

Reducing Anomalous Hysteresis in Perovskite Solar Cells by Suppressing the Interfacial Ferroelectric Order

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ABSTRACT: Despite the booming research in organometal halide perovskite solar cells (PSCs) of recent years, considerable roadblocks remain for their large-scale deployment, ranging from undesirable current–voltage hysteresis to inferior device stability. Among various plausible origins of hysteresis, interfacial ferroelectricity is particularly intriguing and warrants a close scrutiny. Here, we examine interfacial ferroelectricity in MAPbI₃ (FAPbI₃)/TiO₂ and MAPbI₃/phenyl-C61-butyric-acid-methyl-ester (PCBM) heterostructures and explore the correlations between the interfacial ferroelectricity and the hysteresis from the perspective of nonadiabatic electronic dynamics. It is found that the ferroelectric order develops at the MAPbI₃/TiO₂ interface owing to the interaction between the polar MA ions and TiO₂. The polarization switching of the MA ions under an applied gate field would drastically result in different rates in interfacial photoelectron injection and electron–hole recombination, contributing to the undesirable hysteresis. In sharp contrast, ferroelectricity is suppressed at the FAPbI₃/TiO₂ and MAPbI₃/PCBM interfaces, thanks to elimination of the interfacial electric field between perovskite and TiO₂ via substitution of strong polar MA (dipole moment: 2.29 debye) by weak polar FA ions (dipole moment: 0.29 debye) and interface passivation, leading to consistent interfacial electronic dynamics and the absence of hysteresis. The present work sheds light on the physical cause for hysteresis and points to the direction to which the hysteresis could be mitigated in PSCs.

KEYWORDS: perovskite solar cells, hysteresis, ferroelectricity, excited-state electronic dynamics, orientation selectivity, electron–hole recombination



1. INTRODUCTION

Organometal trihalide perovskite solar cells (PSCs) have made remarkable achievements in energy conversion efficiency, rising steadily from 3.8¹ to 25.2% (KRICT/MIT) in just 10 years. This remarkable breakthrough is attributed to the exceptional photophysical properties that the perovskite materials possess, including optimal band gap, excellent photoabsorption,² giant dielectric constant,³ and respectful charge mobilities.^{4–6} Despite unprecedented success, there are still open questions in PSCs that need to be answered in order to further advance the development and eventual deployment of PSCs. Among them, anomalous hysteresis stands out. In PSC devices with hysteresis, the photocurrent–photovoltage (J – V) varies with the photoillumination conditions, the scan direction, and the scan rate.^{7–9} Hysteresis has been observed in both planar and mesoporous structures, irrespective of the hole transport material.

Several explanations for hysteresis have been put forward in the literature: (i) ion migration during J – V scan, resulting in interfacial band bending;^{10,11} (ii) motion of interfacial defects under the device operating conditions, leading to distinct interfacial electronic dynamics;^{12–16} and (iii) ferroelectricity in the active layer originating from either molecular ferroelectric order (FE) of the organic molecules and/or the ionic FE of the inorganic cages.^{17–20} For the past years, great efforts have been

made to eliminate hysteresis and improve the stability of PSCs from the following aspects: additive modification or treatment of the electron-transporting layer (ETL)^{21–26} to optimize the interfacial electronic dynamics in PSCs; changing the element composition of the perovskite intrinsic layer^{27–29} to promote the perovskite quality; and doping of the hole-transporting layer³⁰ to passivate the surface trap states of the perovskite layer.

