Glue-like passivation by the natural alkene lycopene for efficient and stable perovskite solar cells: insights from a theoretical perspective†

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Passivation engineering has been recognized as a brilliant strategy to obtain stable and efficient perovskite solar cells (PSCs). The natural alkene lycopene (LP) extracted from tomatoes is the first heteroatom-free passivator that evidently increased the stability of PSCs in recent experiments, although the mechanism remains unclear. Herein, using density functional theory calculations and ab initio molecular dynamics simulations, we demonstrated that LP successfully passivates Pb with alleviated charge localization by donating π-electrons, which exhibit stable bonding components. LP eliminates detrimental trap states induced by oxygen and suppresses nonradiative electron–hole recombination. Moreover, LP spatially blocks water from perovskite in an effective manner while it also weakens atomic fluctuations triggered by water, thus maintaining an optimum moisture tolerance. More importantly, the horizontal adsorption of LP limits the movement of I atoms, leading to a boosted activation barrier for I migration and a reduced migration rate that was decreased by four orders of magnitude. The satisfactory planarity of π–π-conjugated LP provides tight adsorption with perovskite in parallel, which results in outstanding passivation performance. Delocalized electrons move in the skeleton of LP, leading to distributed and flexible interactions with perovskite that resemble those of glue, and preventing lattice mismatch and regional destruction that results when thumbtack-like heteroatom-containing passivators are used. The established mechanism emphasizes the predominant contribution of conjugated C=C bonds to stability and ion migration for green and efficient PSCs.

1. Introduction

Perovskite solar cells (PSCs) have become superstars in the photovoltaic field over the past two decades due to their remarkable properties such as high visible optical absorption, tunable band gap, long carrier diffusion length, and low-cost production.1–3 Although the photoelectric conversion efficiency (PCE) has currently rocketed to 26.1%,4 stability has been a stumbling block to commercialization. The instability is derived from sensitivity to the extrinsic atmospheric factors of water, oxygen, and ultraviolet (UV) light, as well as the existence of intrinsic surface defects.5–7

Because of the hygroscopic nature of amine salt, H2O molecules vertically penetrate the perovskite structure with ease,6 induce reversible hydrate intermediates,9 and then undergo irreversible decomposition. Degradation routes and products vary with the exposure conditions, but it is conclusive that PbI2 is formed.5,7,10 The detrimental effect of O2 on perovskite is reflected in the physical construction and electronic structure. The O2 is converted to superoxide anions by gaining photo-generated electrons. Then, those oxidative species undergo surface reaction, and collapse of the MAPbI3 framework results.11,12 Furthermore, O2 induces trap states13,14 by acting as electron–hole nonradiative recombination centers in the bandgap, which subsequently decreases the PCE. UV light assists in the oxygen-induced degradation of perovskite by providing photoexcited electrons.11,15 Defects are inevitable in the manufacturing process. They provide a channel for water and oxygen, and research indicated that ion migration caused by iodine vacancy (V_I) defects is the chief culprit for the current–voltage (J–V) hysteresis of perovskite.16,17 Therefore, how to weaken the negative effects of defects while enhancing water and oxygen stability is currently a bottleneck in the development of perovskite.

To overcome these issues, numerous effective strategies have been developed, such as encapsulation,7 process engineering,18...
material compositional modification engineering, and passivation engineering. The Lewis base has been exploited as a passivation additive to achieve efficient and stable perovskite devices because it donates lone electrons to interact with uncoordinated Pb and shield against humidity. Thiophene and pyridine were first used to passivate perovskite as monodentate Lewis bases, followed by the bidentate ligand DTBP and 2-MP molecules. Passivation molecules are not limited to monodentate or bidentate, but multi-site anchoring with multiple functional groups synergistically provides additional possibilities for surface passivation. In fact, most Lewis base passivation additives are heterocyclic chemical compounds, which may be expensive, complex to synthesize, and toxic. An increasing number of natural additives are being incorporated into PSCs, such as caffeine, theophylline, theobromine, capsaicin, and terpineol. These ‘green’ molecules with stable structures derived from nature are eco-friendly and readily accessible, and thus, their use has resulted in the evolution of a new trend of passivation molecules.

