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1. Introduction

Hybrid organic-inorganic perovskite (HOIP) materials are drawing attention in photovoltaic application owing to the rapid rise of power conversion efficiency.^{1,2} To date, HOIPs have achieved a certified power conversion efficiency exceeding 25%.³ The impressive performance of this class of materials is enabled by a unique combination of the desired properties, including a high optical absorption coefficient, high carrier mobility and low electron-hole (e-h) binding energies.⁴ Remarkably, long carrier lifetime and diffusion length have been reported in solution-processed HOIPs,^{5–7} e.g., the methylammonium lead iodide (MAPbI₃ with MA = $CH_3NH_3^+$) which can bear trap densities of up to 10^{17} - 10^{18} cm³.^{8,9} This is in sharp contrast to the picture of a typical semiconductor which shows a rather limited carrier lifetime and diffusion length owing to scattering of defects or impurities. To complete the picture, researchers require an accurate understanding of the



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Hybrid organic–inorganic perovskite materials, such as CH₃NH₃Pbl₃, exhibit substantial potential in a variety of optoelectronic applications. Nevertheless, the interplay between the photoinduced excitations and iodine Frenkel defects which are abundant in CH₃NH₃Pbl₃ films remains poorly understood. Here we study the light-triggered electronic and excitonic properties in the presence of iodine Frenkel defects in CH₃NH₃Pbl₃ by using a combination of density functional theory (DFT) and time-dependent DFT approaches, the latter of which treats electron–hole and electron–nucleus interactions on the same footing. For isolated Frenkel defects, electrons are trapped close to the iodine vacancies and the electron–hole correlation brings the holes in close vicinity to the electrons, yielding tightly bound polaronic excitons. However, in the presence of multiple interactive Frenkel defects, the holes are pulled out from an electron–hole Coulomb well by the iodine interstitials, leading to spatially separated electron–hole pairs. The X-ray photoelectron spectra are then simulated, unravelling the light-triggered charge transfer induced by Frenkel defects at the atomistic level. We also find that the energy and spatial distributions of polaronic excitons at the Frenkel defects can be controlled by the dynamical rotation of organic cations.

nature of the carriers and the role played by defects in the photophysics of HOIPs.

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Significant effort has been devoted to the study of high defect tolerance of HOIPs.4 Several studies indicate a significant probability for the formation of native defects in MAPbI₃, but most typical point defects introduce shallow trap states (i.e. electronic states lying close to the band-edges, comparable to or less than the available thermal energy).¹⁰⁻¹² Electronphonon coupling coupled with long-range Coulomb potentials gives rise to large polarons as a result of extended lattice distortion.¹³ Such polaron formation can protect the photogenerated electrons and holes from recombination and defectscattering. These would explain the limited impact of defects on solar cell performance. Nevertheless, non-negligible channels of electrons and energy losses are experimentally resolved, suggesting the presence of fairly deep trap states.^{14,15} These deep in-gap energy levels may arise from the small polarons which originate from localized lattice reorganizations induced cooperatively by both inorganic lattice distortion and organic cation rotations.¹⁶ It is worth noting that the defect-related lattice distortion can be triggered by photoexcitation^{17,18} and transforming large polarons (shallow traps) in the dark to small polaronic excitons (discrete in-gap traps) in excited states,^{19,20} shedding light on the significant role of exciton-defect interactions on determining the nature of defects in HOIPs. This is consistent with

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photoluminescence and spectroscopy measurements that suggest non-trivial e-h recombination, $^{21-23}$ in particular for HOIPs with non-stoichiometric chemical compositions. $^{24-27}$

So far, a considerable amount of research has been directed to focus on native point defects such as vacancy defects and interstitial defects for iodine elements in MAPbI₃.^{10,28,29} Unlike conventional semiconducting materials, however, MAPbI₃ bears strong ionic bonding features,³⁰ so the defects composed of neutral anion-cation pairs should be considered. Defect migration due to ion diffusion could be the source of Frenkel defects (FDs) that consist of a positively charged vacancy defect and a negatively charged interstitial defect.³¹ To the best of our knowledge, very limited studies have been performed to mainly focus on the activation barriers of Frenkel pairs in HOIPs,³²⁻³⁴ so further studies on the properties of FDs are largely demanded. Notably, with the help of the high-resolution X-ray photoelectron spectroscopy (XPS) technique, an obvious shift of iodine 3d and lead 4f core-level energies has been experimentally resolved in MAPbI₃ films under light irradiation, whereas the core-level spectra before and after light illumination are hardly affected in MAPbI₃ single crystals.³⁵ Such contrasting behaviors in MAPbI₃ films and single crystals demand a careful exploration towards the photophysical properties of FDs in MAPbI₃.

