Supporting Information for:

Unravelling the Effects of Oxidation State of Interstitial Iodine and Oxygen Inhibits Charge Trapping and Recombination in $CH_3NH_3PbI_3$ Perovskite: A Time-Domain Ab Initio Study

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S1 Coupled Kinetic Equations

Here, we consider the following processes that characterize the charge carrier relaxation pathways in pristine $MAPbI_3$, I_i, I_i^{-1}, I_i^{+1} and IO_3^{-1} systems. The schematics of related charge processes are depicted in Figure S1-S4. The obtained charge trapping and recombination dynamics between two states are shown in Figure S5-S13. Here, the transition rate between the conduciton band minimum (CBM) and valence band maximum (VBM), CBM and electron trap, electron trap and VBM, VBM and hole trap is denoted by $k_{(cbm\rightarrow vbm)}$, $k_{(cbm\rightarrow trap)}$, $k_{(trap\rightarrow vbm)}$, $k_{(vbm\rightarrow trap)}$, respectively. The rate constants shown in Figure S5-S13 are obtained by fitting the key state population to an function $f(t) = t/A$. Constant A is depending on the system.

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(a) pristine $MAPbI_3$: electron-hole recombination across CBM and VBM. Figure S1 gives the basis set. The time-dependent populations of excited state (CBM) and ground state (VBM) are described by equations 1-2 and their solutions are given by equations 3-4. Figure S5 gives the ground state population growing and rate constant.

coupled kinetic equations:

$$\frac{d[ES]}{dt} = -k_{(cbm \to vbm)}[ES] \qquad (1)$$

$$\frac{d[GS]}{dt} = k_{(cbm \to vbm)}[ES] \qquad (2)$$

the solutions for this set of equations are:

$$[ES] = e^{-k_{(cbm \to vbm)} * t} \qquad (3)$$

$$[GS] = 1 - e^{-k_{(cbm \to vbm)} * t} \qquad (4)$$

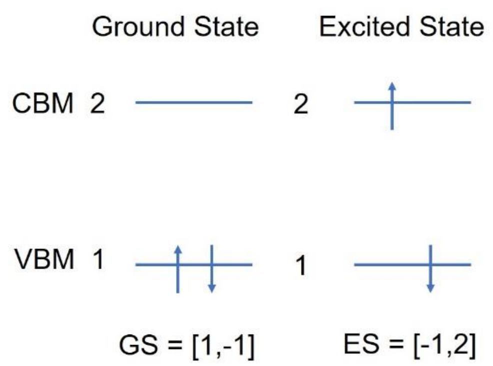


Figure S1. The schematic of electron-hole recombination pathway in pristine $MAPbI_3$.

(b) I_i: electron-hole recombination mediated by trap states. Figure S2 and S3 give the basis set of electron trap- and hole trap-assisted electron-hole recombination. The electron-trap assisted charge recombination is described by equations 5-7 and whose solutions are presented in equations 8-10. The hole-trap mediated electron-hole recombination is described by equations 11-13 and the corresponding solutions are shown in equations 14-16. The dynamics processes and transition constants of $k_{(cbm\rightarrow vbm)}$, $k_{(vbm\rightarrow trap)}$, $k_{(cbm\rightarrow trap)}$ are shown in Figure S6-S8.

coupled kinetic equations for electron-hole recombination containing electron trapping:

$$\frac{d[ES]}{dt} = -(k_{(cbm\rightarrow vbm)} + k_{(cbm\rightarrow trap)})[ES] \quad (5)$$

$$\frac{d[trap]}{dt} = k_{(cbm\rightarrow trap)}[ES] - k_{(trap\rightarrow vbm)}[trap] \quad (6)$$

$$\frac{d[GS]}{dt} = k_{(cbm\rightarrow vbm)}[ES] + k_{(trap\rightarrow vbm)}[trap] \quad (7)$$

the solutions for this set of equations are:

$$[ES] = e^{-(k_{(cbm\rightarrow vbm)}+k_{(cbm\rightarrow trap)})*t} \quad (8)$$

$$[trap] = \frac{k_{(cbm\rightarrow trap)}}{(k_{(cbm\rightarrow vbm)}+k_{(cbm\rightarrow trap)}-k_{(trap\rightarrow vbm)})}\left(e^{-k_{(trap\rightarrow vbm)}*t} - e^{-(k_{(cbm\rightarrow vbm)}+k_{(cbm\rightarrow trap)})*t}\right) \quad (9)$$

