SUPPORTING INFORMATION

Defects Migration in Methylammonium Lead Iodide and their Role in Perovskite Solar Cells Operation

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1. $MAPbI_3$ SIMULATION CELL

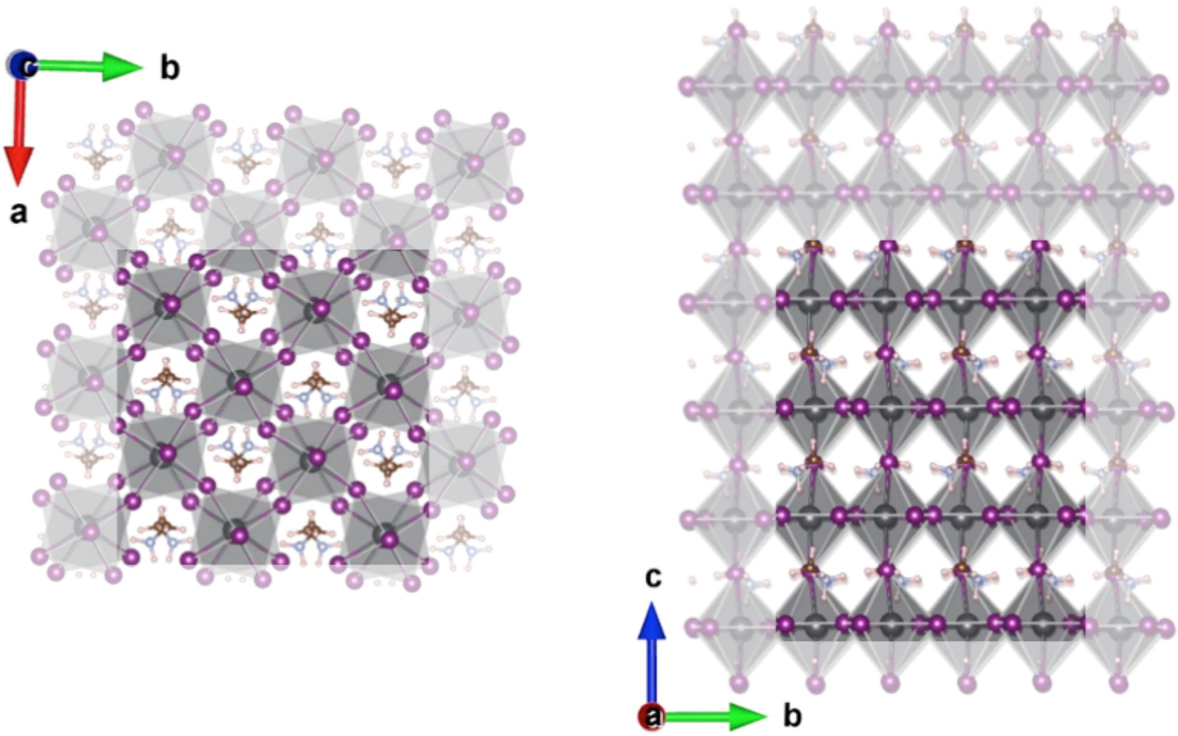

Figure S1. Top (left) and side (right) views of the 384 unit cell employed for calculation of the defect migration energies. The crystallographic axes are highlighted.

2. ALTERNATIVE MIGRATION PATH FOR V_{Pb}

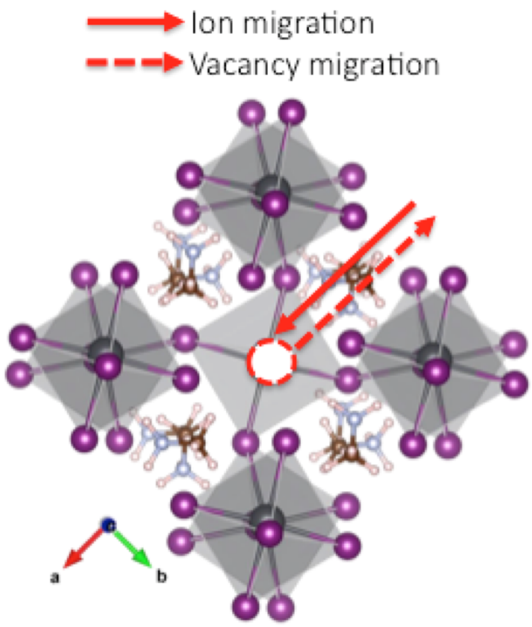

Figure S2. Alternative migration path for V_{Pb}, which walks along the diagonal of the square formed by four Pb and four I in the *ab* plane and implies an activation energy of 1.06 eV.