Iodine-related defects exhibit low formation energies and migration barriers,^{12,36} so the negatively charged iodine interstitial (I_i^-) and positively charged iodine vacancy (V_I^+) pairs are relatively abundant in MAPbI₃ films as supported by experiments.²¹ Here, we sought to combine density functional theory (DFT) and time-dependent DFT (TDDFT) approaches to study the behavior of MAPbI₃ in the presence of iodine FDs. We show the spatial extent of photogenerated e–h pairs in MAPbI₃ with one isolated iodine FD, labeled as MAPbI₃-FD1, and two interactive iodine FDs, referred to as MAPbI₃-FD2. These results are also compared with those of MAPbI₃ with iodine point defects, which provides a deep insight of FDs into the e–h dissociation and electron transfer in MAPbI₃ films.

2. Computational details

While the MAPbI₃ in the tetragonal phase is stable at room temperature,³⁷ the MAPbI₃ in the cubic phase is adopted in this work based on the considerations below. Firstly, the theoretical calculations suggested that the properties of traps are not affected by crystalline phases.^{12,20,38} Secondly, the lattice parameters of the $4 \times 4 \times 4$ supercells in the cubic phase (a = 6.33 Å) are larger than the screening radius (~0.8 nm) around a point defect,³⁹ so the interactions between the native point defects and their images are largely negligible. Thirdly, the screening distance between different Frenkel defects is enlarged as much as possible to weaken their interactions. Fixing the cell parameters of the cubic crystalline phase,⁴⁰ the primitive cell



Fig. 1 Effects of photoexcitation in MAPbI₃-FD1. (a) The positions of one Frenkel pair in MAPbI₃-FD1. The ion in magenta represents the position of the V_1^+ defect and the ion in orange represents the position of the I_i^- defect. (b) Lowest excited-state charge densities of MAPbI₃-FD1 in the ground-state (GS) geometry. (c) Lowest excited-state charge densities of MAPbI₃-FD1 in the excited-state (ES) configuration. In (b and c), the electron (hole) density is shown in red (yellow) and the value of the iso-surface is $2.0 \times 10^{-3} \text{ e } \text{Å}^{-3}$. (d) DOS of MAPbI₃-FD1 in both the ground-state and excited-state geometries. The discrete trap state is highlighted with the arrow. (e) Atomic displacements in MAPbI₃-FD1 from the ground-state geometry in (b) to the excited-state geometry in (c). (f) The ions with the largest displacements. Pb²⁺ ions (solid black) and I⁻ ions (solid red) in (e) are shown with the same color.

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is periodically expanded, generating a $4 \times 4 \times 4$ supercell (namely 64 MAPbI₃ units) with 768 ions in the paraelectric configuration where the MA cations have random orientation in the supercell. One or two Frenkel defects are then created in different spatial domains. Based on the projected augmented wave pseudopotentials and the Perdew-Burke-Ernzerhof (PBE) functional, the ground-state geometric optimization is carried out by using the DFT approach with a plane-wave basis set, as implemented in the Vienna ab initio simulation package (VASP).⁴¹ The valence electrons of 4, 7, 4, 5 and 1 are treated for atoms of Pb, I, C, N and H species, respectively. All the DFT calculations are performed with a cutoff energy of 400 eV at the Γ point which has been shown to be sufficient in predicting the band gap and defective properties for the lead halide perovskites.¹¹ The convergence criteria for energy and forces are set to be 10^{-4} eV and 0.04 eV Å⁻¹, respectively. Based on the fully optimized ground-state geometries, a recently developed large-scale TDDFT approach is employed to assess the photoinduced excited-state geometries and primary excitations.42 In this scheme, the ionic forces and charge densities in the excited state are calculated by the derivatives of the Lagrangian functional with respect to the ionic position and external potential, respectively. In both the ground-state and excitedstate calculations, the semi-empirical DFT-D2 method is used