$$[GS] = 1 - \frac{1}{(k_{(cbm\rightarrow vbm)}+k_{(cbm\rightarrow trap)}-k_{(trap\rightarrow vbm)})}\left\{k_{(cbm\rightarrow trap)} * e^{-k_{(trap\rightarrow vbm)}*t} - (k_{(cbm\rightarrow vbm)} - k_{(trap\rightarrow vbm)}) * e^{-(k_{(cbm\rightarrow vbm)}+k_{(cbm\rightarrow trap)})*t}\right\} \quad (10)$$

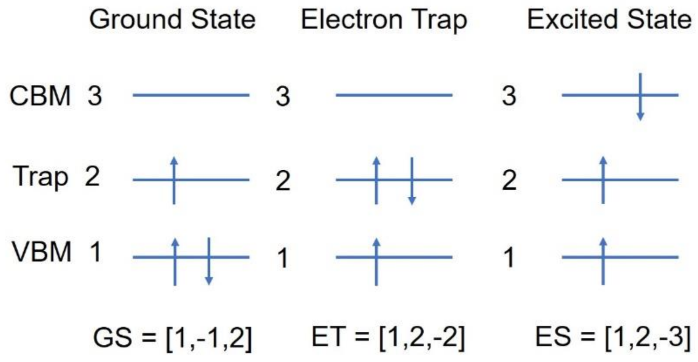


Figure S2. The schematic of electron-hole recombination containing electron trapping pathways in I_i.

coupled kinetic equations for electron-hole recombination containing hole trapping:

$$\frac{d[ES]}{dt} = -(k_{(cbm\to vbm)} + k_{(vbm\to trap)})[ES] \quad (11)$$

$$\frac{d[trap]}{dt} = k_{(vbm\to trap)}[ES] - k_{(cbm\to trap)}[trap] \quad (12)$$

$$\frac{d[GS]}{dt} = k_{(cbm\to vbm)}[ES] + k_{(cbm\to trap)}[trap] \quad (13)$$

the solutions for this set of equations are:

$$[ES] = e^{-(k_{(cbm\to vbm)}+k_{(vbm\to trap)})*t} \quad (14)$$

$$[trap] = \frac{k_{(vbm\to trap)}}{(k_{(cbm\to vbm)}-k_{(cbm\to trap)}+k_{(vmb\to trap)})}\left(e^{-k_{(cbm\to trap)}*t} - e^{-(k_{(cbm\to vbm)}+k_{(vbm\to trap)})*t}\right) \quad (15)$$

$$[GS] = 1 - \frac{k_{(vbm\to trap)}}{(k_{(cbm\to vbm)}-k_{(cbm\to trap)}+k_{(vbm\to trap)})}\left(e^{-k_{(cbm\to trap)}*t}\right) - \frac{((k_{(cbm\to vbm)}-k_{(cbm\to trap)}}{(k_{(cbm\to vbm)}-k_{(cbm\to trap)}+k_{(vbm\to trap)})}\left(e^{-(k_{(cbm\to vbm)}+k_{(vbm\to trap)})*t}\right) \quad (16)$$

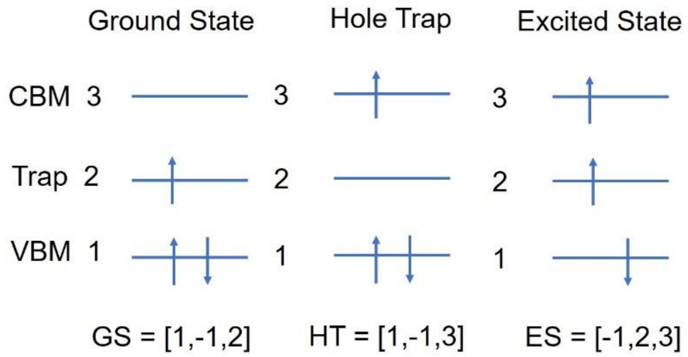


Figure S3. The schematic of electron-hole recombination containing hole trapping pathways in I_i.