Although much effort has been made to better understand the potential causes for the hysteresis and to suppress it, the hysteresis in PSCs has been disputed, especially the existence of ferroelectricity in perovskites and its influence on hysteresis. For example, researchers from the University of Bath have calculated the ferroelectric polarization of the methylammonium (CH₃NH₃⁺, MA) lead tri-iodide (MAPbI₃) perovskite (as large as 38 $\mu\text{C}/\text{cm}^2$) and observed the rotation of the MA ions at room temperature using ab initio molecular dynamics (MD). They postulated that the ferroelectricity

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could be responsible for the hysteresis of PSCs.^{19,31} On the other hand, Zheng et al. revealed that the antiferroelectric order was more stable in the tetragonal phase of MAPbI₃ with nearly zero overall polarization.³² Stoumpos^{20,33} and Kutes³⁴ have directly observed ferroelectricity in MAPbI₃ by polarization–electric field (*P*–*E*) measurements and piezo-response force microscopy (PFM). However, more recent works^{11,35} have detected no room-temperature ferroelectricity in MAPbI₃ with either *P*–*E* loop measurements or PFM. Moreover, Snaith et al. have observed a giant low-frequency magnitude of the hysteretic charge density (over 1000 $\mu\text{C}/\text{cm}^2$) and ruled out the ferroelectricity as the main cause of hysteresis in PSCs.³⁶ Therefore, it would be of significant importance to ascertain the presence of ferroelectricity in PSCs and to elucidate the correlation between the ferroelectricity and hysteresis in PSCs.

In this work, we focus on the presence of interfacial ferroelectricity between the active layer and ETL and examine the relationship between the interfacial ferroelectricity and the anomalous hysteresis from *ab initio* time-domain nonadiabatic molecular dynamics (NAMD) simulations.^{37–40} We find that the freestanding MAPbI₃ perovskite slab shows zero ferroelectric polarization. However, when it forms an interface with the TiO₂ ETL, interfacial FEs are developed between MAPbI₃ and TiO₂ with two distinct metastable orientations of the MA ions. The two metastable interfacial configurations are thermodynamically stable at 300 K, thanks to the high transition barrier between them. Most importantly, the two metastable structures could lead to 50 times difference in recombination rates at the interfaces. Consequently, the structural transformations between these two structures during *J*–*V* scans could yield distinct current–voltage characteristics associating with the scanning directions. Substitution of MA by formamidinium (H₂N=CHNH₂⁺, FA) ions can lead to a negligible interfacial FE between FAPbI₃ and TiO₂, effectively reducing the hysteresis undesirably. Interface passivation by phenyl-C61-butyric-acid-methyl-ester (PCBM) is found to efficiently eliminate the interfacial electric field between TiO₂ and the perovskite, reducing the interfacial FE, leading to consistent interfacial electronic dynamics and the absence of hysteresis. Our findings are consistent with the experimental observations that the FAPbI₃-based devices⁴ and PCBM-passivated MAPbI₃-based PSCs^{41,42} are nearly free of hysteresis, while pure MAPbI₃-based PSCs suffer severe voltage–current hysteresis. Therefore, the interfacial ferroelectricity is recognized as one of the microscopic reasons for the hysteresis in MAPbI₃-based PSCs.

2. THEORETICAL MODELS AND COMPUTATION PARAMETERS

We choose a 84-atom (2 × 2) perovskite (001) slab and a 96-atom (2 × 4) rutile TiO₂(110) surface to model the perovskite/TiO₂ interfaces. The bottom two atomic layers of the TiO₂ slab are fixed at their corresponding bulk positions to effectively represent the bulk geometry of TiO₂. The thickness of the vacuum layer is ~15 Å to ensure that there are no interactions between the repeating periodic units. To simulate the MAPbI₃/PCBM heterojunction, a 189-atom (3 × 3) surface slab of MAPbI₃ is employed. The distance between PCBM and the MAPbI₃ surface is 3.65 Å. First-principles calculations based on density functional theory (DFT) are performed to examine the geometric and electronic properties of the heterojunctions, implemented with the VASP code.⁴³ The plane wave basis, the Perdew–Burke–Ernzerhof (PBE)