Natural lycopene (LP) extracted from tomatoes was employed in PSCs as a passivator, and a breakthrough in efficiency and stability was achieved by two research teams. There was an increase in the PCE from 20.57% to 23.62% with vastly enhanced short-circuit current ($J_{sc}$) and open-circuit voltage ($V_{oc}$). Long-term stability was obtained when 90% of the original PCE value was exceeded after exposure to oxygen and moisture. Almost all Lewis bases contain N, O, P, and S heteroatoms to contribute lone pair electrons, as reported in previous studies. The first-principles calculation results by Zhang and Long emphasize the key role of N, S, and O heteroatoms in the passivation of Lewis bases. LP was first used as a passivator because of its natural characteristics of being an alkane without heteroatoms, and its performance was no less than that of heteroatom-containing passivators. The passivation effects of alkenes have been previously underestimated. Now, LP paves a new road for the selection of passivators. How does an alkene without heteroatoms passivate perovskite? The microscopic mechanism governing how alkenes without heteroatoms passivate perovskite is currently vague, and an explanation is urgently required.

Our calculation results indicated that delocalized $\pi$-$\pi$-conjugated C–C bonds endow LP molecules with satisfactory planarity and a broad, uniform force similar to that obtained with glue. Such interaction originates from the donation of the $\pi$-electrons of C–C to coordinate with Pb. LP successfully passivates the Pb that undergoes aggravated charge localization induced by I$_s$. It eliminates the trap states introduced by oxygen and shields water, which results in increased stability. More importantly, the compressed space due to the robust adsorption of LP on MAPbI$_3$ in parallel narrows the freedom of I$_s$, leading to boosted activation barriers for I atom migrations and a reduced migration rate.

2. Computational details

In consideration of the high temperature of PSCs exposed to illumination, MAPbI$_3$ was constructed in the cubic phase, which is the dominant structure when $T_c > 330.4$ K. The PbI$_2$-terminated (001) MAPbI$_3$ in cubic formation with an I$_s$ defect contains 143 atoms. The supercell possesses three layers, and the bottom layer was frozen while the others were fully relaxed during the optimizations. Vacuum layers in the z direction were more than 20 Å to prevent mirror interactions. The constants of the supercell were 12.58 Å, 12.54 Å, and 41.88 Å along the x, y, and z directions, respectively.

The geometry optimization and electronic property analysis were implemented in the Vienna ab initio Simulation Package (VASP) code. The spin-polarized generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange correlation function was employed. The weak van der Waals interactions were treated by the Grimme DFT-D3 approach. Projector-augmented wave (PAW) approaches were performed with a 400 eV plane-wave energy cutoff to describe the electron–ion core interactions. The convergence threshold was $10^{-5}$ eV for energy and 0.02 eV Å$^{-1}$ for force. A $3 \times 3 \times 1$ Γ-centered Monkhorst–Pack $k$-point mesh grid was used for geometry optimization and electronic structure calculations.

The activation energies for migrations were calculated using the climbing image nudged elastic band (CI-NEB) method. Eight images were inserted between the initial and final states of the diffusion paths. The convergence threshold was $10^{-5}$ eV for energy and 0.05 eV Å$^{-1}$ for force. The configuration and properties of LP molecules were obtained by Gaussian 16 software at the B3LYP/6-311G(d,p) level. The Crystal Orbital Hamilton Population (COHP) was produced using the LOBSTER package. The ab initio molecular dynamics (AIMD) simulation was carried out on the CP2K package. The cutoff energy for the hybrid Gaussian plane-wave basis was set to 400 Ry to ensure accuracy. A trajectory of 20 ps was obtained in the NVT ensemble with a time step of 1 fs at a fixed temperature of 300 K that was carried out using a Nose–Hoover thermostat.