(c) I_i^{-1}: electron-hole recombination across CBM and VBM of the system. The transition rate $k_{(cbm\rightarrow vbm)}$ is obtained by fitting the ground state (VBM) population (Figure S9). The kinetic processes and basis set are same to the pristine $MAPbI_3$, see equations 1-4 and Figure S1.

(d) I_i^{+1}: electron-trap assisted electron-hole recombination. The time-dependent populations of the excited state (CBM), trap state, and ground state (VBM) are described by equations 17-19 and whose solutions are presented in equations 20-22. The basis set is shown in Figure S4. The transition rates $k_{(cbm\rightarrow vbm)}$, $k_{(trap\rightarrow vbm)}$, $k_{(cbm\rightarrow trap)}$ are obtained by fitting the key state population shown in Figure S10-S12.

coupled kinetic equations:

$$\frac{d[ES]}{dt} = -(k_{(cbm\rightarrow vbm)} + k_{(cbm\rightarrow trap)})[ES] \tag{17}$$

$$\frac{d[trap]}{dt} = k_{(cbm\rightarrow trap)}[ES] - k_{(trap\rightarrow vbm)}[trap] \tag{18}$$

$$\frac{d[GS]}{dt} = k_{(cbm\rightarrow vbm)}[ES] + k_{(trap\rightarrow vbm)}[trap] \tag{19}$$

the solutions for this set of equations are:

$$[ES] = e^{-(k_{(cbm\rightarrow vbm)}+k_{(cbm\rightarrow trap)})*t} \tag{20}$$

$$[trap] = \frac{k_{(cbm\rightarrow trap)}}{(k_{(cbm\rightarrow vbm)}+k_{(cbm\rightarrow trap)}-k_{(trap\rightarrow vbm)})}\left(e^{-k_{(trap\rightarrow vbm)}*t} - e^{-(k_{(cbm\rightarrow vbm)}+k_{(cbm\rightarrow trap)})*t}\right) \tag{21}$$

$$[GS] = 1 - \frac{1}{(k_{(cbm\rightarrow vbm)}+k_{(cbm\rightarrow trap)}-k_{(trap\rightarrow vbm)})}\{k_{(cbm\rightarrow trap)} * e^{-k_{(trap\rightarrow vbm)}*t} - (k_{(cbm\rightarrow vbm)} - k_{(trap\rightarrow vbm)}) * e^{-(k_{(cbm\rightarrow vbm)}+k_{(cbm\rightarrow trap)})*t}\} \tag{22}$$

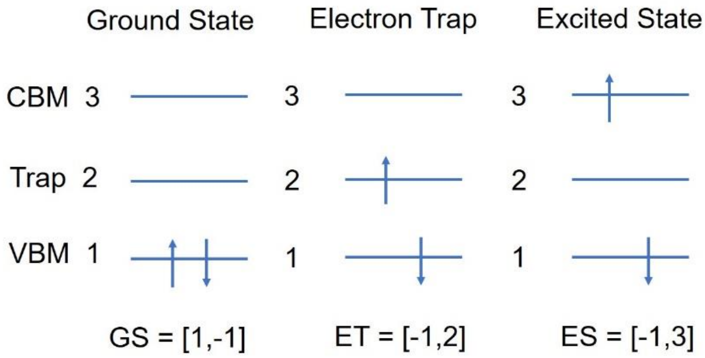


Figure S4. The schematic of electron-hole recombination and electron trapping pathways in I_i^{+1}.

(e) IO_3^{-1}: electron-hole recombination across CBM and VBM of the system. The transition rate $k_{(cbm \rightarrow vbm)}$ is obtained by fitting the ground state (VBM) population (Figure S13). The kinetic equations, solutions and basis set is same to the pristine $MAPbI_3$, see equations 1-4 and Figure S1.