exchange–correlation functional,^{44,45} and the projector augmented wave potentials^{46,47} are employed. The cutoff energy is set to be 500 eV to ensure the simulating precision. The lattice vectors for the MAPbI₃/TiO₂ simulation system are *a* = 12.90 Å and *b* = 13.17 Å. Considering the fact that FAPbI₃ exhibits a trigonal *P3m1* space group,⁴⁸ which is almost cubic when it was grown on the TiO₂ surface, we adopt a 84-atom (2 × 2) (001) surface of trigonal *P3m1* FAPbI₃ perovskite above the rutile TiO₂ (110) surface to model the FAPbI₃/TiO₂ heterojunction. The lattice vectors for the FAPbI₃/TiO₂ simulation system are *a* = 12.53 Å and *b* = 13.17 Å. Geometries were fully relaxed until forces on nonfixed atoms are below 0.01 eV Å^{−1} per atom.

Here, we also tested spin–orbital coupling (SOC) corrections for perovskites. We have calculated the energy band structure of bulk perovskite MAPbI₃ with and without SOC corrections included (Figure S1). The calculated energy gap *E_g* is 1.65 eV for bulk perovskites with pure PBE functional used, in good accordance with the experimental result of ~1.54 eV. If the SOC corrections were included using the PBE functional, *E_g* decreases to 0.54 eV. This behavior results from the fact that DFT with the PBE functional would underestimate *E_g* of semiconductors while neglecting SOC corrections would overestimate *E_g*. Apparently, these errors cancel each other in the energy gap calculations with the PBE functional without consideration of SOC correction, thus leading to minor discrepancy between results of PBE and GW + SOC or HSE + SOC, confirmed by many works on the MAPbI₃ perovskite.^{49,50} Therefore, for simplicity and to avoid affordable computational costs in SOC and GW calculations, we choose to use the simplified PBE approximation without SOC.

The excited-state interfacial electronic dynamics of perovskite/TiO₂ and perovskite/PCBM heterostructures are studied by NAMD simulations. The simulation systems are heated from 0 to 300 K by velocity rescaling. Then, a 5 ps adiabatic MD run with a time step of 1 fs in the microcanonical ensemble is implemented. The MD trajectories are subsequently utilized in NAMD surface hopping simulations. More detailed descriptions of the NAMD computations can be acquired in refs 37 and 38.

3. RESULTS AND DISCUSSION

3.1. Geometric Properties of the MAPbI₃/TiO₂ Interface. Figure 1a,b show the optimized geometries of the pristine MAPbI₃ slab and the MAPbI₃/TiO₂ interface. Both MAPbI₃ and MAPbI₃/TiO₂ start with the initial structures where the eight MA moieties have an orientation of $\theta = 90^\circ$ (the C–N bonds are parallel to the perovskite/TiO₂ interface, namely, the *XY* plane), where θ is the vectorial angle between the *Z*-axis and the vector C–N (pointing from C atom to N atom). From Figure 1a, the four MA moieties of the top layer and the four MA groups of the bottom layer in the lattice of the optimized MAPbI₃ slab show distinct orientations, with $\theta = 120^\circ$ for the top layer and $\theta = 60^\circ$ for the bottom layer MA ions. This special arrangement of MA ions would decrease the surface polarity of MAPbI₃ and help to stabilize the slab structures.⁵¹ Surprisingly, when the MAPbI₃ slab has been put onto the TiO₂ rutile (110) substrate, the eight MA ions show the same orientation with $\theta = 60^\circ$ (Figure 1b). This unexpected orientation selectivity of MA ions is induced by the effective electric field at the MAPbI₃/TiO₂ interface. Kelvin probe force microscopy and contact potential difference results

