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Electronic structure of Li$^+@C_{60}$ adsorbed on methyl-ammonium lead iodide perovskite CH$_3$NH$_3$PbI$_3$ surfaces

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Abstract

It was recently shown by Jeon et al. [Angewandte Chem. 2018, 57, 4607] that air stability more than 1000 hours under light illumination can be achieved in methyl-ammonium (MA) lead iodide perovskite solar cells, when Li$^+$ is replaced by Li$^+@C_{60}$ in a dopant material used in the p-type donor layer. In order to demonstrate the role of Li$^+@C_{60}$ in the hole transporting material, we carry out first-principles electronic structure calculations of Li$^+@C_{60}$ adsorbed on MAPbI$_3$ using the van der Waals corrected density functional theory. We use finite slab models of tetragonal MAPbI$_3$ (001) surfaces with MAI terminations. Using the most stable MAPbI$_3$ surfaces, we introduced one Li$^+@C_{60}$ molecule on various position of the MAI surface and performed geometrical optimizations. Then, we found that the Li$^+@C_{60}$ is adsorbed at the aboveC position with almost 100% ionized. There is not much difference between the top and bottom positions of Li$^+$ inside C$_{60}$, but the bottom position is slightly more stable than the top position. In the MAPbI$_3$/Li$^+@C_{60}$ system, the Kohn-Sham (KS) wave functions of the HOMO and HOMO-1 levels are spread out in MAPbI$_3$ and those of the LUMO, LUMO+1, LUMO+2 levels are localized in Li$^+@C_{60}$; the energy gap between these levels is 0.6 eV. Thus, in the neutral, spin-polarized MAPbI$_3$/Li$^+@C_{60}$ system, the KS wave functions of the HOMO (SOMO, - spin) and LUMO (+ spin) levels are both localized in Li$@C_{60}$ and their energy gap of 0.125 eV is very small. This HOMO (SOMO) level behaves as a hole level when it loses an electron to become Li$^+@C_{60}$. Since there are three almost degenerate LUMO+1 and LUMO+2 levels, it is expected to behave as a good hole conductor. Due to this fact, we conclude that the use of Li$^+@C_{60}$ molecules in place of the bare Li ions as dopant materials in the MAPbI$_3$ solar cells can prevent from degradation. In any case regardless to the adsorption geometry, our results clearly show the existence of the energetically isolated hole level localized in the Li$@C_{60}$, which may successfully contribute to the suppression of the oxidation of the MAPbI$_3$ surface.
Introduction

Methyl-ammonium (MA) lead halide perovskites such as CH$_3$NH$_3$PbI$_3$ (hereafter abbreviated to MAPbI$_3$) have attracted significant attention since the discovery of an efficient photovoltaic behaviour of the heterojunction of MAPbI$_3$ and TiO$_2$ by Miyasaka’s group in 2009.$^{1-3}$ So far, various heterojunction systems overlaid with SnO$_2$, C$_{60}$, C$_{60}$ derivatives like PCBM, and so on have been proposed by many researchers, and the light-current energy conversion efficiency has rapidly increased from 3.8%$^1$ to over 20%$^3$-$^7$. In a typical architecture of perovskite solar cells (PSCs), MAPbI$_3$ works as a photo-absorber and is sandwiched by an $n$-type acceptor layer and a $p$-type donor layer. The former is made of the electron transporting material (ETM) such as C$_{60}$ and C$_{60}$ derivatives and the latter is made of the hole transporting material (HTM) such as 2,2’,7,7’-tetrakis(N,N-di-p-methoxyphenylamine)-9,9’-spirobi-fluorene (spiro-MeOTAD) and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)$^2, 8$-$^{11}$.