S2 Additional Figures

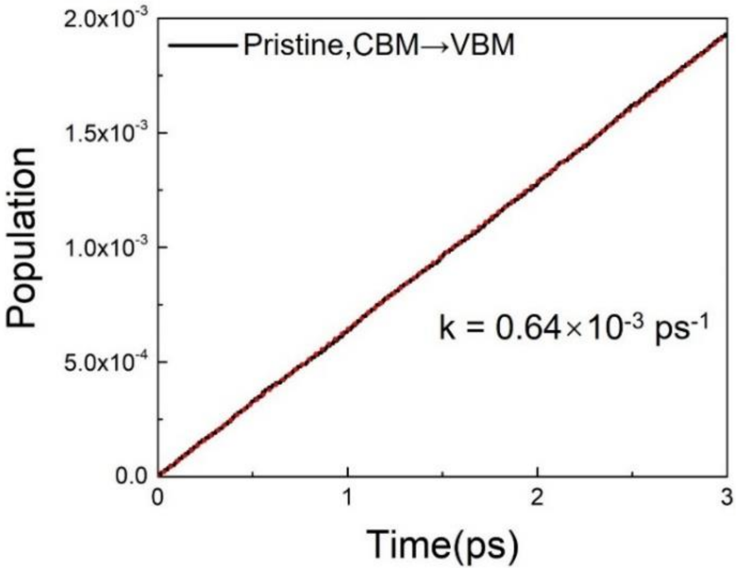


Figure S5. Time evolution of the ground state's population due to recombination of the valence band hole with conduction band electron in pristine $MAPbI_3$. The fitting function is $f(t) = t/(1.554 \times 10^6)$.

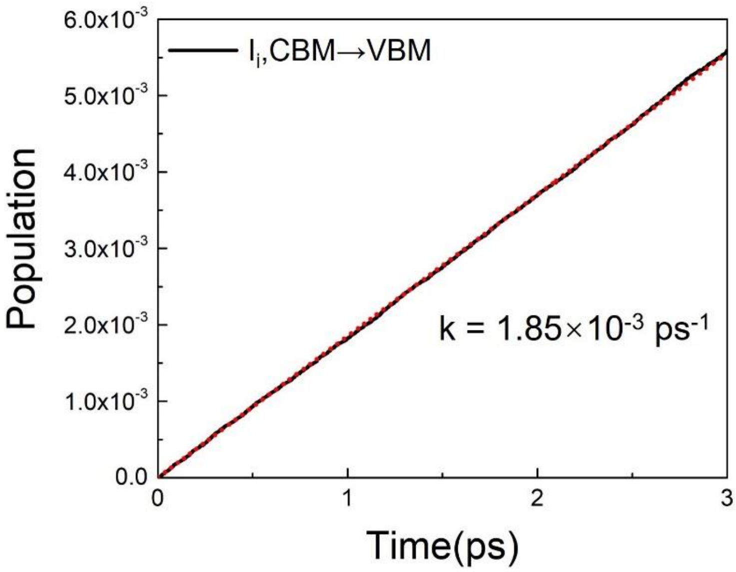


Figure S6. Time evolution of the ground state's population due to recombination of the valence band hole with conduction band electron in I_i. The fitting function is $f(t) = t/(0.540 \times 10^6)$.

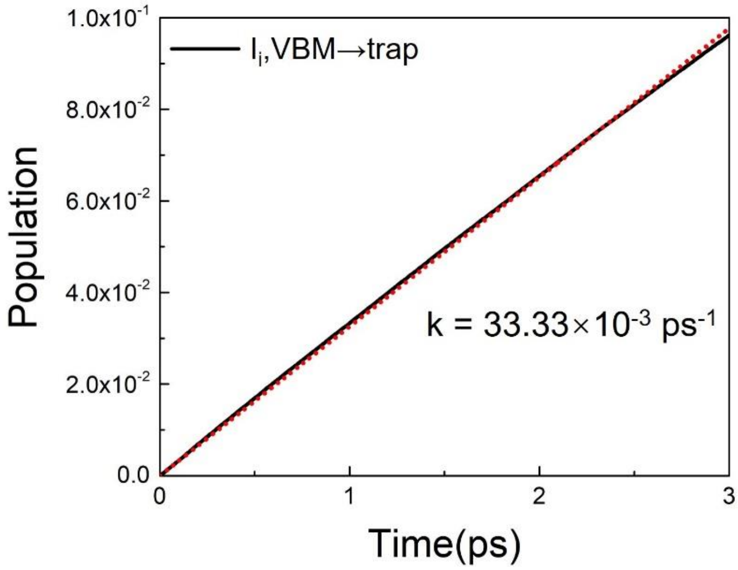


Figure S7. Time evolution of the trap state's population due to hole trapping form valence band maximum (VBM) to trap state in I_i. The fitting function is $f(t) = t/(0.030 \times 10^6)$.