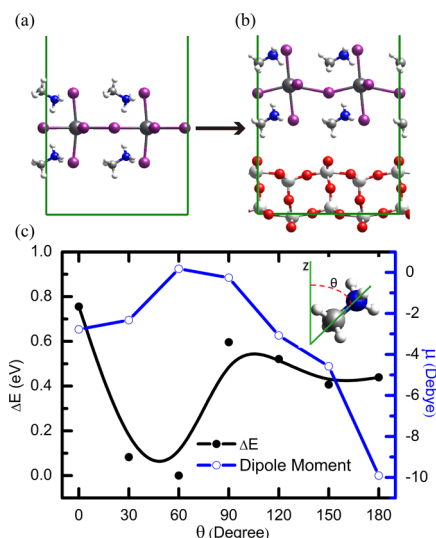


Figure 1. Atomic structures of the (a) thin MAPbI₃ slab and (b) MAPbI₃/TiO₂ heterojunction. (c) Relative energy differences and dipole moments for different MA orientations of the MAPbI₃/TiO₂ heterojunction. Here, we used the spline curve to connect the data points showing a smooth black curve, therefore some data points are not precisely on the curve. The inset shows the schematic diagram of θ , which is defined as the angle between vector C–N (pointing from C to N atom) and the Z-axis (the surface normal direction).

revealed the existence of a nonnegligible electric field ($\sim 10^6$ V·m⁻¹) at the mesoporous MAPbI₃/TiO₂ interface, extending hundreds of nanometers.^{52–54} Being influenced by the interfacial electric field, polar MA ions in the Pb–I skeleton would realign with identical orientations.

We further sweep the potential energy surface (PES) of the MAPbI₃/TiO₂ heterostructure as a function of θ , with θ varying in the range of 0°–180° ($\theta > 180^\circ$ are symmetric with $\theta < 180^\circ$) by fixing the C and N atoms of the MA ions while keeping other atoms fully relaxed. Figure 1c shows the relative energy differences and interfacial dipole moments μ as a function of MA orientation θ of the MAPbI₃/TiO₂ heterojunction. Here, we define the lowest energy of the conformation with $\theta = 60^\circ$ as zero. Note that the relative energy difference ΔE has been averaged over the eight MA cations. We find two local minima on the PES: $\theta = 60^\circ$ and $\theta = 150^\circ$. The energy difference between the two local minima is 407 meV per MA moiety and the estimated energy barrier for structural transformation between these two conformations is 635 meV per MA ion, which indicates that the orientation switches of MA ions can hardly happen at room temperature but probably occur under the applied external electric field during voltage scans.

3.2. Kinetic Stability of Orderly Aligned MA Ions at the MAPbI₃/TiO₂ Interface. To verify the kinetic stability of the two ordered aligned structures at room temperature, we have performed MD runs of the two conformations. Starting from the initial relaxed structures of $\theta_0 = 60^\circ$ and $\theta_0 = 150^\circ$, the temperatures of the two configurations increase from 0 to 300 K with a 100 fs MD run and are maintained at 300 K for 1000 fs to attain the thermodynamic equilibrium. Last, another 5000 fs microcanonical MD run is carried out to investigate the statistical structural properties of the two conformations. Note that all atoms of the MAPbI₃ perovskite are free to move during the whole MD process. By tracing the variation of θ during the 5 ps MD simulations, we find that the MA cations

on the top layer of the perovskite/TiO₂ heterostructure (the MAI atomic layer close to the vacuum) and the interface layer (the MAI atomic layer close to the TiO₂ substrate) show distinct dynamic behaviors. From Figure 2a, the θ of the four