Although the application of Spiro-MeOTAD as a HTM in PSCs$^2, 12$ has made an important step in improving the energy conversion efficiency, the low long-term stability under light illumination and coexistence of oxygen and water has been a serious drawback of PSCs for a commercial use$^{13}$-$^{15}$. In particular, the dopants used in the HTM suffer from degradation.$^{13}$-$^{17}$ In order to reduce degradation, Jeon et al.$^{18}$ proposed to use Li ion encapsulated C$_{60}$ (Li$^+$@C$_{60}$)
instead of bare Li ion (Li\(^+\)) in combination with bis(trifluoromethanesulfonylimide (TFSI\(^-\)) as a p-type dopant. Using this dopant, they reported that spiro-MeOTAD\(^+\)TFSI\(^-\) functions as an effective HTM and Li\(^+@C_{60}\) functions as an antioxidant, reacting with intruding oxygen. By preventing unnecessary oxidation in the device system, [Li\(^+@C_{60}\)]TFSI\(^-\) devices achieved stability approximately 7-fold that of conventional Li\(^+\)TFSI\(^-\) devices in MAPbI\(_3\)-based PSCs, and 10-fold in a more stable mixed ion lead halide PSCs. Consequently, the passivated PSCs showed no decrease in the energy conversion efficiency for more than 1000 hours while being continuously illuminated under ambient conditions.

Atomistic modelling and simulation based on first-principles density functional theory (DFT) can play an important role to reveal the underlying mechanisms of the high performance of PSCs.\(^{19-21}\) Yin et al.\(^{22}\) studied the energy alignment and charge transfer properties at the interface between MAPbI\(_3\) perovskites and Spiro-MeOTAD and PCBM. They found that the MAPbI\(_3\) (001) and (110) surfaces favor hole injection to the hole acceptor Spiro-MeOTAD, whereas the polar MAPbI\(_3\) (001) surface facilitates electron transfer to the PCBM. However, concerning the reduction of degradation of PSCs, the role of Li\(^+@C_{60}\) adsorbed on the MAPbI\(_3\) surface in the experiment by Jeon et al.\(^{18}\) remains unclear. Therefore, the purpose of this paper is to investigate the electronic structure of Li\(^+@C_{60}\) adsorbed on the MAPbI\(_3\) surface. The mass production of Li\(^+@C_{60}\) was achieved by a plasma shower method,\(^{23}\) which was suggested by a first-principles molecular dynamics study\(^{24}\) and experiments\(^{25, 26}\). The maximum production ratio in this method is theoretically estimated to be about 3.7\%.\(^{27}\) Now Li\(^+@C_{60}\) has many possibilities of applications.\(^{28-33}\)

**Computational Methods**
First-principles all-electron calculations were performed by using DMol³ package, which adopts numerical atomic orbitals. A standard DFT dispersion (DFT-D) correction was employed to take into account van der Waals interaction in the Tkatchenko-Scheffler (TS) scheme. This method is formally identical to DFT-D2 method of Grimme but the dispersion coefficients and damping function are charge-density dependent. The DFT-TS method can therefore handle the change in the vdW contribution of atoms due to their chemical environment.

In the present study, we consider a slab model of tetragonal phase of MAPbI₃ (001) with MAI-terminated surfaces. The slab model has a 2 × 2 periodicity in-plane and four MAI-layer thick with 50 Å vacuum regions between the slabs are assumed, which are large enough to avoid the interaction between periodic images. The MAPbI₃ slab model and endohedral Li⁺@C₆₀ fullerene were first optimized to achieve the minimum energy. We introduce one Li⁺@C₆₀ molecule on the MAPbI₃ (001) layer, forming a hybrid MAPbI₃/Li⁺@C₆₀ structure with a total of 445 atoms. For the MAPbI₃/Li⁺@C₆₀ interface, the dipole slab correction for the electrostatic potential is taken into account in the calculations due to the existence of polar bonds.

All calculations (except for perovskites with bare surfaces) were performed based on the spin unrestricted, i.e., spin-polarized, approach using the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) form for the exchange-correlation functional. We have ignored spin-orbit coupling (SOC) because the PBE functional can provide reasonable estimation on structural, electronic and optical properties. The double-numerical quality basis, i.e., double numerical plus polarization (DNP) function, was employed for all calculations. The size of these DNP basis set is comparable to that of the Gaussian 6-31G**. In the calculation, the geometrical optimization was performed with the Fermi smearing of 0.005 hartree. The tolerances
of the energy, gradient, and displacement convergences were set at $1 \times 10^{-5}$ Ha, $2 \times 10^{-3}$ Ha/Å, and $5 \times 10^{-3}$ Å, respectively.