3. DERIVATION OF THE MIGRATION KINETICS

As one might notice from the energy landscapes depicted in Figure 2 of the paper, in absence of any field the activation energies for a forward and a backward step are exactly the same, which, according to the Arrhenius equation, deliver a migration rate constant of:

$$k = \frac{k_B T}{\hbar} e^{-\frac{E_a}{RT}} \quad (1)$$

Under the influence of an electrostatic field, however, the defect has to surmount an energy barrier of E_a - $\varepsilon/2$ to move forwards, while the backward step has an associated activation energy of E_a - $\varepsilon/2$. ε stands for the gain in electrostatic energy due to a forward step of the defect across a crystal unit cell. Therefore, the migration rates constant for the forward and backward hops read as:

$$k_{for} = \frac{k_B T}{\hbar} e^{-\frac{(E_a - \varepsilon/2)}{RT}} \quad (2)$$

$$k_{for} = \frac{k_B T}{\hbar} e^{-\frac{(E_a + \varepsilon/2)}{RT}} \quad (3)$$

and the ratio between them (ρ) amounts to:

$$\rho = \frac{k_{for}}{k_{back}} = \frac{\frac{k_B T}{\hbar} e^{-\frac{(E_a - \varepsilon/2)}{RT}}}{\frac{k_B T}{\hbar} e^{-\frac{(E_a + \varepsilon/2)}{RT}}} = e^{-\frac{(E_a - \varepsilon/2 - (E_a + \varepsilon/2))}{RT}} = e^{\frac{\varepsilon}{RT}} \quad (4)$$

As it is immediately clear from Eq. 4, the ratio depends exclusively on ε, which in turn is determined by the potential across the PSC and the thickness of the perovskite layer. For a typical 300 nm thick film and a potential of 1 V, ε equals to $3.3 \cdot 10^{-3}$ V/nm. Since the unit cell of $MAPbI_3$ comprises 6.5 Å, a *singly charged* defect gains 2.2 meV each forward step made towards the electrode. This number, plugged in Eq. 4, delivers a ρ of about 1.08, meaning that the forward step is 1.08 faster than the backward step. Assuming a one-dimensional path, this means that each 208 hops the defect will advance 8 steps towards the electrode (208/8 ratio). A defect located in the middle of a 300 nm thick perovskite layer should perform ~230 forward hops to reach the selective contact. Multiplied by 208/8 it provides a total number of 5980 hops. V_I and I_i, which perform a hop each $7.7 \cdot 10^{10}$ s^{-1}, would reach the electrode in 5980 / $7.7 \cdot 10^{10}$ = $7.7 \cdot 10^{-8}$ s = 77 ns. Similarly, the V_{Br}, with a calculated rate constant of $1.2 \cdot 10^{12}$ s^{-1}, would instead last 5980 / $1.2 \cdot 10^{12}$ = $5.0 \cdot 10^{-9}$ s = 5 ns. Regarding V_{MA}, the migration times amount to 5980 / $6.5 \cdot 10^{5}$ = $9.2 \cdot 10^{-3}$ s = 9 ms and 5980 / $1.3 \cdot 10^{4}$ = 0.46 s for $MAPbI_3$ and $MAPbBr_3$, respectively. The situation is slightly different for V_{Pb}, which is *doubly charged* (-2). Therefore, the corresponding ε is 4.4 meV, and ρ amounts to 1.17. Following the reasoning above, a V_{Pb} requires a total number of (217/17)*230 = 2936 hops to reach the electrode. With a calculated rate constant of 1.2 s^{-1}, this delivers a total migration time of 2936 / 1.2 = 2553 s = 41 min.