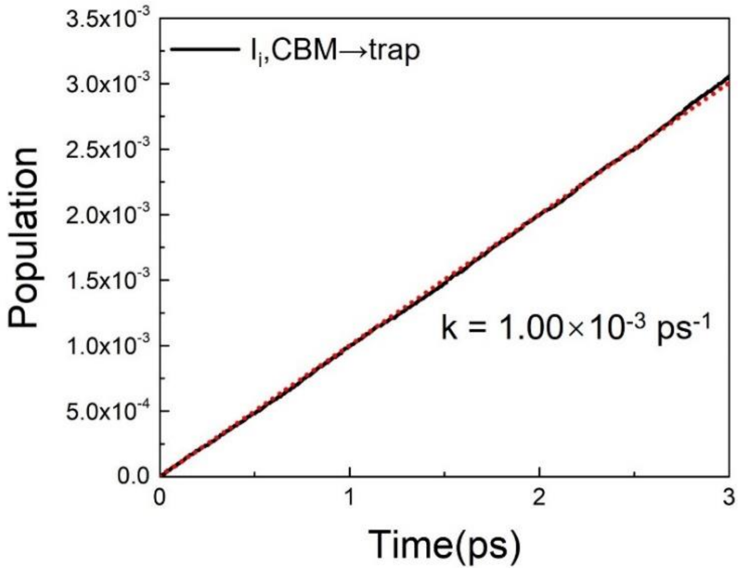


Figure S8. Time evolution of the ground state's population due to recombination of the trapped hole with conduction band electron in I_i. The fitting function is $f(t) = t/(1.000 \times 10^6)$.

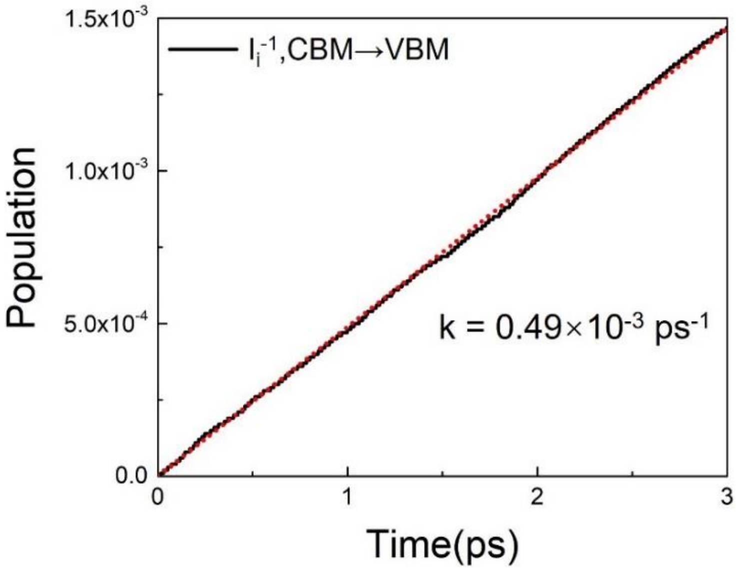


Figure S9. Time evolution of the ground state's population due to recombination of the valence band hole with conduction band electron in I_i^{-1}. The fitting function is $f(t) = t/(2.045 \times 10^6)$.

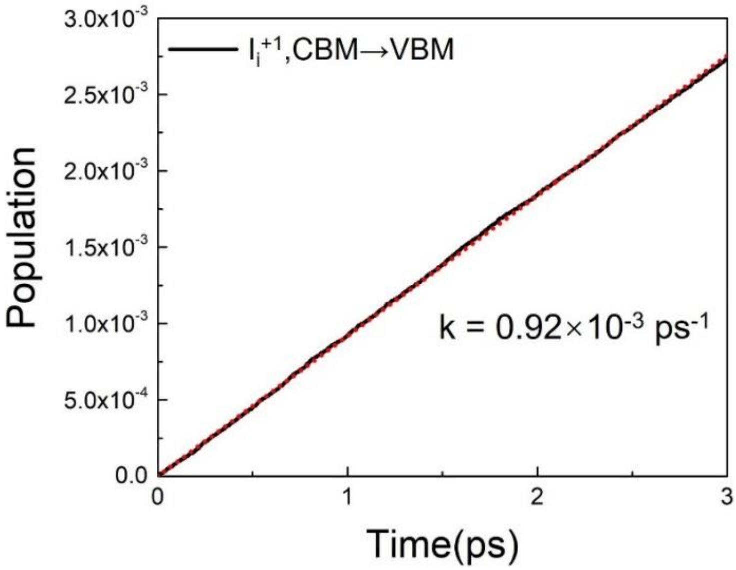


Figure S10. Time evolution of the ground state's population due to recombination of the valence band hole with conduction band electron in I_i^{+1}. The fitting function is $f(t) = t/(1.088 \times 10^6)$.