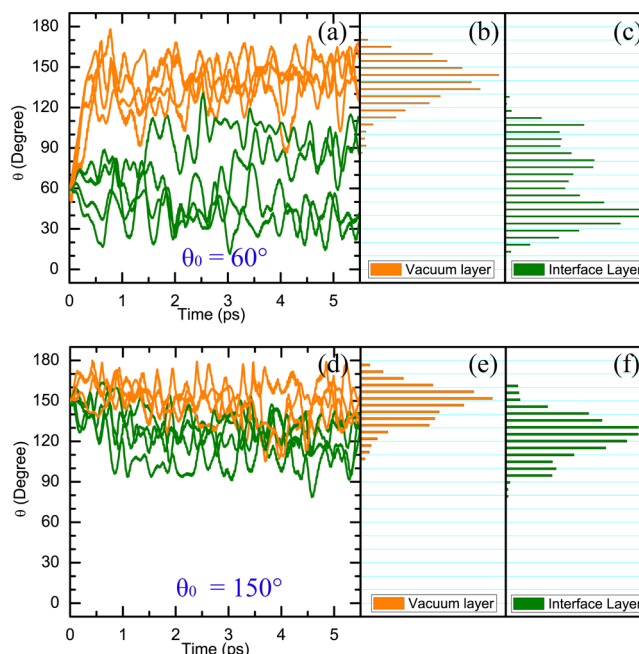


Figure 2. (a) Time evolution of θ of the top layer and interface layer MA moieties in the MAPbI₃/TiO₂ heterojunction during MD simulations with the initial structure with MA orientations of $\theta_0 = 60^\circ$. (b,c) Occurrence frequency of θ of the top layer and interface layer MA moieties in the MAPbI₃/TiO₂ heterojunction during 5 ps MD simulations with the initial structure of $\theta_0 = 60^\circ$. (d) Time evolution of θ of the top layer and interface layer MA moieties in the MAPbI₃/TiO₂ heterojunction during MD simulations with the initial structure of $\theta_0 = 150^\circ$. (e,f) Occurrence frequency of θ of the top layer and interface layer MA moieties in the MAPbI₃/TiO₂ heterojunction during 5 ps MD simulations with the initial structure of $\theta_0 = 150^\circ$.

MA groups in the interface layer oscillate around 60° during the 5 ps MD run, which are in line with their initial structure at the ground state (0 K). The interfacial electric potential-induced orientation selectivity of MA ions is well retained at 300 K, whereas the θ of the four organic groups in the top layer increases from 60 to 150° and reaches the equilibrium value of 150° . For the heterojunction with the initial $\theta = 150^\circ$, the θ of both the top layer and interface layer stabilizes at around 150° (Figure 2b). Therefore, resulting from the interfacial electric field, the orientation selectivity of MA cations in the interface layer can persist at 300 K, while the orientation of MA moieties in the layer away from the perovskite/TiO₂ interface are not stabilized because of weaker interactions between MA and the TiO₂ substrate.

3.3. Ultrafast Charge Dynamics of the MAPbI₃/TiO₂ Heterojunction. Furthermore, to look into the interfacial electronic structures of the two heterojunctions, the projected density of states (PDOS) are calculated (Figure 3a). The energy levels displayed in Figure 3a are measured with reference to the vacuum energy level. Note that the MAPbI₃ model we adopted in our simulations is somehow thin (only containing three atomic layers); as a consequence, the conduction band (CB) and valence band of the thin MAPbI₃

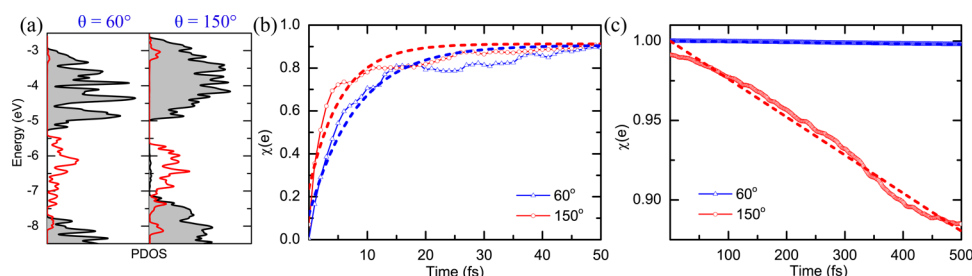


Figure 3. (a) PDOSs of MAPbI₃/TiO₂ heterojunctions with MA orientations of $\theta = 60^\circ$ and $\theta = 150^\circ$, respectively. (b) Total ET fraction χ from the MAPbI₃ LUMO to the TiO₂ CBs as a function of time for MA orientations of $\theta = 60^\circ$ and $\theta = 150^\circ$ at the MAPbI₃/TiO₂ interface. The dashed lines are exponential fittings of the injection process. (c) ET χ as a function of time back from TiO₂ CBM to the MAPbI₃ HOMO during the recombination process at the MAPbI₃/TiO₂ interface for MA orientations of $\theta = 60^\circ$ and $\theta = 150^\circ$. Dashed lines are linear fittings of the interfacial electron–hole recombination process.