to account for the van der Waals corrections.43 Since the

reasonable band gap produced by the PBE functional originates

from a cancelation of two effects, namely the lack of spinorbital interactions and the self-interaction error inherent to pure DFT functionals,⁴⁴ the results obtained by the PBE functional are validated by carrying out calculations including spin-orbital coupling (SOC) corrections and applying an optimally tuned range-separated hybrid (OT-RSH) functional.⁴⁵ In order to reproduce the fundamental band gap from the GW calculations,^{46,47} the range-separation parameter is set to be zero which has been used in our recent work for MAPbI₃.²⁰ The XPS core level energies of ions in both the ground-state and excitedstate geometries are simulated with the initial-state approach,⁴⁸ which is performed in the VASP by recalculating the Kohn–Sham eigenvalues of the core states subsequent to the self-consistent determination of the charge density associated with the valence electrons.⁴⁹

3. Results and discussion

It is noted that a tightly bound I_i^-/V_I^+ pair could dissociate *via* successive diffusion of iodine ions,³² but the iodine ion diffusion is complicated by coupling with the orientational MA cations which occurs in sub-picoseconds.^{50,51} Hence, the mechanism of iodine ion diffusion in MAPbI₃ is beyond the scope of this work. For simplicity, we study paraelectric MAPbI₃-FD1 which holds spatially separated I_i^-/V_I^+ pairs (Fig. 1a). While the concentration



Fig. 2 Charge densities and DOS in MAPbl₃-FD1. (a and b) Lowest excited-state charge densities of MAPbl₃-FD1 with the l_i^- defect oriented by the nearest $-NH_3$ moieties of MA cations in ground-state and excited-state geometries, respectively. (c) DOS of ground-state geometry in (a) and excited-state geometry in (b). (d and e) Lowest excited-state charge densities of MAPbl₃-FD1 with the l_i^- defect oriented by the nearest $-CH_3$ groups of MA cations in ground-state geometries, respectively. (f) DOS of ground-state geometry in (d) and excited-state geometry (e). The discrete in-gap states are highlighted with the arrows in (c and f). The electron (hole) density is shown in red (yellow) and the value of the iso-surface is 2.0×10^{-3} e Å⁻³ in (a), (b), (d) and (e).

of the iodine FDs is as high as 10^{19} – 10^{20} cm⁻³ in this work, Walsh et al. have suggested that the defect concentrations in MAPbI₃ can reach this level.⁵² At any given "instantaneous" configuration for which the MA ions are static, the electronic excitation in the ground-state configuration is delocalized (Fig. 1b), yielding both shallow hole and electron trap states as supported by the density of states (DOS) (Fig. 1d). In the excitedstate geometry, however, the electronic excitation turns to be rather localized in the vicinity of the V_I⁺ defect (Fig. 1c). A discrete in-gap electron trap resolved in the excited state (Fig. 1d) originates from the local geometric deformation (Fig. 1e) in the vicinity of the V_{I}^{+} defect (Fig. 1f) when comparing the ground-state and excited-state geometries. Due to the Coulomb attraction between the photogenerated e-h pairs, the holes are trapped by the electrons in the trap, forming a tightly bound polaronic exciton surrounding the V_I^+ defect. We note that the I_i⁻ defect itself has a marginal effect on the charge localization (Fig. S1a and b, ESI⁺), whereas the V_I⁺ defect itself promotes the crossover of charge densities from the spatial extension to local confinement (Fig. S1c and d, ESI⁺).²⁰ Therefore, the tightly bound polaronic exciton in the excited state is induced by the V_I^+ defect.

Since the dipolar MA cations can affect the charge distributions in the vicinity of defects by interacting with the inorganic lattice,⁵³ the effect of the dynamical MA cations on the nature of the e–h pairs is explored by reorienting the first neighboring MA cations