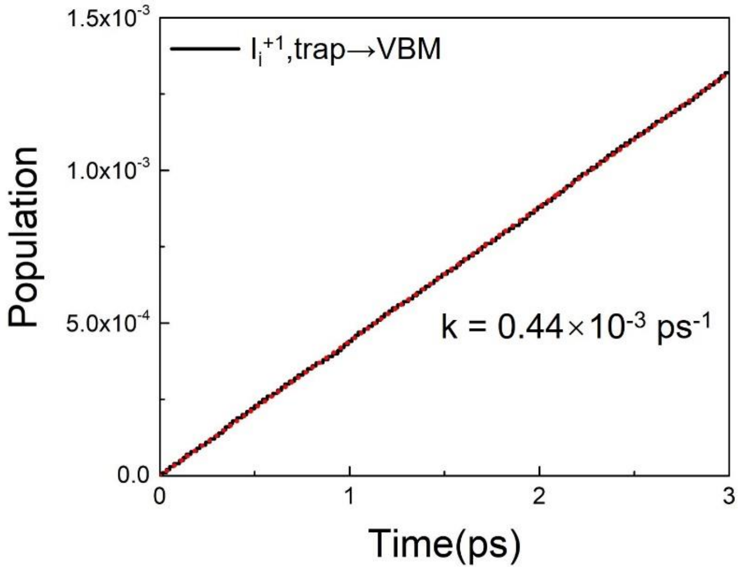


Figure S11. Time evolution of the ground state's population due to recombination of the trapped electron with valence band hole in I_i^{+1}. The fitting function is $f(t) = t/(2.271 \times 10^6)$.

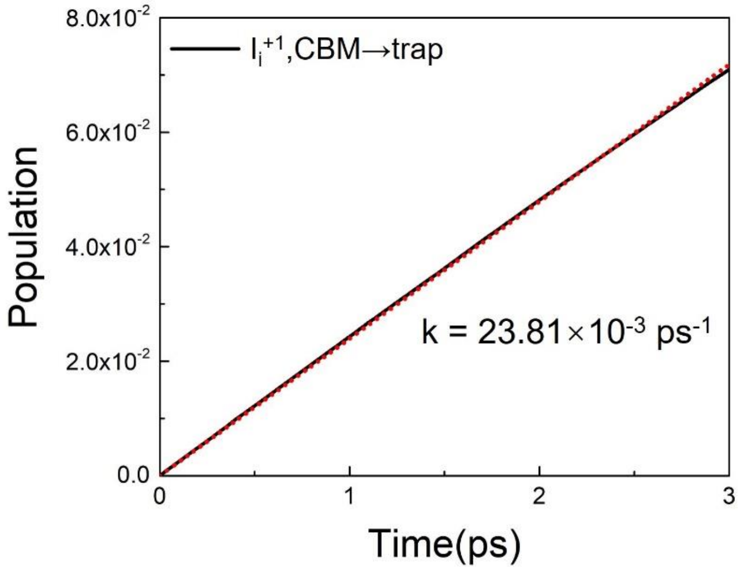


Figure S12. Time evolution of the ground state's population due to electron trapping form conduction band minimum (CBM) to trap state in I_i^{+1}. The fitting function is $f(t) = t/(0.042 \times 10^6)$.