3. Results and discussion

3.1. Adsorption configuration and bonding properties

MAPbI$_3$ can act as either a MAI-terminated ($S_{MAI}$) or PbI$_2$-terminated ($S_{PbI_2}$) surface (ESI, Fig. S1). Greater negative adsorption energy indicated that LP prefers to adsorb on the $S_{PbI_2}$-terminated pristine surface. Defects would inevitably exist on the crystal surface during manufacturing. Therefore, based on the PbI$_2$-terminated (001) cubic perovskite, widespread iodine vacancy with low formation energy was introduced, and named MAPbI$_3$-I$_s$.

Highly symmetric LP is composed of 11 conjugated C–C and 2 unconjugated C–C units. To decrease the length of the molecule but retain the functional groups of conjugated C–C, LP was replaced with a fragment containing four conjugated C–C moieties, which is depicted in the green transparent area of Fig. 1a.

Differing from heteroatom-containing passivators centered on points, the $\pi$-$\pi$ conjugation of LP causes electron clouds to be exposed above and below the molecular plane (Fig. 1c). The negative electrostatic potential (ESP) is distributed throughout the molecular skeleton of LP (Fig. 1b), which indicates that LP
is willing to donate electrons. Therefore, the interaction between LP and the surface of perovskite is deemed to be broader and facile.

The adsorption energy of LP on the perovskite is $-2.26 \text{ eV}$. The dihedral angle between the LP molecule and the perovskite surface is approximately $167.85^\circ$, which indicates that the LP molecule adsorbs on the perovskite surface nearly in parallel (see Fig. 2). The distance between the LP molecule and perovskite is approximately $3.03 \ \text{Å}$. After passivation, the average length of the double bonds in LP increases from $1.36 \ \text{Å}$ to $1.38 \ \text{Å}$, which remains in the range of double bonds. This is highly consistent with the experimental observation captured by Fourier transform infrared (FTIR) spectroscopy that indicates a shift (but not a disappearance) of the characteristic vibration of the $\text{C} = \text{C}$ bond peaks from $1630 \ \text{cm}^{-1}$ to $1643 \ \text{cm}^{-1}$. LP caused an increase in the Pb–I bond length from $3.17 \ \text{Å}$ to $3.20 \ \text{Å}$ in the vertical direction near the I vacancy, and thus, the Pb–I–Pb angle became slightly deformed. A change in structure is the epitome of interaction between LP and perovskite. To explore this interaction in detail, a series of analyses was carried out.

The charge density difference (CDD) in Fig. 3a shows a noticeable charge accumulation and loss between LP and Pb atoms near the I vacancy defect, which indicates strong covalent bonding.56 Surprisingly, there was a significant charge distribution between the C–H of the methyl group at the left tail of LP and I, which indicated that the interaction between C–H and I synergistically assisted the binding between LP and Pb. Polarized by the rich electrons of the conjugated $\text{C} = \text{C}$ beside $-\text{CH}_3$, the activity of H was enhanced, forming a strong interaction with the I of the PbI$_2$ octahedron involved in the covalent effect. The Bader charge and planar-averaged CDD in the $z$ direction (ESI† Fig. S2) demonstrated that electrons were transferred from the LP side to the perovskite side.

The electron localization function (ELF) is used to characterize the degree of electronic localization.57 The defect results in uninvolvement of Pb electrons, which precipitates aggravated localization as opposed to bare perovskite. The introduction of LP alleviates the localization of Pb near the vacancy shown in Fig. 3b because Pb donates electrons to participate in bonding, indicating successful passivation. The distribution of delocalized charges between the $-\text{CH}_3$ in the tail of LP and I observed in the ELF also confirms the existence of strong interaction between C–H and I.

The COHP can be used to qualitatively analyze bond strength by extracting bonding and antibonding components.58 COHP

Fig. 1 (a) Molecular configuration, (b) electrostatic potential (ESP), and (c) highest occupied molecular orbital (HOMO) of lycopene. The green transparent area represents simplified lycopene molecules.

Fig. 2 Side (left) and top (right) views of optimized configurations for LP@MAPbI$_3$–I$_v$. The values in red and black indicate the length (Å) of C–Pb and the distance (Å) between LP and the perovskite surface, respectively. The circle in red denotes the iodine vacancy location.

Fig. 3 (a) The charge density difference (CDD), Bader charge analysis for LP@MAPbI$_3$–I$_v$, and (b) electron localization function (ELF) for bare MAPbI$_3$, MAPbI$_3$–I$_v$, and LP@MAPbI$_3$–I$_v$. The blue and yellow regions correspond to charge depletion and accumulation, and the isosurface level is set to be $0.001 \ \text{eBohr}^{-3}$ for the CDD. The circle in red represents the interaction between C–H and I.
analysis of C–Pb contact in Fig. 4 indicates that C–Pb chemical bonding is indeed stable due to the existence of bonding states in the vicinity of the Fermi level. Combined with the projected density of states (PDOS), it was found that the p orbital of C in LP plays a major role in bonding in the conduction band minimum (CBM), which again verifies the contribution of π electrons to bonding.

Several groups reported that passivation molecules may lead to deep trap states in band gaps of perovskite, which is disastrous for passivation effects. As shown in Fig. 4, LP has a negligible effect on the band structure of perovskite, and no deep trap state appears. Such a phenomenon mainly occurs because LP molecules do not contain heteroatoms with high electronegativity that would lower the energy of the electronic levels, resulting in trap states.

In experiments, LP passivated perovskite as an additive or interlayer in devices. There is no doubt that the charge transfer property of the insert layer would affect the overall performance of PSCs. The insulating properties of passivation molecules with a long alkyl chain may hinder interfacial charge transport. However, the obvious charge distribution in the CDD and charge transfer with 0.10 electrons between LP and MAPbI₃ demonstrates that unlike alkanes, LP as an alkene possesses a strong charge transfer ability due to delocalization of the molecular electric orbitals induced by the conjugated C=C structure.

3.2. Oxygen stability
Oxygen will be captured by I vacancy defects and stably adsorbed on it, whose procedure is depicted in ESI† Fig. S4a. Considering that the procedure for the passivation interlayer or additive is carried out under a nitrogen atmosphere in the laboratory, the device would not contact the air until the fabrication was completed. Therefore, the LP molecule in the adsorption configuration (see ESI† Fig. S4b) is closer to perovskite than oxygen. After LP treatment, the adsorption energy of oxygen on perovskite decreased from 2.21 eV to 1.13 eV. The distance of O-O in molecular oxygen lengthens from 1.29 Å to 1.31 Å (see ESI† Fig. S4). There is a difference between the spin-down and spin-up of the DOS. We only focus on the spin-down component of the PDOS because it can clearly present the midgap.

Oxygen introduces deep midgap states (electron-trap and hole-trap) in the bandgap of perovskite (Fig. 5a), which is consistent with previous calculations. These trap states can capture the electrons in the CBM and the holes in the VBM, respectively, and the trapped charge carrier undergoes additional recombination, as shown in Fig. 5b, which reduces the PCE of PSCs. In addition, the trap state can be further transformed into oxidation species, which prepare for the subsequent degradation of perovskite. When passivated by LP, the trap state is eliminated (see Fig. 5c), and there is no additional access (see Fig. 5d) for the recombination of electrons and holes. Nonradiative recombination is suppressed, resulting in a prolonged carrier lifetime and enhanced PCE. This is mainly attributed to the strong interaction between LP and the perovskite surface, and more importantly, LP itself is harmless to the electronic structure. Therefore, LP inhibits the physical degradation and the destruction of the electronic structure by preventing direct contact between oxygen and perovskite, and forming a layer of double protection.