**Results & Discussion**

MAPbI$_3$ undergoes a structural phase transition from a cubic to a tetragonal phase at temperature $\sim 330$ K, and it becomes an orthorhombic structure at temperature below 160K. In the present study, the room-temperature tetragonal phase of MAPbI$_3$ is chosen as the model structure for studying the structural and electronic properties in the Li@C$_{60}$ adsorbed geometries. The computationally optimized cell parameters for the bulk tetragonal phase of MAPbI$_3$ are $a = 8.70$ Å, $b = 8.72$ Å and $c = 12.83$ Å, which are comparable to experimental values. A typical PSC has asymmetric interfaces ETM/MAPbI$_3$/HTM. Therefore, we consider an asymmetric slab model with the MAI as the top surface layer (facing the vacuum layer) and the PbI layer as the bottom layer of MAPbI$_3$. Here, the MAI-terminated surface is set as the MAPbI$_3$ top surface because this surface facilitates the electron transfer to the C$_{60}$ ETM.

Many studies show that the MA orientation play important role in governing the stability and electronic structures of MAPbI$_3$. The orientation of MA molecule has a significant effect on the charge mobility, the bandgap change and photo-energy conversion efficiencies. Neutron scattering measurements suggested the formation of either antiferroelectric or ferroelectric domains in these perovskites based on the ordered orientation of MA cations. However, the highly disordered orientation of MA cation at room temperature excludes the possibility of spontaneous polarization in the antiferroelectrics or ferroelectrics due to the ordered orientation of MA cations. In order to take into account the MA orientations effect, we consider
three orientations of MA cation with respect to the top surface as shown in Fig. 1: (i) the topC model with the CH$_3$ group pointing up in all layers, (ii) the topN model with the NH$_3$ group pointing up in all layers, and (iii) the apolar model with half of -NH$_3$ or -CH$_3$ groups pointing up and half pointing down. We first look at the energetics of the slab models. In Table 1, we summarize the valence band edge (VBE), conductance band edge (CBE), band gap, and the total relative energies of the tetragonal MAPbI$_3$ perovskites with bare surface. The calculated VBE and CBE for the bare-surface tetragonal MAPbI$_3$ are -4.66 to -5.37 eV and -3.55 to -3.88 eV, respectively. Among them, the topC orientation is the most stable structure with the bandgap of 1.48eV in agreement to other works.$^{49}$ Since the topC model is the most stable structure, we will focus on the tetragonal MAPbI$_3$ perovskites with the topC orientation by introducing a Li$^+$@C$_{60}$ molecule on various MAPbI$_3$ surfaces: the aboveC, aboveI and bridge positions (see Fig. S1-S3 of the Supplementary Information). In each case, we examine the effect of the Li$^+$ located at the off-central top and bottom inside the C$_{60}$ cage on the electronic structures of the MAPbI$_3$/ Li$^+$@C$_{60}$ system. Hereafter, we denote the Li$^+$(top)$@C_{60}$ and Li$^+$(bottom)$@C_{60}$ molecules as the lithium-Ion endohedral fullerene with the Li$^+$ located at the off-central “top” and “bottom” inside the C$_{60}$ cage, respectively.