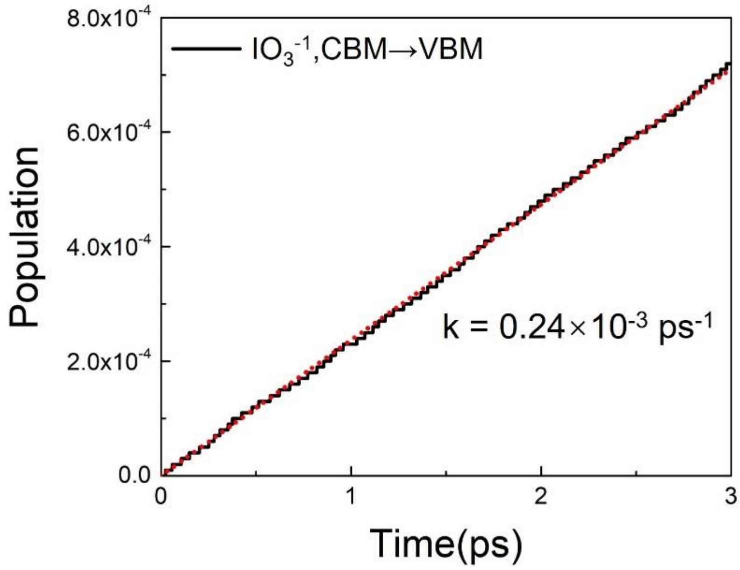


Figure S13. Time evolution of the ground state's population due to recombination of the valence band hole with conduction band electron in IO_3^{-1}. The fitting function is $f(t) = t/(4.221 \times 10^6)$.

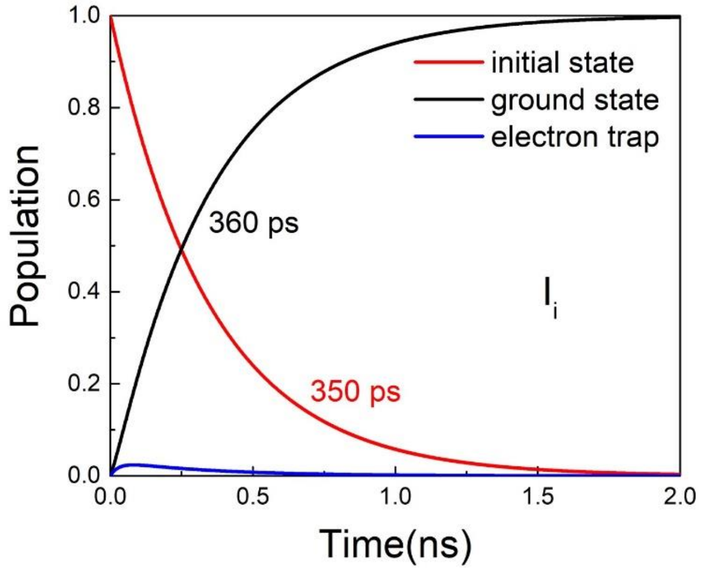
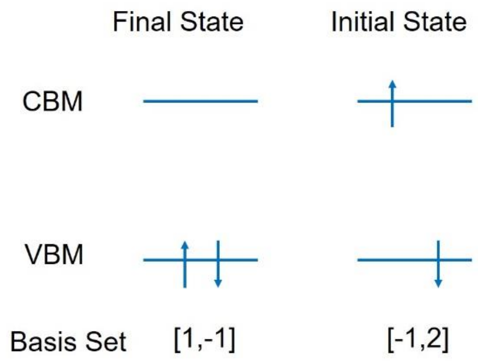


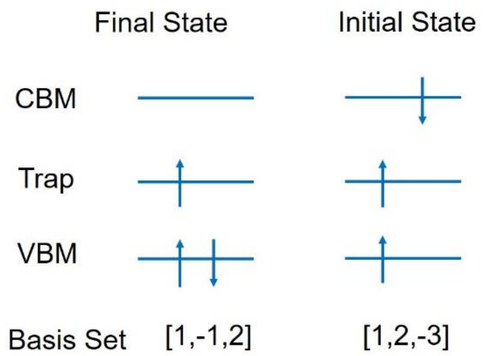
Figure S14. Evolution of populations of the key states for electron trapping in I_i.

Electronic configurations of product (final) and reactant (initial) states.