3.3. Moisture stability
When exposed to humidity, water molecules diffuse from the surface into the interior of perovskite because of the affinity
between H$_2$O and MA$_x$ which can be simulated with AIMD. A large coverage of water molecules would form a hydrogen-bonded network with each other, while the water diffusion process is more obvious in small amounts. Based on low coverage, two and four water molecules were considered in this work. The energy and temperature fluctuate within a small range, and thus, the systems are in a steady state (Fig. S5, ESI†).

Fig. 6 describes the evolution of the height of O atoms in water over time. When the system was exposed to environments with two H$_2$O molecules, one H$_2$O molecule began to rapidly invade at 2.5 ps into the pristine MAPbI$_3$–I$_v$ surface, and at 16 ps, both H$_2$O molecules remained in the inner surface. Combined with the AIMD trajectory (ESI† Fig. S6), the water interacted with MA and formed bonds with the Pb at the surface, leading to structural deformation. Upon LP treatment, two H$_2$O molecules were shielded by LP and had no opportunity to advance to the perovskite surface.

Diffusion was more pronounced when exposed to four H$_2$O molecules: at 2 ps, the first H$_2$O molecule began to penetrate, and at 7 ps, all four H$_2$O molecules remained inside the perovskite. At 13 ps, the diffusion trend intensified. Finally, the location of the water was deeper than that with the coverage of two H$_2$O molecules. After LP passivation, three H$_2$O molecules were blocked far away at the surface, and only one H$_2$O molecule penetrated the interior of the perovskite at 18 ps, with a slow trend. Thus, LP effectively blocks perovskite from water and prevents subsequent degradation, thereby exhibiting remarkable moisture resistance. The results of AIMD in our work are consistent with previous experimental observations of long-term moisture stability.\(^{31,32}\)

Atomic fluctuation is usually used to evaluate the stability relative to degradation due to oxygen exposure and moisture, as reported in the literature,\(^{13,33,67}\) which is characterized by the average standard deviation ($\sigma$) of the positions for the I/MA/Pb particles calculated using the following formula:\(^{69–71}\)

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} (r_{ij} - r_i)^2}{n - m}}$$

where $r_{ij}$ represents the position of MA/I/Pb particles $i$ at step $j$, $r_i$ denotes the average location of particles $i$ along $m$-step AIMD trajectories, and $n$ refers to the total number of MA/I/Pb particles in the system.

The boosted fluctuation results in accelerated degradation of the perovskites, whereas suppressed atomic fluctuation indicates enhanced perovskite stability.\(^{13}\) For the MAPbI$_3$–I$_v$ surface, the atomic fluctuation deviation induced by water was more significant, with the values of 0.552, 0.790, and 1.089 for MA, I, and Pb particles, respectively (see Fig. 7).

Therefore, LP not only spatially blocks water from perovskite, but it also increases the stability of the system against atomic fluctuations. Such remarkable moisture tolerance is due to the hydrophobicity of LP molecules, as well as the tight and sheltered adsorption on perovskite, which plays a dominant role in durable water-blocking effects.

### 3.4 Ion migration inhibition

Suppression of iodide migration significantly contributes to the operational stability of the PSCs.\(^{72}\) Compared with Pb$^{2+}$ and MA$^-$ species, I$^-$ can easily diffuse with the lowest energy barrier.\(^{73,74}\) I atom migration can occur within the layer or between layers.\(^{17,72–74}\) Because passivation mostly affects the surface of perovskite, the migration path in our work mainly considers I atom migration within the top plane. The specific migration path refers to previous work,\(^{54,72}\) as shown in Fig. 8a. The migration rate constant ($k$) can be estimated by the Arrhenius equation:\(^{17,75}\)

$$k = \frac{k_B T}{h} e^{-\frac{E_a}{RT}}$$

![Fig. 6](image1.png) **Fig. 6** Evolution of the height of the O atoms in water molecules over time for (a) 2H$_2$O@MAPbI$_3$–I$_v$, (b) 2LP–2H$_2$O@MAPbI$_3$–I$_v$, (c) 4H$_2$O@MAPbI$_3$–I$_v$, and (d) 2LP–4H$_2$O@MAPbI$_3$–I$_v$. Blue areas and dashed lines indicate perovskite bulk and LP heights, respectively.