Using the most stable topC model, we introduced one Li$^+@C_{60}$ molecule on the aboveC, aboveI and bridge positions of the MAI surface and performed geometrical optimizations. Figure 2(a) shows the total energy of the MAPbI$_3$/Li$^+@C_{60}$ system relative to the case with a Li$^+$(bottom)$@C_{60}$ on the aboveC geometry. The corresponding HOMO, LUMO and band gap are shown in Fig. 2(b). The binding energy of the MAPbI$_3$/Li$^+@C_{60}$ system for three different geometries and the binding energy of the MAPbI$_3$/Li@C$_{60}$ system for the aboveC geometry is shown in Fig. 3. In general, the stability of the MAPbI$_3$/Li$^+@C_{60}$ system is in the order of a
Li\(^+\)@C\(_{60}\) on the aboveC > bridge > aboveI position. From Fig. 3, the binding energy of the MAPb\(_3\)/Li\(^+\)@C\(_{60}\) system also increases in the order of a Li\(^+\)@C\(_{60}\) on the aboveC > bridge > aboveI geometry, which further confirm the stability of the MAPb\(_3\)/Li\(^+\)@C\(_{60}\) system. In addition, the MAPb\(_3\)/Li\(^+\)@C\(_{60}\) system is energetically more stable than the MAPb\(_3\)/ Li\(^+\)@C\(_{60}\) system for the same geometry (see Fig. 2(a)), which is also consistent with the binding energies of the MAPb\(_3\)/Li\(^+\)@C\(_{60}\) system (see Fig. 3)). Although the iodine has a high electronegativity, a Li\(^+\)@C\(_{60}\) adsorbed on the aboveI position of CH\(_3\)NH\(_3\)PbI\(_3\) surfaces is energetically less favorable compared to other geometries. Among the MAPb\(_3\)/Li\(^+\)@C\(_{60}\) system, a Li\(^+\)(bottom)@C\(_{60}\) absorbs on the aboveC geometry of MAPb\(_3\) surface is the most stable structure with the strongest binding energy of -3.193 eV (Fig. 3) and the highest bandgap value of 0.626 eV (Fig. 2(b)).

For the MAPb\(_3\)/Li\(^+\)(bottom)@C\(_{60}\) system, the LUMO varies from -5.708 eV to -5.763 eV and the HOMO has a value range from -6.322 eV to -6.369 eV, leading to a bandgap value in the range from 0.575 eV to 0.626 eV. Compared with the MAPb\(_3\)/Li\(^+\)@C\(_{60}\) system, the MAPb\(_3\)/Li\(^+\)(top)@C\(_{60}\) system has a slightly lower bandgap ranging from 0.563 eV to 0.603 eV; the LUMO varies from -5.672 eV to -5.706 eV and the HOMO varies from -6.260 to -6.309 eV. It is interesting to note here that the MAPb\(_3\)/Li\(^+\)@C\(_{60}\) system with the aboveC (aboveI) geometry has the largest (smallest) bandgap value of 0.603 (0.563) eV and 0.626 (0.575) eV for the Li\(^+\) located at the off-central “top” and “bottom” inside the C\(_{60}\) cage, respectively.

Since the MAPb\(_3\)/Li\(^+\)@C\(_{60}\) system with the aboveC geometry is the most stable structure, we calculate and compare the electronic structures of the MAPb\(_3\)/Li\(^+\)@C\(_{60}\) system with a neutral lithium endohedral fullerene Li@C\(_{60}\) absorbed on the aboveC geometry of MAPb\(_3\) surface (MAPb\(_3\)/Li@C\(_{60}\)). The total energy relative to the MAPb\(_3\)/Li(bottom)@C\(_{60}\) with the aboveC geometry is depicted in Fig. 2(a), which is very small, i.e. ~0.008 eV, compared to the
MAPbI$_3$/Li$^+@C_{60}$ system. Since the binding energy of the MAPbI$_3$/Li$^+@C_{60}$ system is smaller than that of the MAPbI$_3$/Li$^+@C_{60}$ system by over 1.5 eV as shown in Fig. 3, Li$^+@C_{60}$ has a great tendency to become a good hole conductor by absorbing a hole. From Fig. 2(b), it is seen that the MAPbI$_3$/Li(top)$@C_{60}$ has a small band gap of 0.125 eV, which is independent of the off-central position of Li and is smaller than the bandgap of the MAPbI$_3$/Li$^+@C_{60}$ system by a factor of 5. The LUMO and HOMO (SOMO) of the MAPbI$_3$/Li$^+@C_{60}$ system are ~ -5.0 eV and ~ -5.1 eV, respectively, which are relatively higher than those of the MAPbI$_3$/Li$^+@C_{60}$ system (see Fig. 7).