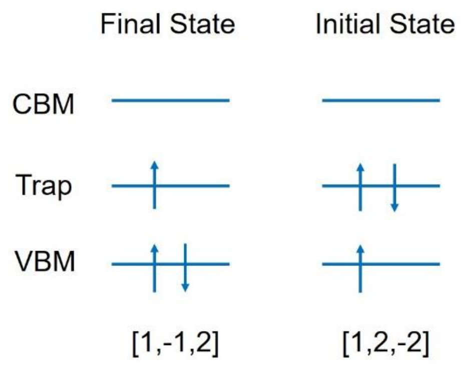
(1) The electronic configuration of product (final) and reactant (initial) states in the pristine $MAPbI_3$, I_i^{-1} and IO_3^{-1} systems during electron-hole recombination between VBM and CBM:



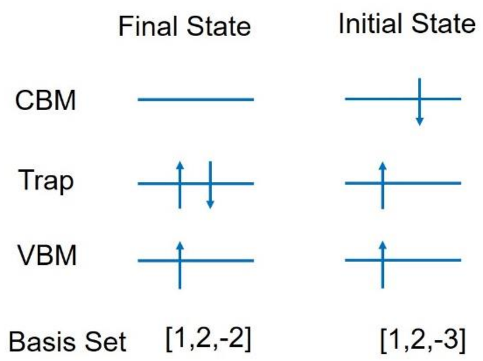
(2) The electronic configuration of product (final) and reactant (initial) states in the I_i system for electron-hole recombinaiton between CBM and VBM bypassing the trap state:



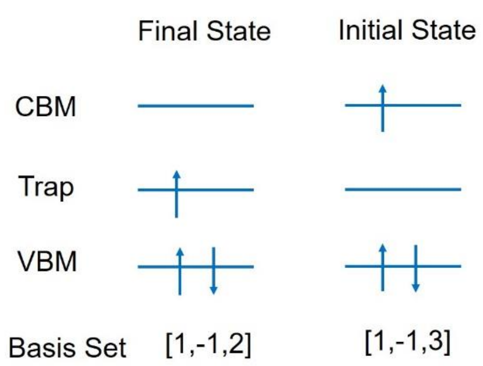
(3) The electronic configuration of (final) and reactant (initial) states in the I_i system for recombinaiton between VBM and the trap state:



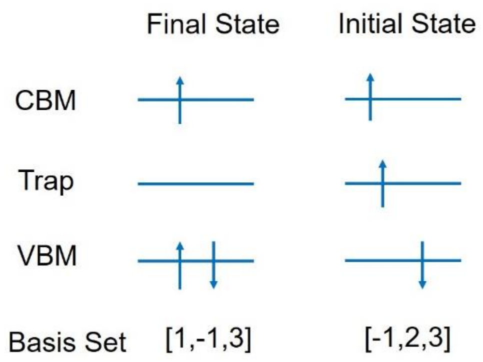
(4) The electronic configuration of (final) and reactant (initial) states in the I_i system for electron trapping between CBM and the trap state:



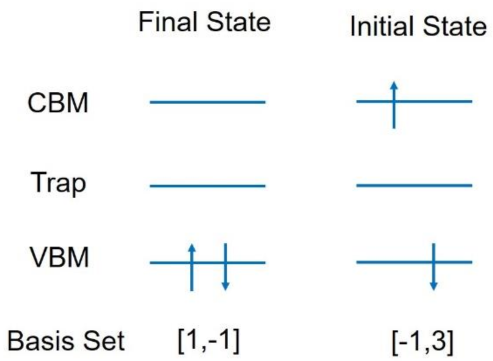
(5) The electronic configuration of (final) and reactant (initial) states in the I_i system for hole trapping assisted recombiation between CBM and trap state:



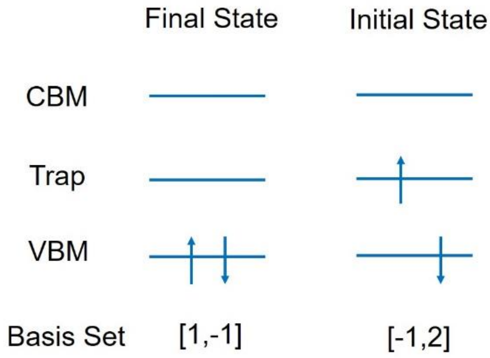
(6) The electronic configuration of (final) and reactant (initial) states in the I_i system for hole trapping between VBM and trap state:



(7) The electronic configuration of (final) and reactant (initial) states in the I_i^{+1} for electron-hole recombinaiton between CBM and VBM bypassing the electron trap state:



(8) The electronic configuration of (final) and reactant (initial) states in the I_i^{+1} for recombination between VBM and electron trap state:



(9) The electronic configuration of (final) and reactant (initial) states in the I_i^{+1} for electron between CBM and the electron trap state: