (d) spin-down WCs (shown as dark green spheres) assigned to the OH species in the structure in Figure 5h. The parentheses show the number of WCs for different species. There is no unpaired electron in the O_2 species, and the charge states of the O_2 species is -2. Two excess electrons in the $MAPbI_3$ surface were abstracted by the O_2 species. The charge states of the OH species is -1. Two excess electrons in the $MAPbI_3$ surface were abstracted by the two OH species. The color codes for the atoms are the same as those in Figure 1. The Pb ions originally bonded to the removed iodine are marked as green spheres.

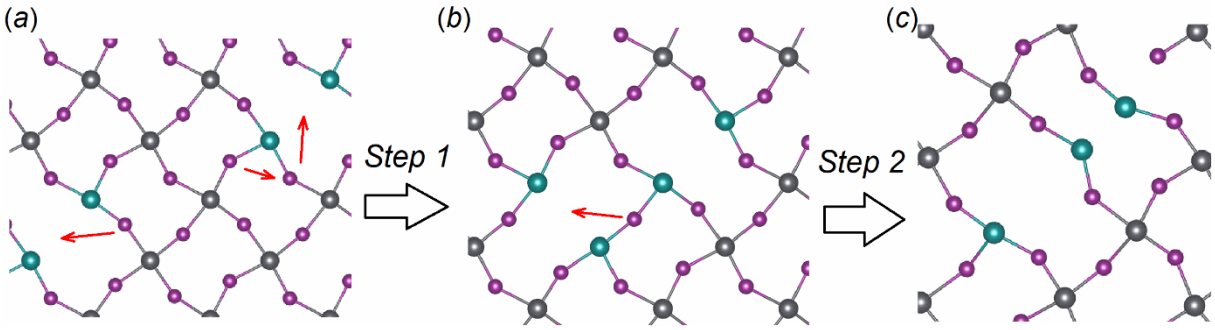

Figure SI16 Schematic diagram of long-range iodine migration in bulk $MAPbI_3$. (a) nonadjacent iodine vacancies separated by a long distance, (b) next-nearest nonadjacent iodine vacancies, and (c) adjacent iodine vacancies. We proposed that there are two steps for the long-range iodine migration to proceed: from Figure a to b (Step 1), and from Figure b to c (Step 2). The red arrows in (a) and (b) denote the possible directions of the iodine diffusion. The Pb ions bonded to the removed iodine are marked as dark cyan spheres. The color codes for the other atoms are the same as those in Figure 1.

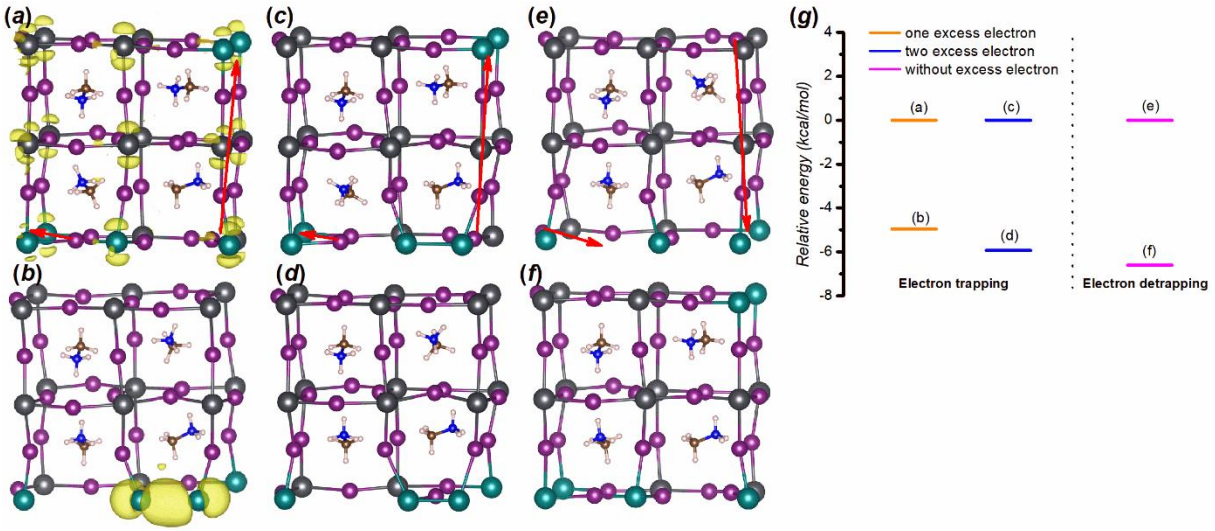

Figure SI17 (a) & (b) three nonadjacent iodine vacancies and three adjacent iodine vacancies in bulk $MAPbI_3$ with one excess electron, respectively. (c) & (d) three nonadjacent iodine vacancies and three adjacent iodine vacancies in bulk $MAPbI_3$ with two excess electrons, respectively. (e) & (f) three adjacent iodine vacancies and three nonadjacent iodine vacancies

in bulk $MAPbI_3$ without excess electron, respectively. (g) The relative energy for the above three cases. Herein, we used a larger 2 × 2 × 2 tetragonal $MAPbI_3$ supercells with the Gamma point sampling of the Brillouin zone. The red arrows in (a), (c) and (e) denote the possible directions of the iodine. By electron trapping, the structures in (b) and (d) are more stable by -5.0 and -6.0 kcal/mol than that of in (a) and (c), respectively. However, by electron detrapping, the structure in (f) is more stable by -6.6 kcal/mol than that in (e). The Pb ions bonded to the removed iodide are marked as dark cyan spheres. The spin densities are shown as the yellow contour surfaces. The color codes for the other atoms are the same as those in Figure 1.