Table 1. Estimation of Driving Forces ΔG^0 , Coupling Strength $|S_{DA}|$, Charge-Transfer Distances d , and Rates k^{-1} for Electron Injection and Charge Recombination of Different MA Orientations

θ (deg)	HOMO (eV)	LUMO (eV)	VBM (eV)	CBM (eV)	ΔG_{inj}^0 (eV)	ΔG_{rec}^0 (eV)	d (Å)	$ S_{DA} _{inj}$	$ S_{DA} _{rec}$	k_{inj}^{-1} (fs)	k_{rec}^{-1} (ps)
60	−5.50	−3.24	−7.86	−5.20	1.96	0.30	5.60	2.46×10^{-2}	1.96×10^{-2}	8.17	225.20
150	−5.73	−3.19	−7.21	−4.90	1.71	0.83	3.24	3.60×10^{-2}	0.37	5.55	4.18

slab are separated by a broad E_g of 2.26 eV (2.54 eV) for $\theta = 60^\circ$ ($\theta = 150^\circ$) as a result of the quantum confinement effect, which is larger than the E_g of cubic MAPbI₃ (1.69 eV) in the previous DFT calculations and experiments.^{55–57} This can also be demonstrated by the fact that the calculated E_g of ~ 1.96 eV for the thin MAPbI₃(001) film (Figure S2) is much larger than the energy gap for bulk cubic MAPbI₃. Although in principle a thicker perovskite layer should be utilized to attain more accurate results, it causes unaffordable simulation costs in the present work for MD and nonadiabatic electron dynamics simulations.

The lowest unoccupied molecular orbital (LUMO) levels of both structures lie above the CB minimum (CBM) of TiO₂, ensuring efficient electron injection from MAPbI₃ into the TiO₂ electrode. The energetic driving force ΔG_{inj}^0 for electron injection, namely, the energy difference between the LUMO and the TiO₂ CBM ($\Delta G_{inj}^0 = E_{LUMO} - E_{CBM}$), for the case of $\theta = 60^\circ$ (1.96 eV) is larger than that for $\theta = 150^\circ$ (1.71 eV). The diversity in band offsets is triggered by the distinct dipole moments, which arise from the ordered alignment of the MA moieties at the perovskite/TiO₂ interface. The dipole moments are $\mu = 0.17$ debye for $\theta = 60^\circ$ (the same direction with the vectorial direction of the Z-axis) and $\mu = -4.58$ debye for $\theta = 150^\circ$, respectively. Regarding the interfacial dipole as a parallel-plate capacitor, the potential energy drop across the capacitor is estimated as $\Delta E = \Delta\mu/\epsilon_0 S$, where S is the surface area of the plate. Here, we have $S = 12.90 \text{ Å} \times 13.17 \text{ Å} = 169.89 \text{ Å}^2$. Using the dipole difference $\Delta\mu = 4.75$ debye, we obtain $\Delta E = 0.08$ eV, comparable to the difference in ΔG_{inj}^0 of 0.25 eV quoted above.