When two atoms of opposite charge form two molecular species are in proximity within the sum of their van der Waals (vdW) radii, a non-covalent intermolecular interaction may form between the molecules.$^{50-52}$ At the interface between the Li$^+@C_{60}$ (or the Li$@C_{60}$) molecule and the topC-oriented MAPbI$_3$, the C atoms of C$_{60}$ may interact with MAPbI$_3$ surface via the I atoms of PbI$_3$ and H (or C) atoms of MA, as shown in Figs. 4 and S4-S11 (Supplementary Information). The vdW radii of C, H and I are 1.77 Å, 1.20 Å and 2.04 Å, respectively.$^{53}$ This indicates that any C···H(-C) distance < 2.97 Å, C···C(-H3) distance < 3.54 Å, or C···I(-Pb) distance < 3.81 Å may signify a potential interaction between Li$^+@C_{60}$ and MAPbI$_3$ surface. Based on this criterion, we conduct a simple analysis on the interactions at the MAPb$_3$I/Li$^+@C_{60}$ interface for three different geometries. We also examine the MAPbI$_3$/Li$@C_{60}$ system with a neutral lithium endohedral fullerene Li$@C_{60}$ absorbed on the aboveC geometry of MAPbI$_3$. In Table 2, we summarize the atomic distance of selected atoms/molecules (fragments) located at the MAPbI$_3$/Li$^+@C_{60}$ interface, as well as the MAPbI$_3$/Li$@C_{60}$ interface. A more comprehensive analysis of results can be found in Figs. S4-S11 in Supplementary Information.

Let us now correlate the findings in Table 2 with the stability (Fig. 2(a)) and the binding energy (Fig. 3) of the MAPbI$_3$/Li$^+@C_{60}$ system. From Fig. 2(a), we found that the energetically
most stable geometry of the MAPbI₃/Li⁺@C₆₀ system is the aboveC geometry and the next stable geometry is the aboveI position. However, both the aboveC and bridge geometries have the C···H(-C), C···C(-H) and C···I(-Pb) interactions. The results from Table 2 shows that the main difference between these two geometries is the C···H(-C) atomic distance: the aboveC geometry is in the ranges of 2.612Å – 2.660 Å, whereas it is in the ranges 2.791Å – 2.990 Å for the aboveI geometry. This suggest that the C···H(-C) interaction, i.e. the π-CH interaction, plays a crucial role in governing the stability of the MAPbI₃/Li⁺@C₆₀ system and the strength of binding between the MAPbI₃ and Li⁺@C₆₀. The MAPbI₃/Li⁺@C₆₀ system with the aboveI geometry is the least stable structure among the three geometries (though they have six C···I(-Pb) interactions with high-electronegative iodines), implying that the C···I(-Pb) interactions, i.e. the π-I interaction, contribute lesser compared with the C···H(-C) interactions. All the atomic distances C···H(-C), C···C(-H) and C···I(-Pb) of the MAPbI₃/Li⁺(bottom)@C₆₀ system are shorter than those of the MAPbI₃/Li⁺(top)@C₆₀ system. Therefore, the MAPbI₃/Li⁺(bottom)@C₆₀ system is energetically more stable than the MAPbI₃/Li⁺(top)@C₆₀ system for the structure with the same geometry (Fig. 2(a)). For the same geometry, the binding energies of the MAPbI₃/Li⁺(bottom)@C₆₀ system is also stronger than that of the MAPbI₃/Li⁺(top)@C₆₀ system. Although the MAPbI₃/Li⁺@C₆₀ system has a weak binding energy (Fig. 3), both the MAPbI₃/Li(top)@C₆₀ system and the MAPbI₃/Li(bottom)@C₆₀ system have six bond distance within the vdWs interactions (Figs. S4 and S5), i.e. three C···H(-C) in the ranges 2.618Å-2.673Å, two C···C(-H) in the ranges 3.538Å - 3.547Å, and one C···I(-Pb) in the ranges 3.744Å - 3.782Å, with a small energy difference of ~0.008 eV (Fig. 2(a)). Obviously, the stability of the Li@C₆₀ molecule is another important factor that contributes to the strength of binding between the MAPbI₃ perovskite and the Li@C₆₀ molecule, besides the atomic distances at the MAPbI₃/Li⁺@C₆₀ interface. Although this simple analysis may
provide a rough picture on the interaction at the MAPbI$_3$/Li$^+@C_{60}$ (or Li@$C_{60}$) interface, it is important to note that the calculated atomic distances using the GGA-PBE may not accurate. In addition, the lattice dynamics play an important role in determining the structural and electronic properties of these halide perovskites,$^{54-56}$ and the tetragonal structure of MAPbI$_3$ perovskite at room temperature is strongly anharmonic.$^{57}$