surrounding the I_i^- and V_I^+ defects, respectively. In the case of MAPbI₃-FD1 with the I_i⁻ defect oriented by the nearest -NH₃ moieties, both charge densities and DOS show a similar crossover to those in Fig. 1 when going from the ground state to the excited state (Fig. 2a-c), yielding a tightly bound polaronic exciton in the excited state. When the I_i^- defect is oriented by the nearest $-CH_3$ moieties, however, hole densities turn to be slightly confined in the ground state (Fig. 2d) and become rather localized in the excited state (Fig. 2e). In this case, the e-h pair gets separated in the excited state and both hole and electron in-gap traps are resolved (Fig. 2f). Due to the attractive (repulsive) interactions between the positively (negatively) charged -NH₃ (-CH₃) groups and I_i^- defect, the former case is ~15 meV nm⁻³ smaller than the latter case in the excited state, indicating that a tightly bound polaronic exciton is preferably formed. In the case of MAPbI₃-FD1 with the V_{I}^{+} defect oriented by the nearest -NH₃ groups, MAPbI₃-FD1 shows similar charge distribution (Fig. 3a and b) and DOS (Fig. 3c) to those in Fig. 1. By contrast, the reversed MA cations closely surrounding the V_I^+ defect, namely the $-CH_3$ groups oriented towards the VI⁺ defect, prompt the spatially extended charge densities (Fig. 3d and e); concurrently, the discrete in-gap trap cannot be resolved in the excited state (Fig. 3f). The excited-state energy of the latter configuration is energetically $\sim 20 \text{ meV nm}^{-3}$ smaller than the former configuration because of the attractive (repulsive) interactions between the negatively (positively) charged $-CH_3$ ($-NH_3$) groups and V_1^+ vacancy. This is in



Fig. 3 Charge densities and DOS in MAPbl₃-FD1. (a and b) Lowest excited-state charge densities of MAPbl₃-FD1 with the V_1^+ defect oriented by the nearest $-NH_3$ groups of MA cations in ground-state and excited-state geometries, respectively. (c) DOS of ground-state geometry in (a) and excited-state geometry in (b). (d and e) Lowest excited-state charge densities of MAPbl₃-FD1 with the V_1^+ defect oriented by the nearest $-CH_3$ moieties of MA cations in ground-state geometries, respectively. (c) DOS of ground-state geometry in (a) and excited-state geometry in (b). (d and e) Lowest excited-state charge densities of MAPbl₃-FD1 with the V_1^+ defect oriented by the nearest $-CH_3$ moieties of MA cations in ground-state and excited-state geometries, respectively. (f) DOS of ground-state geometry in (d) and excited-state geometry in (e). The discrete in-gap state in (c) is highlighted with the arrow. The electron (hole) density is shown in red (yellow) in (a), (b), (d) and (e). The value of the iso-surface is 2.0×10^{-3} e Å⁻³ in (a and b) as well as 1.0×10^{-3} e Å⁻³ in (d and e).

line with our recent work which reports that the deep electron traps (Fig. 1c and d) could be healed by the reorientation of MA cations. Taken together, the tightly bound polaronic exciton formed in paraelectric MAPbI₃-FD1 is largely controlled by the electrostatics between the dipolar MA cations and the charged native point defects.

We then move to MAPbI₃-FD2 by generating an iodine FD in MAPbI₃-FD1. The two iodine FDs in MAPbI₃-FD2 are interactive by keeping their distance smaller than the screening radius $(\sim 0.8 \text{ nm})$ ³⁹ so the change of defect properties in MAPbI₃-FD2 with respect to MAPbI₃-FD1 is contributed by the newly created Frenkel pair. It is noted that, when the iodine ion of the second Frenkel pair is close to the iodine ion of the first Frenkel pair, the I_i⁻ defect in MAPbI₃-FD1 moves to an adjacent inorganic cavity (Fig. 4a), indicating the correlation of the relative positions of iodine ions owing to their repulsive interactions. In analogy to MAPbI₃-FD1, the delocalized electronic excitation in the ground state is sustained (Fig. 4b and d). Very strikingly, however, MAPbI₃-FD2 in the excited state exhibits spatially separated hole-rich and electron-rich domains (Fig. 4c), which is sharply different from the case in MAPbI₃-FD1, which confines both holes and electrons in the vicinity of the V_{I}^{+} defect. We verify that regardless of the position of I_i⁻ defects (Fig. S2a, ESI^{\dagger}) and V_I⁺ defects (Fig. S2b, ESI^{\dagger}) of the second Frenkel pair, a fraction of holes and electrons remain spatially separated (Fig. S2c and d, ESI[†]). These suggest consistently that