In the following, we conduct NAMD simulations to explore the impact of MA orientations on the electron-transfer (ET) process at the MAPbI₃/TiO₂ interface using the mixed quantum-classical fewest switching surface hopping method.^{37,38,58,59} Figure 3b shows the total ET fraction χ from MAPbI₃ to TiO₂ as a function of time for different MA orientations. Both adiabatic ET and nonadiabatic ET are considered in the simulations, which are shown in Figure S3. The two heterostructures exhibit ultrafast electron injection into the TiO₂ substrate, with a lifetime of 8.17 fs for $\theta = 60^\circ$ and 5.55 fs for $\theta = 150^\circ$, respectively. The injection rates are

obtained via exponential fittings of the ET fraction χ from the MAPbI₃ LUMO to the TiO₂ CB as a function of time t with the following equation^{37,38}

$$\chi(t) = \chi_f(1 - \exp[-(t + t_0)/\tau]) \quad (1)$$

Here, χ_f is the final amount of ET and τ is the calculated elapsed time for ET. Influenced by the electronic coupling between MAPbI₃ and TiO₂, little portion of PE state distributes in TiO₂ at t_0 . Here, t_0 can be viewed as the ET time corresponding to the pretransfer amount.

Although the structure of $\theta = 60^\circ$ owns a larger ΔG_{inj}^0 , it possesses a slightly slower injection dynamic from MAPbI₃ to ETL. To find out the reason behind this discrepancy between injection rates and ΔG_{inj}^0 , we have calculated the nonadiabatic electronic coupling strength S_{DA} between the electron donor state and acceptor state, which is known as another critical factor influencing ET^{37,38,60}

$$S_{DA} = \int d^3r \psi_D(\mathbf{r}) \psi_A(\mathbf{r}) \quad (2)$$

The donor state of injection is the LUMO of the perovskite, and the acceptor state is TiO₂ CBM. As shown in Table 1, the calculated electronic coupling strength for the perovskite layer and TiO₂ surface in the structure of $\theta = 60^\circ$ is slightly weaker than that in the structure of $\theta = 150^\circ$ (0.025 vs 0.036), leading to a slower injection dynamic accordingly.

The recombination dynamics for the two conformations are shown in Figure 3c. We observe a dramatic difference (as large as 50 times) in recombination rates between the two interface configurations. The lifetimes for recombination are 225.20 ps for $\theta = 60^\circ$ and 4.18 ps for $\theta = 150^\circ$. The timescales for the charge recombination are estimated by a linear extrapolation of the ET fraction χ from TiO₂ CBM to MAPbI₃ HOMO when all electrons are transferred back to MAPbI₃. The initial amounts of ET from TiO₂ to perovskite in the two configurations during the recombination process are calculated, which are 0.0001 for $\theta = 60^\circ$ and 0.0075 for $\theta = 150^\circ$. In comparison with the case of $\theta = 60^\circ$, the greater initial fraction of the PE electron located in the MAPbI₃ layer in the structure of $\theta = 150^\circ$ suggests a stronger electronic coupling between the perovskite and the semiconductor substrate, which is

demonstrated by a stronger delocalization of the PE state onto the perovskite. This strong delocalization can also be verified by the exciton charge density plots in Figure 4. The electron

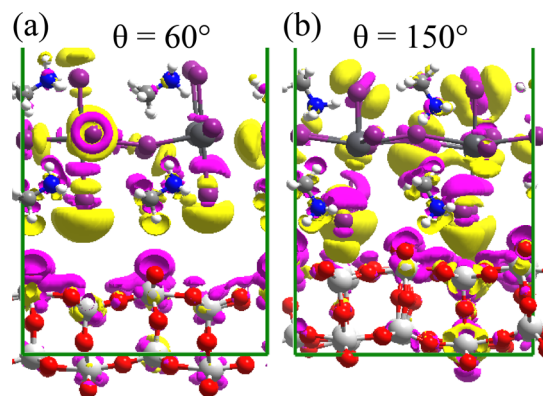


Figure 4. Exciton charge densities of MAPbI₃/TiO₂ heterojunctions with (a) $\theta = 60^\circ$ and (b) $\theta = 150^\circ$, respectively. The value of the isosurface is 0.0001 e/Å³. The electron and hole densities are colored in magenta and yellow, respectively.