After gaining an understanding on the correlation between the stability and the vdW interactions at interface, we now investigate the atomic charge distribution at the interface between the MAPbI$_3$ perovskite and Li$^+@C_{60}$ (or Li@$C_{60}$). We perform an atomic charge analysis using the geometrical optimized structure of the MAPbI$_3$/Li$^+@C_{60}$ (and MAPbI$_3$/Li@$C_{60}$) system. We employ the Hirshfeld atomic population analysis, which is based on the electron density at individual atoms.$^{58,59}$ The Hirshfeld charges of individual Li@$C_{60}$ molecule and MAPbI$_3$ slab are 0.0e and - 0.005e, indicating that they possess neutral charge. On the other hand, the calculated Hirshfeld charge of individual Li$^+@C_{60}$ molecule has 0.998e ~ +1e, as expected. Table 3 summarizes the Hirshfeld atomic charges of selected fragments [CH$_3$] and [I] at the MAPbI$_3$/Li$^+@C_{60}$ interface. Q is the charge transferred from [MAPbI$_3$] to [Li$^+@C_{60}$]. [Li$^+@C_{60}$] and [MAPbI$_3$] denote the calculated Hirshfeld fragments of the MAPbI$_3$/Li$^+@C_{60}$ system. Calculated Hirshfeld atomic charges of a MAPbI$_3$ with a neutral lithium endohedral fullerene Li@$C_{60}$ are for only the aboveC position. A more detail analysis of Hirshfeld atomic charges of fragments [CH$_3$], [I], [Li], [Li$^+$] and [C] at the MAPbI$_3$/Li$^+@C_{60}$ interface with the Li$^+@C_{60}$ can be found in Table S2 of Supplementary Information. From Table 3, the MAPbI$_3$/Li@$C_{60}$ system also possess neutral charge similar to the Hirshfeld charge of individual Li@$C_{60}$ molecule and the MAPbI$_3$ slab, as expected. For the MAPbI$_3$/Li$^+@C_{60}$ system, the calculated Hirshfeld charge for all three
geometries including the Li$^+$ located at the off-central top and bottom positions inside the C$_{60}$ cage is $\sim +1.0e$ charge, which is the same as the isolated Li$^+@C_{60}$ molecule. In the MAPbI$_3$/Li$^+@C_{60}$ system, the amount of charge transfer Q from the MAPbI$_3$ to Li$^+@C_{60}$ increases in the order of bridge $>$ aboveI $>$ aboveC geometry. The most stable MAPbI$_3$/Li@C$_{60}$ system with the aboveC geometry has the highest amount of charge transfer Q, and therefore possessing the strongest binding energy. However, the amount charge transfer of the MAPbI$_3$/Li$^+@C_{60}$ system with the aboveI position is higher than that of the MAPbI$_3$/Li$^+@C_{60}$ system with the bridge position, though the system with the aboveI position is more stable and possesses a stronger binding energy. This is because the charge transfer of MAPbI$_3$ to the Li$^+@C_{60}$ on the aboveI position is facilitated by the iodine which has a high electronegativity. This can be evidenced by the fragment [I1] of the aboveI geometry possesses the Hirshfeld charges of -0.169e to -0.177e, whereas the Hirshfeld charges of fragment [I1] of the aboveC and bridge geometries have the Hirshfeld charges of $> -0.2e$. This implies that more charges are transferred by the fragment [I1] in the MAPbI$_3$/Li$^+@C_{60}$ system with the aboveI position than that of the system with the aboveC or bridge position. Since the MAPbI$_3$/Li@C$_{60}$ system is neutral, there is almost no transfer of charge Q $\sim 0e$.