![Fig. 7](image2.png) **Fig. 7** The average standard deviation (Å) of the positions for I/MA/Pb particles for the 2H$_2$O–MAPbI$_3$–I$_v$ and 2LP–2H$_2$O–MAPbI$_3$–I$_v$ systems.
LP@MAPbI$_3$–I$_v$ system, but the value decreased to 16.96 Å after LP
adsorption of the surface in a tilted orientation. This diminishes the shielding effect of oxygen and water, resulting in unsatisfactory passivation upon stability. However, intelligently shrouded adsorption of LP occurs on perovskite, thus surpassing the inefficient adsorption of other natural molecules. Moreover, other alkenes possessing satisfying planarity and a satisfactory match between C–C bonds and Pb would achieve glue-like passivation similar to that of LP.

In addition, the satisfactory passivation of LP for MAPbI$_3$ perovskites would apply to other perovskite materials, because one passivation molecule can accomplish passivation on all inorganic or organic–inorganic hybrid PSCs, according to related experiments. For example, benzylamine successfully passivated FAPbI$_3$ and MAPbI$_3$ perovskites and pyridine derivatives achieved remarkable performance on CsPbI$_3$ and FA$_{0.88}$Cs$_{0.12}$PbI$_3$-based PSCs. Furthermore, as determined by theoretical calculations, the valence and conduction bands were contributed by the PbI$_3$–octahedral framework. Therefore, although our work is based on MAPbI$_3$, the results can be applied to other perovskite materials such as CsPbI$_3$ or FAPbI$_3$.

It is worth mentioning that our computational results clarify the passivation effects on stability in terms of H$_2$O/O$_2$ resistance and ion migration, but the component of aging is not involved. Chemical species change with aging, and aging of precursors may result in unsatisfactory reproducibility and deteriorative device performance of the PSC. Thus, there is a great need for future experiments exploring the exact aging process of perovskite precursors.

### 5. Conclusion

Based on DFT calculations and AIMD simulations, the passivation effects of natural LP on the iodine vacancy of MAPbI$_3$ were investigated and involved the exploration of geometric configuration, bonding characteristics, electronic properties, oxygen stability, moisture tolerance, and ion migration. The results indicated that π–π-conjugated LP molecules were adsorbed on the surface of perovskite in parallel. LP donates π electrons to coordinate with Pb, and this interaction is indeed stable due to the existence of bonding states near the Fermi level, as verified by COHP analysis. In addition, the CDD and ELF captured strong –CH$_2$–I interaction polarized by the conjugated C–C assisting in the Lewis acid–base coordination. LP prevents direct contact between oxygen and

![Fig. 8](image-url) (a) Top and side views of the I atom migration path. (b) Activation barriers for the migration of I ions within the MAPbI$_3$–I$_v$ and LP@MAPbI$_3$–I$_v$ systems.

<table>
<thead>
<tr>
<th>Systems</th>
<th>$E_{ab}$ (eV)</th>
<th>$k$ (s$^{-1}$)</th>
<th>$h_0$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI$_3$–I$_v$</td>
<td>0.19</td>
<td>2.56 × 10$^{-6}$</td>
<td>17.21</td>
</tr>
<tr>
<td>LP@MAPbI$_3$–I$_v$</td>
<td>0.45</td>
<td>1.37 × 10$^{-6}$</td>
<td>16.96</td>
</tr>
</tbody>
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Table 1 Activation barriers ($E_{ab}$), migration rate constants ($k$) at 300 K, and averaged height ($h_0$) of the migrating I atom for the migration procedure on the MAPbI$_3$–I$_v$ and LP@MAPbI$_3$–I$_v$ systems.

where $k_B$ represents the Boltzmann constant, $T$ refers to the temperature, $h$ denotes the reduced Planck constant, and $R$ denotes the ideal gas constant.