4. ENERGY PROFILES FOR THE HALIDE VACANCY MIGRATION IN $MAPbI_3$ AND $MAPbBr_3$

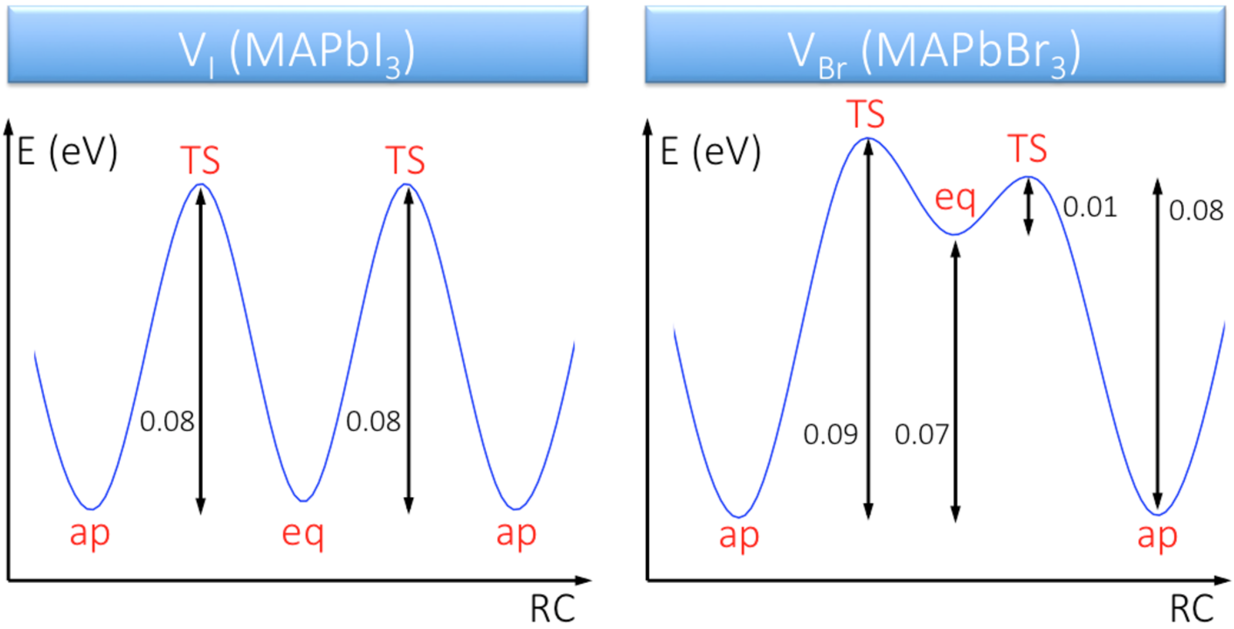

Figure S3. Energy profiles for V_I and V_{Br} migration in $MAPbI_3$ and $MAPbBr_3$, as they hop between two apical sites, passing through a equatorial position. Notice that for $MAPbI_3$, the V_I in the apical and equatorial positions are almost isoenergetic, giving rise to a symmetric reaction profile. For $MAPbBr_3$, instead, the equatorial defect lies 0.07 eV higher in energy than the apical one, leading to an asymmetric path.

5. ENERGY PROFILES FOR THE Pb VACANCY MIGRATION IN $MAPbI_3$

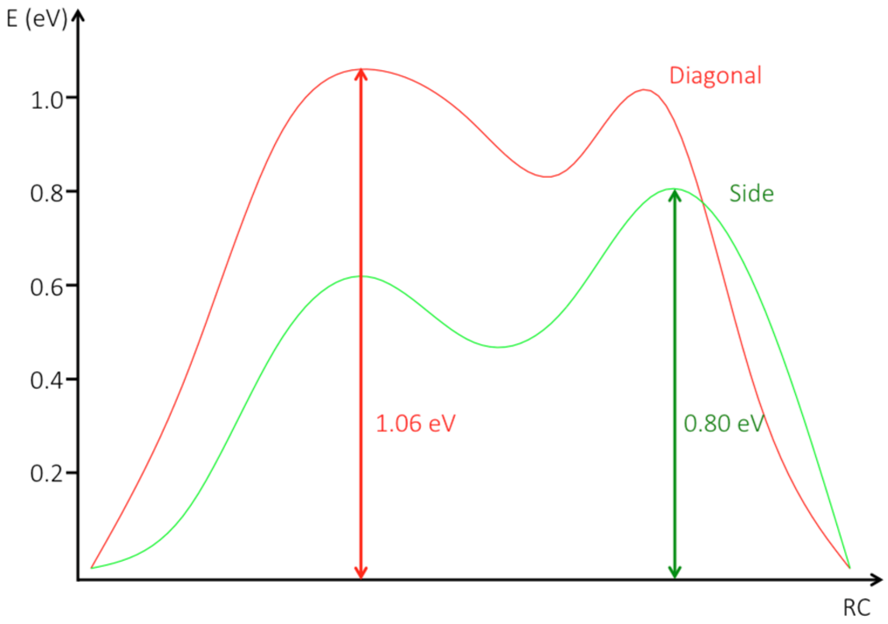

Figure S4. Energy profiles for V_{Pb} migration in $MAPbI_3$, which may walk along the side (green) or the diagonal (red) of the square formed by four Pb and four I in the *ab* plane.