a fraction of holes is pulled out from the V_I⁺ defects in MAPbI₃-FD2, manifesting that the second Frenkel pair promotes the e-h separation. The reasons are analyzed as follows. Analogous to MAPbI₃-FD1, the ions with the largest distortions (Fig. 4e) are located in the vicinity of the V_I^+ defects (Fig. 4f) when going from the ground state to the excited state. The geometric deformation is thus excluded from contributing to the separated e-h pair. Since the MAPbI₃ with two I_i⁻ defects shows spatially extended hole and electron excitation (Fig. S3a and b, ESI^{\dagger}) and the MAPbI₃ with two V_I⁺ defects confines both holes and electrons in the vicinity of V_1^+ defects (Fig. S3c and d, ESI⁺), we attribute the spatially confined holes and electrons in different domains of MAPbI3-FD2 to the enhanced Coulomb attraction between the two Ii⁻ ions and hole densities. While the trapped electrons tend to attract holes, the Coulomb interaction between Ii⁻ ions and hole densities is increased in MAPbI₃-FD2 compared to MAPbI₃-FD1, thus pulling out the holes from the electron traps. This is supported by the separated e-h pair when the Ii⁻ defect is oriented by the nearest -CH₃ groups of MA cations (Fig. 2e). We validate that (i) the discrete in-gap traps in Fig. 1 and 4 are not affected by including SOC corrections (Fig. S4a and d, ESI[†]) and by treating the long-range e-h interactions with the OT-RSH functional⁴⁵ (Fig. S4b and e, ESI[†]); (ii) the charge distributions predicted by the OT-RSH functional (Fig. S4c and f, ESI†) differ weakly from those predicted by the PBE functional (Fig. 1c and 4c), which is



Fig. 4 Effects of photoexcitation on MAPbI₃-FD2. (a) The positions of two Frenkel pairs in MAPbI₃-FD2. The ions in magenta represent the position of V_1^+ defects and the ions in orange represent the position of I_1^- defects. (b) Lowest excited-state charge densities of MAPbI₃-FD2 in ground-state geometry. (c) Lowest excited-state charge densities of MAPbI₃-FD2 in the excited-state configuration. In (b and c), the electron (hole) density is shown in red (yellow) and the value of the iso-surface is 2.0×10^{-3} e Å⁻³. (d) DOS of MAPbI₃-FD2 in both the ground-state and excited-state geometries. The discrete trap state is highlighted with the arrow. (e) Atomic displacements in MAPbI₃-FD2 from the ground-state geometry in (b) to the excited-state geometry in (c). (f) The ions with the largest displacements. Pb²⁺ ions (solid black) and I⁻ ions (solid red) in (e) are shown with the same color.

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likely due to the large dielectric permittivity (thus strong electrostatic screening) in MAPbI₃.^{54,55} Therefore, the most important finding in this study is that multiple interactive iodine FDs can promote the dissociation of the tightly bound polaronic excitons induced by the isolated iodine FDs in MAPbI₃.

Notably, the XPS technique has resolved that the I 3d and Pb 4f core levels exhibit ~ 0.69 eV energy shifts toward lower binding energy in MAPbI₃ films and are marginally affected in MAPbI₃ single crystals under light illumination.³⁵ As the experimentally prepared MAPbI₃ single crystals are expected to have much lower trap density as compared to the MAPbI₃ films, MAPbI₃-FD1 bearing isolated iodine FDs may correspond to the experimentally prepared MAPbI₃ single crystals and MAPbI₃-FD2 which holds interactive iodine FDs may map to the experimentally prepared MAPbI3 films. According to such correspondence, our simulated XPS results are consistent with the experimental findings. When comparing the simulated XPS results between pristine MAPbI₃ and MAPbI₃-FD1, the binding energies of I 3d and Pb 4f core levels in pristine MAPbI₃ are weakly affected in the ground state (Fig. 5a and b) because a tiny fraction of electrons moves from the ions in the vicinity of the V_{I}^{+} defect to the ions surrounding the I_{i}^{-} defect (Fig. 6a).

Since the charge carriers reshuffle upon photoexcitation, a fraction of electrons belonging to the iodine and lead ions in the vicinity of the V_I^+ defect is captured by the electron traps (Fig. 6b). Therefore, the binding energies of I 3d and Pb 4f core levels show asymmetric variations in the excited state, namely a weak change toward low binding energy and a strong shift toward high binding energy (Fig. 5c and d). Importantly, the isolated iodine FDs can hardly lower the binding energies of I 3d and Pb 4f core levels, which is in line with the experimentally resolved I 3d and Pb 4f core levels in MAPbI₃ single crystals under light irradiation.³⁵

