Supplementary Information

Frenkel Defects Promote Polaronic Exciton Dissociation in Methylammonium Lead Iodide

Perovskites

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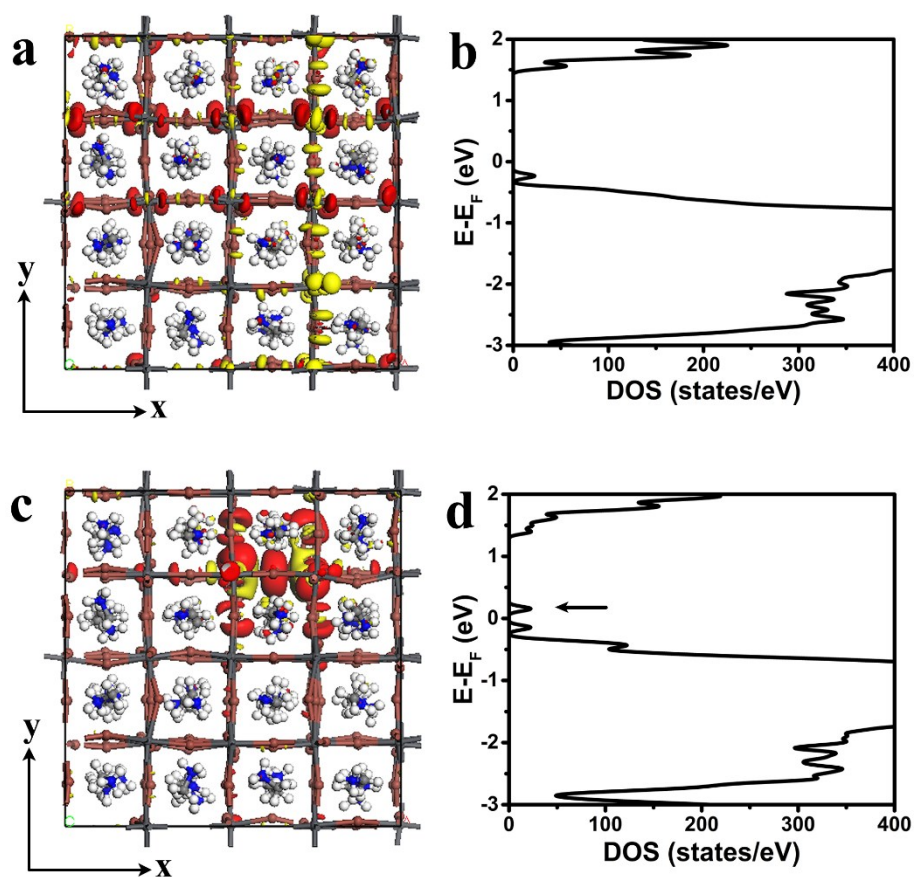*Corresponding author

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Figure S1. Charge densities and DOS in MAPbI$_3$ with native point defects. (a)-(b) Lowest excited-state charge densities and DOS in excited-state configuration for MAPbI$_3$ in presence of one I$_i^-$ defect. (c)-(d) Lowest excited-state charge densities and DOS in excited-state configuration for MAPbI$_3$ in presence of one V$_I^+$ defect. The positions of I$_i^-$ and V$_I^+$ defects are identical to the positions in Figure 1a. The discrete in-gap states are highlighted with the arrow in (d). In (a) and (c), the electron (hole) density is shown in red (yellow) and the value of iso-surface is 1.5×10^{-3} e Å^{-3}.
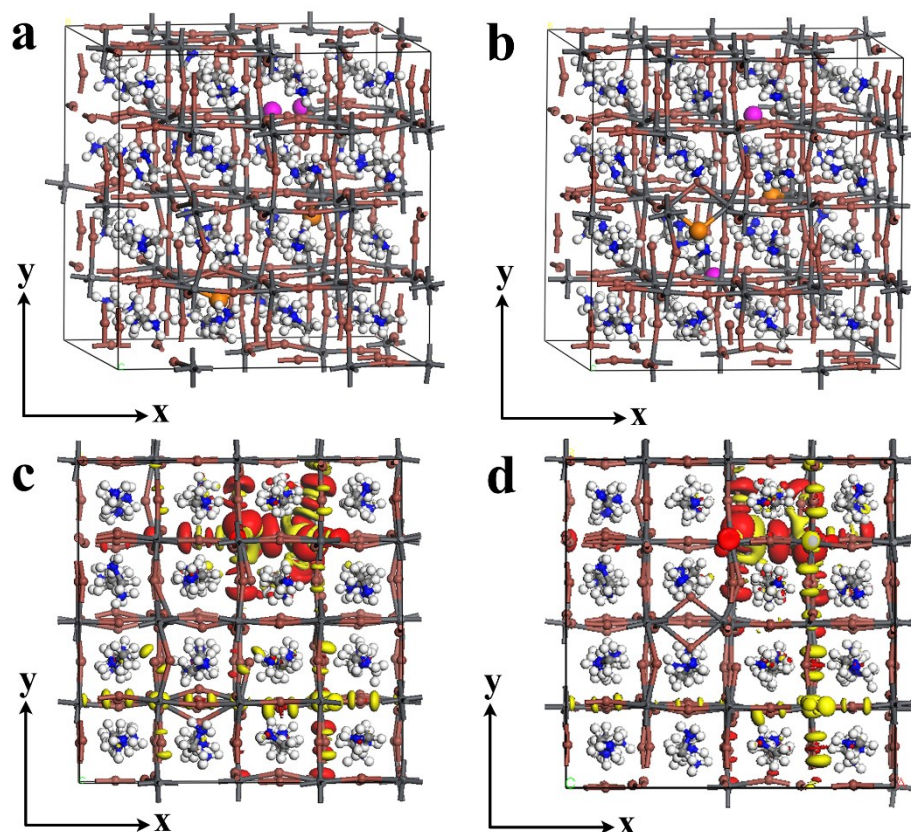
Figure S2. (a) MAPbI$_3$-FD2 configuration which shows different positions of I$_i^-$ defects with respect to MAPbI$_3$-FD2 configuration in Figure 4a. (b) MAPbI$_3$-FD2 configuration which shows different positions of V$_I^+$ defects with respect to MAPbI$_3$-FD2 configuration in Figure 4a. (c) Charge densities in the excited-state geometry of MAPbI$_3$-FD2 configuration in (a). (d) Charge densities of the excited-state geometry for MAPbI$_3$-FD2 configuration in (c). The electron (hole) density is shown in red (yellow) in (c) and (d). The value of iso-surface is 2.0×10^{-3} e Å^{-3} in (c) and (d).

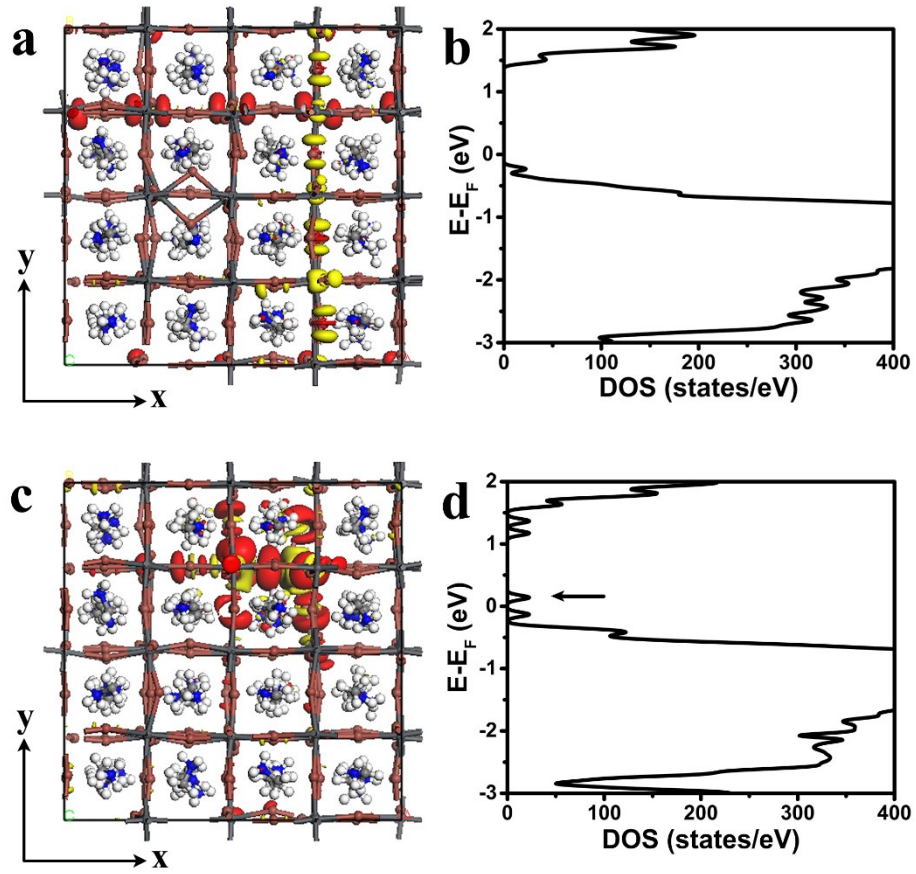Figure S3. Charge densities and DOS in MAPbI$_3$ with native point defects. (a)-(b) Charge densities and DOS in excited-state configuration for MAPbI$_3$ in presence of two I$_i^-$ defects. (c)-(d) Charge densities and DOS in excited-state configuration for MAPbI$_3$ in presence of two V$_I^+$ defects. The discrete in-gap state in (d) is highlighted with the arrow. The positions of I$_i^-$ defects in (a) and V$_I^+$ defects in (c) are the same to those in Figure 4a. In (a) and (c), the electron (hole) density is shown in red (yellow) and the value of iso-surface is 2.0×10^{-3} e Å^{-3}.
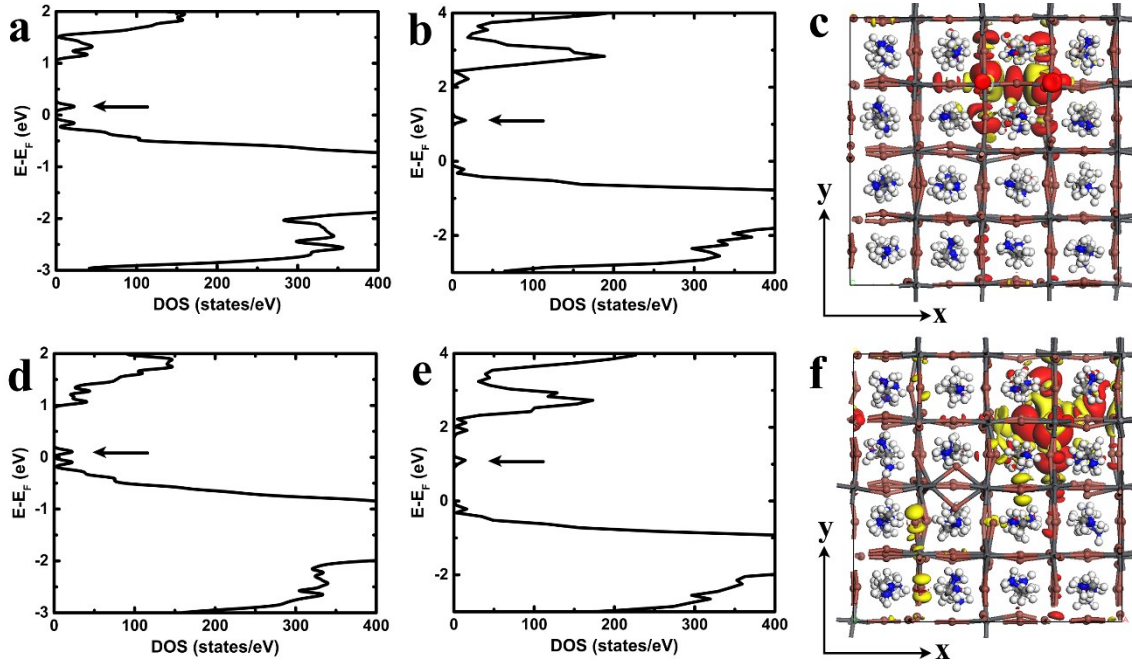
Figure S4. DOS and charge densities with SOC corrections and OT-RSH functional for defective MAPbI$_3$. (a) DOS with SOC corrections for the excited-state geometry of MAPbI$_3$-FD1 in Figure 1c. (b)-(c) DOS and charge densities calculated with the OT-RSH functional for the excited-state geometry of MAPbI$_3$-FD1 in Figure 1c. (d) DOS with SOC corrections for the excited-state configuration of MAPbI$_3$-FD2 in Figure 4c. (e)-(f) DOS and charge densities calculated with the OT-RSH functional for the excited-state geometry of MAPbI$_3$-FD2 in Figure 4c. The discrete in-gap states are highlighted with the arrows in (a), (b), (d) and (e). In (c) and (f), the electron (hole) density is shown in red (yellow) and the value of iso-surface is 2.0×10^{-3} e Å^{-3}.