6. IMPACT OF I VACANCIES ON THE CRYSTAL STRUCTURE OF $MAPbI_3$

Crystal axis	Perfect $MAPbI_3$	$MAPbI_3$ with V_I
a	8.694	8.480
b	8.630	8.390
c	12.825	12.171
c/b	1.486	1.451

7. ELECTRONIC STRUCTURE OF THE SINGLY DEFECTIVE MODELS

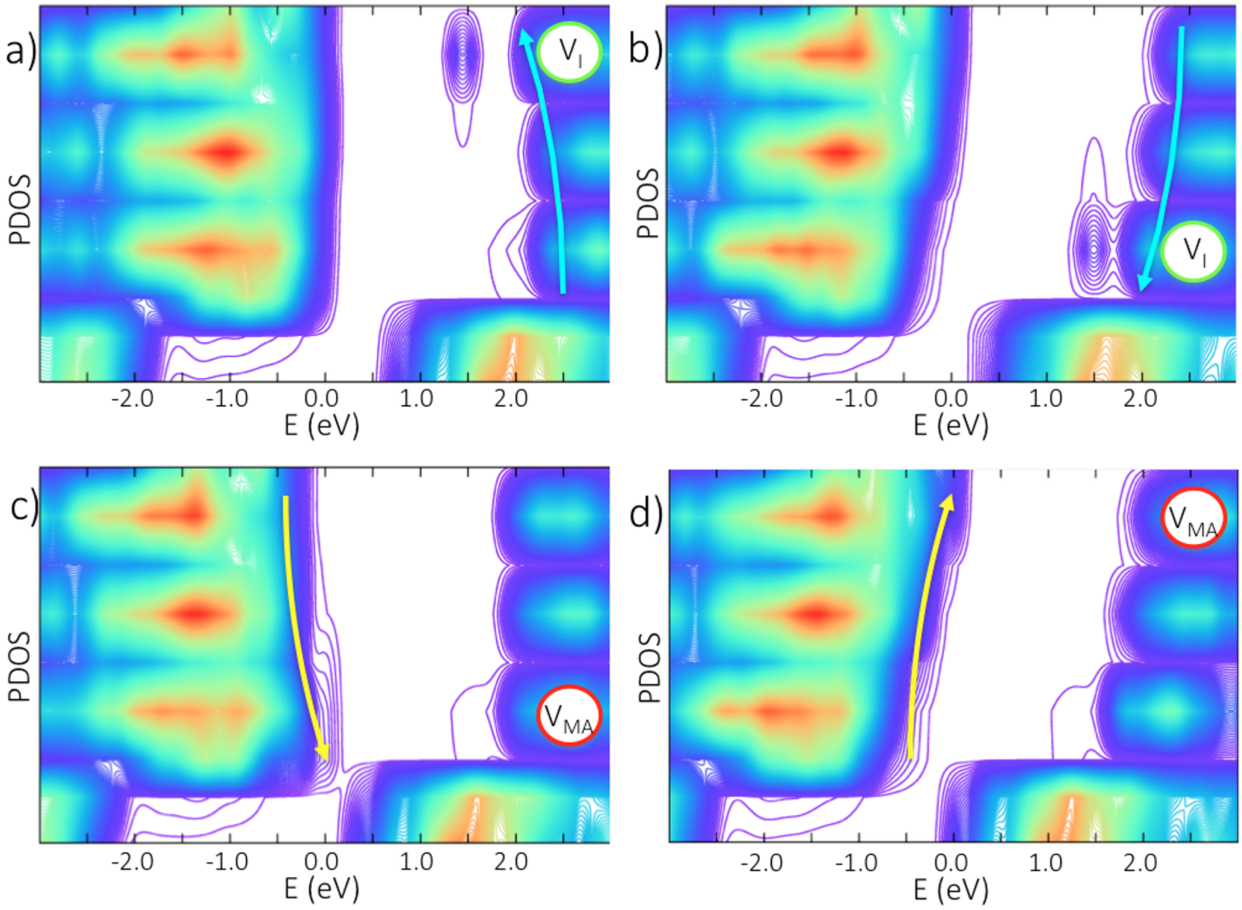

Figure S5. Local Density of States (DOS), projected along the direction orthogonal to the perovskite/TiO_2 interface, for the singly defective models. The position of the vacancy is highlighted in each case. Light-blue (yellow) arrows eye-guide the evolution of photogenerated electrons (holes).

8. ELECTRONIC STRUCTURE OF THE DOUBLY DEFECTIVE MODELS

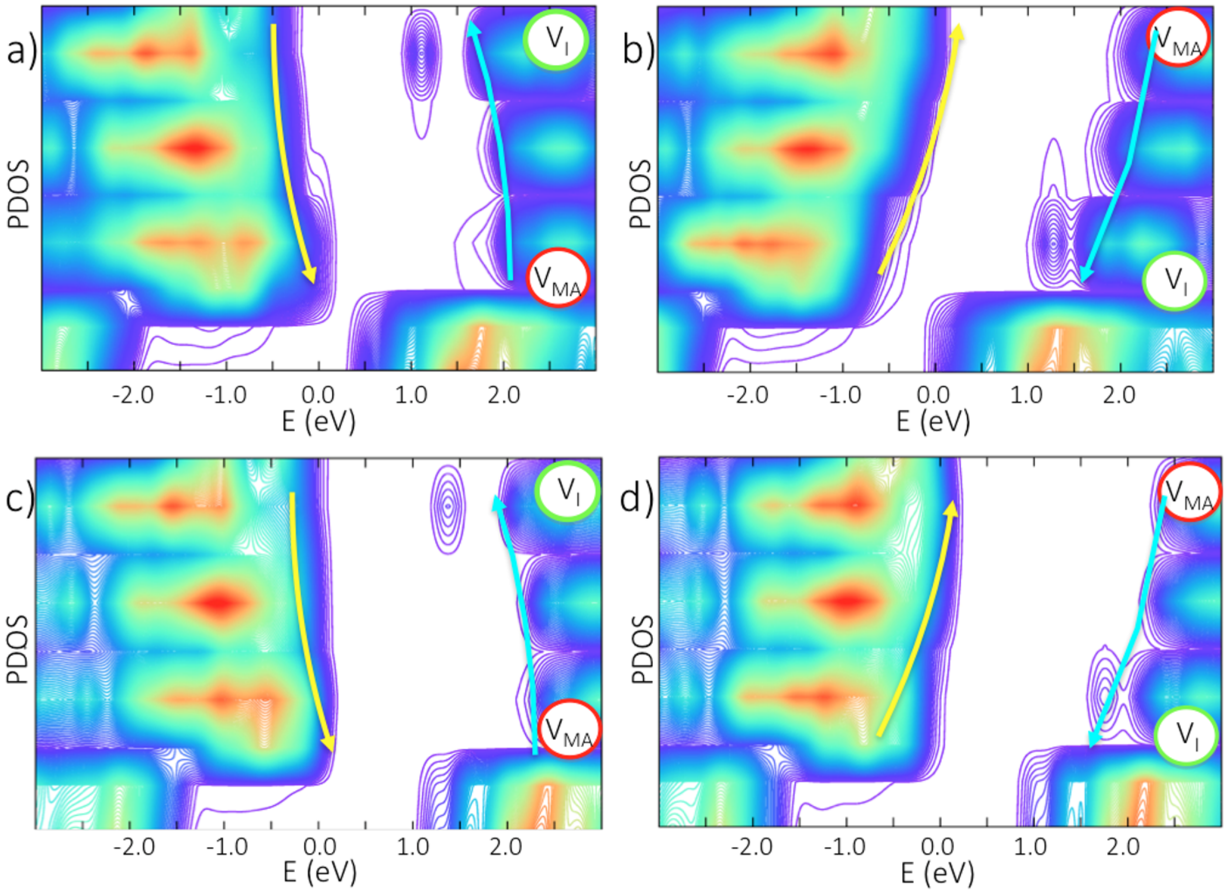

Figure S6. Local Density of States (DOS), projected along the direction orthogonal to the perovskite/TiO_2 interface, for the doubly defective models 1 (left panels) and 2 (right panels), in their singlet ground (top panels) and triplet excited (bottom panels) states. The position of the vacancies is highlighted in each case. Light-blue (yellow) arrows eye-guide the evolution of photogenerated electrons (holes).