The picture changes a lot when focusing on MAPbI₃-FD2. Compared to MAPbI₃-FD1, there is a slightly stronger electron redistribution within the inorganic framework for MAPbI₃-FD2 in the ground state (Fig. 5a and b). The electrostatics induce the electron densities from the ions in the vicinities of the two V_I^+ defects to the ions surrounding the two I_i^- defects (Fig. 6c). In the excited state, the two V_I^+ defects tend to localize the electrons which could in turn have tendency to attract the holes. However, the electron-rich domain (Fig. 6d) contributed by the two I_i^- defects in MAPbI₃-FD2 has stronger attraction to the holes than the case in MAPbI₃-FD1, so a fraction of holes is pulled out from the electron traps (Fig. 4c). Resultantly, the



Fig. 5 DFT-calculated core-level energies of pristine and defective MAPbI₃. (a) I 3d core-level energies for pristine MAPbI₃, MAPbI₃-FD1 and MAPbI₃-FD2 in the ground-state geometries. (b) Pb 4f core-level energies for pristine MAPbI₃, MAPbI₃-FD1 and MAPbI₃-FD2 in the ground-state geometries. (c) I 3d core-level energies for pristine MAPbI₃-FD1 and MAPbI₃-FD2 in the excited-state geometries. (d) Pb 4f core-level energies for pristine MAPbI₃-FD2 in the excited-state geometries. (d) Pb 4f core-level energies for pristine MAPbI₃-FD1 and MAPbI₃-FD2 in the excited-state geometries. (d) Pb 4f core-level energies for pristine MAPbI₃-FD2 in the excited-state geometries.



Fig. 6 The charge transfer from pristine MAPbl₃ to defective MAPbl₃ in both the ground state and excited state. (a) Charge transfer in the ground-state configurations from pristine MAPbl₃ to MAPbl₃-FD1. (b) Charge transfer in the excited-state configurations from pristine MAPbl₃ to MAPbl₃-FD1. (c) Charge transfer in the ground-state configurations from pristine MAPbl₃ to MAPbl₃-FD2. (d) Charge transfer in the excited-state configurations from MAPbl₃ to MAPbl₃-FD2. The ions in magenta and in orange represent the positions of V₁⁺ and I_i⁻ defects, respectively. The ions in larger size highlighted by the lines in magenta lose electrons, leading to the increase of binding energies in Fig. 5. By contrast, the ions in larger size highlighted by the lines in orange obtain electrons, leading to the decrease of binding energies in Fig. 5.

binding energies of I 3d and Pb 4f core levels become significantly lower in the excited state (Fig. 5c and d) than those in the ground state (Fig. 5a and b). The ~ 0.60 eV energy shifts toward lower binding energy (Fig. 5c and d) are consistent with the experimental findings in MAPbI₃ films, implying that the experimentally resolved electron transfer may be induced by the interactive iodine FDs.

4. Conclusions

In this work, MAPbI₃ in the presence of both isolated and interactive iodine FDs is investigated with the combination of DFT and TDDFT approaches. In MAPbI₃ with isolated iodine Frenkel pairs, charge transfer occurs weakly in the ground-state geometries from the neighborhood of V_I⁺ defects to the neighborhood of I_i⁻ defects. Upon photoexcitation, substantial geometric distortions are resolved in the vicinity of V_I⁺ defects which yield deep in-gap electron traps. The electrons are thus trapped close to the V_I^+ defects, manifested by the increase of binding energies of iodine and lead ions in the vicinity of V_1^+ defects. Owing to the e-h correlation, the holes are pulled to the proximity of the spatially confined electrons in MAPbI₃ with isolated iodine FDs, thus forming the tightly bound polaronic excitons. Strikingly, a fraction of holes and electrons become spatially separated in the excited-state geometries of MAPbI₃ in the presence of interactive iodine FDs, which is ascribed to the stronger Coulomb attraction of I_i^- defects to the holes. Hence, multiple FDs could promote the dissociation of the polaronic excitons in defective MAPbI₃, providing a plausible explanation for the long carrier lifetime and diffusion length in MAPbI₃ films. The photoinduced electron transfer in MAPbI₃-FD2 is in line with the changes of I 3d and Pb 4f core levels resolved by the XPS technique in MAPbI₃ films under light irradiation. Besides, the charge distributions in defective MAPbI₃ are largely affected by the dipolar MA cations, suggesting that the optoelectronic behavior in defective MAPbI₃ is complicated by the electrostatics between defects and the organic cations.

Conflicts of interest

There are no conflicts of interest to declare.

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