Table 1 shows that the energy barrier is 0.19 eV for the pristine MAPbI$_3$–I$_v$ surface, which is similar to the value reported in previous studies and the migration rate is 2.56 × 10$^{-6}$ s$^{-1}$. After passivation by LP, the migration barrier increased to 0.45 eV, and the migration rate was reduced by four orders of magnitude with a value of 1.37 × 10$^{-6}$ s$^{-1}$. In addition, the average height of the migrating I atom was 17.21 Å during the migration process within the pristine MAPbI$_3$–I$_v$ system, but the value decreased to 16.96 Å after LP passivation. Such a phenomenon indicates that the horizontal adsorption of LP narrows the migration space of I in the z direction and restrains the freedom of I, which increases the difficulty of migration, resulting in an increased migration energy barrier.

### 4. Discussion

For traditional heteroatom-containing passivators, the anchoring sites are concentrated on heteroatoms, and this passivation is similar to the action of thumbtacks. For monodentate heteroatom-containing passivators such as pyridine and thiophene, their single-site anchoring would lead to unsustainable passivation. For bidentate heteroatom-containing passivators such as 2-mercaptopyridine (2-MP) and D-4-tert-butyl-phenylalanine (Phe) (D4TPB), the distance between the two anchoring sites must be well matched with the perovskite lattice, which increases the difficulty of selection of the bidentate ligands. For multidentate ligands such as terpyridine (Tpy) with high electronegativity, local interaction that is too intense would severely damage the regional lattice of perovskite, which was confirmed in our previous work. In contrast, the π–π conjugation of LP endows molecules with satisfactory planarity, and the flowing π-electron cloud in LP determines the diffuse, extensive, and non-local force. These facts together result in the adsorption of LP on the perovskite in a plane-covered, flexible, and larger-scale state that is comparable to that of glue. Such glue-like interaction can effectively shield oxygen, prevent the diffusion of water, and inhibit I atom migration, with remarkable photoelectric properties and durable stability.

Natural passivation molecules such as theophylline, caffeine, and capsaicin all contain C–O or C–N double bonds as well as benzene rings, which constrain molecular flexibility and increase the hindrance of coordination. To provide a preferable match for the lattice of perovskite, these natural molecules tend to adsorb on the surface in a tilted orientation. This diminishes the shielding effect of oxygen and water, resulting in unsatisfactory passivation upon stability. However, intelligently shrouded adsorption of LP occurs on perovskite, thus surpassing the inefficient adsorption of other natural molecules. Moreover, other alkenes possessing satisfying planarity and a satisfactory match between C–C bonds and Pb would achieve glue-like passivation similar to that of LP.

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perovskite and eliminates the trap state induced by \( \text{O}_2 \), resulting in a prolonged carrier lifetime when exposed to oxygen.

AIMD simulation illustrated that LP can block water invasion by acting like an umbrella and suppressing the atomic fluctuation induced by water. This greatly enhances moisture resistance, which is mainly ascribed to the tight bonding with perovskite, as well as the satisfactory hydrophobicity of LP. CINEB showed that the horizontal adsorption of LP narrows the bandgap, with distributed force, flexible form, and larger scope. The thumbtack-like anchoring of heteroatom-containing passivators results in a mismatch with the lattice, regional destruction of the surface, and a detrimental trap state. In contrast, the electron clouds of LP are distributed throughout the molecular skeleton in a manner that resembles glue, with distributed force, flexible form, and larger scope. The molecular planarity of LP and the Lewis acid–base coordination between the C—C and Pb are all attributed to the π–π conjugation of LP. Our work is in satisfactory agreement with the experimentally observed trend, which not only reveals the passivation mechanism of conjugated C—C bonds represented by natural LP but also provides an illuminating inspiration for the selection of efficient, green passivation molecules.

Author contributions

Na Chen: writing – original draft. Quan-Song Li: review and editing.

Conflicts of interest

There are no conflicts to declare.

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