Figures 5 and 6 illustrate the Kohn-Sham (KS) orbitals and energy eigenvalues of the topC heterojunction with a Li$^+@C_{60}$ on the aboveC, aboveI, and bridge positions for Li$^+$ located at the off-central top and bottom inside the C$_{60}$ cage, respectively. From the KS orbitals and energy eigenvalues, we find that the energy gap of MAPbI$_3$ is between the HOMO and LUMO+3 levels and amounts to 1.6 -1.7 eV. Under light illumination, electrons are excited by this energy and transferred to the ETM. Then holes are produced at the HOMO and HOMO-1 levels in the HTM.
If there is no other level in the wide band gap of MAPbI$_3$, the created holes can promote following reactions similar to the case of TiO$_2$:\textsuperscript{60}

\begin{align*}
\text{MAPbI}_3 (h^+) + H_2O & \rightarrow \text{MAPbI}_3 + HO^+ + H^+ \\
\text{MAPbI}_3 (h^+) + OH^- & \rightarrow \text{MAPbI}_3 + HO^-
\end{align*}

(1a) (1b)

Inside the band gap of MAPbI$_3$, however, there are the LUMO, LUMO$+1$, and LUMO$+2$ levels localized at Li$^+@C_{60}$. The location of these levels is about 0.6 eV higher than the HOMO level (see also Table S1). These levels reflect the situation after an electron is transferred from Li@$C_{60}$ to infinitely far away, and a hole is created in the system. The KS energy levels of the neutral, spin-polarized MAPbI$_3$/Li@$C_{60}$ system (before an electron is transferred from Li@$C_{60}$) are shown in Figs. 7 and 8, respectively, for off-central bottom and top Li positions. The neutral Li@$C_{60}$ in this system may be regarded as Li$^+@C_{60}$ in Ref. [61]. The HOMO (SOMO, $-$ spin) and LUMO ($+$ spin) levels are localized at Li@$C_{60}$, and the latter is higher than the former by 0.125 eV; see also the values in the parentheses in Table 2. This is much smaller than the energy difference (0.336 eV for top Li position and 0.476 eV for bottom Li position) between the HOMO (SOMO, $-$ spin) and HOMO$-1$ ($+$ spin) levels. Therefore, the hole can easily migrate between Li@$C_{60}$ molecules, not deep inside the MAPbI$_3$. This is a critical reason that the hole does not directly attack the MAPbI$_3$ surface when Li$^+@C_{60}$ exists on the surface.

**Conclusions**

In summary, we have performed first-principles DFT calculations on the electronic structure of MAPbI$_3$/Li$^+@C_{60}$ heterojunctions. Finite slab models of tetragonal MAPbI$_3$ (001) surfaces with MAI terminations are considered. A Li$^+$ (or Li) endohedral fullerene Li$^+@C_{60}$ (or
Li@C_{60}) is introduced to different positions on the MAPbI\textsubscript{3} surface. We found that the energetically most stable topC geometry of the tetragonal MAPbI\textsubscript{3} surface. We found that the Li\textsuperscript{+}@C_{60} is adsorbed at the aboveC position with almost 100\% ionized. There is not much difference between the top and bottom positions of Li\textsuperscript{+} inside C\textsubscript{60}, but the bottom position is slightly more stable than the top position. In the MAPbI\textsubscript{3}/Li\textsuperscript{+}@C_{60} system, the KS wave functions of the HOMO and HOMO-1 levels are spreaded out in MAPbI\textsubscript{3} and those of the LUMO, LUMO+1, LUMO+2 levels are localized in Li\textsuperscript{+}@C_{60}; the energy gap between these levels is 0.6 eV. Thus, in the neutral, spin-polarized MAPbI\textsubscript{3}/Li@C_{60} system, the KS wave functions of the HOMO (SOMO, - spin) and LUMO (+ spin) levels are both localized in Li@C_{60} and their energy gap of 0.125 eV is very small. This HOMO (SOMO) level behaves as a hole level when it loses an electron to become Li\textsuperscript{+}@C_{60}. Since there are three almost degenerate LUMO+1 and LUMO+2 levels, it is expected to behave as a good hole conductor. Due to this fact, we conclude that the use of Li\textsuperscript{+}@C_{60} molecules in place of the bare Li ions as dopant materials in the MAPbI\textsubscript{3} solar cells can prevent from degradation. In any case regardless to the adsorption geometry, our results clearly show the existence of the energetically isolated hole level localized in the Li@C_{60}, which may successfully contribute to the suppression of the oxidation of the MAPbI\textsubscript{3} surface. Thus, the present study reveals the stability of the MAPbI\textsubscript{3} surfaces.

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