and hole densities are colored in magenta and yellow, respectively. Obviously, the exciton charge density for $\theta = 150^\circ$ is more delocalized, spreading over to both TiO₂ and MAPbI₃ layers, in sharp contrast to that of $\theta = 60^\circ$. To dig into the potential reasons for this disparity in recombination behavior, we have calculated the driving force ΔG_{rec}^0 and electronic coupling S_{DA} for the recombination process. From Table 1, both the ΔG_{rec}^0 (0.83 eV) and S_{DA} (0.37) of $\theta = 150^\circ$ are significantly larger than that of $\theta = 60^\circ$ ($\Delta G_{\text{rec}}^0 = 0.30$ eV, $S_{\text{DA}} = 0.02$). As a result, the recombination rate of $\theta = 150^\circ$ is almost 50 times faster than that of $\theta = 60^\circ$. It should be noted that the timescales of interfacial electronic dynamics we acquired show notable differences from the experiments.^{61–66} This difference arises from the discrepancy between computation models and the realistic system, where the perovskite layer is ultrathin (~ 1 nm) and owns idealistic geometry in theoretical modeling, while in experiments the electrons have to migrate to a much thicker perovskite film (~ 200 nm) and may be trapped by the defects at the interface. In addition, the absolute value of the timescales is not the kernel in the present work but the relative difference in dynamical rates between the two configurations. We have shown in the previous work that the relative difference in dynamical rates is correctly reproduced by NAMD.¹⁵

Given the polar properties of MA moieties, MA near the MAPbI₃/TiO₂ interface is orderly aligned under the effective interfacial electric field when a perovskite slab is put onto the TiO₂ substrate. This regular alignment of MA cations is kinetically stable at room temperature. However, when an external electric field is applied during the J – V scanning,^{31,67} the MA ions may rotate and structural transformation is likely to take place, thus leading to distinct interfacial electronic dynamics influenced by the orientation of the MA cations. Therefore, the FE of MAPbI₃ might be one of the underlying causes of the anomalous hysteresis observed in PSCs. In the forward scan which starts from the open-circuit voltage V_{oc} , the external electric field across the PSCs is pointing from MAPbI₃ to the ETL; most of the MA ions would align at around $\theta = 60^\circ$, causing less electron–hole recombination, thus leading to a better photovoltaic performance. When the scan starts from

the short-circuit current J_{sc} , the direction of the external electric field reverses, triggering the MA ions to rotate to a different orientation with $\theta = 150^\circ$; more electrons are lost in the rapid electron–hole recombination, resulting in poor device performance.

3.4. Reducing Interfacial FE via Substitution of MA by FA Ions. To reduce the interfacial FE, we study the possibility to replace the strong polar MA cations with alternative weak polar organic cations. For this purpose, the FA ions are employed as the substitute of the MA groups in the perovskite lattice. We first examine whether the regular alignment of FA ions also exists in the FAPbI₃ structure. We define a standard angle φ , which is the dihedral angle between the surface where the FA group resides and the XY plane, to demarcate the orientation of FA cations. The static geometry of the pristine thin FAPbI₃ slab and the FAPbI₃/TiO₂ interface are calculated (Figure 5a,b). Both conformations start with the initial

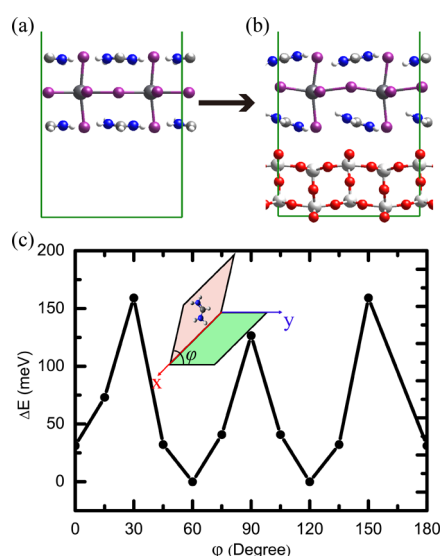


Figure 5. Atomic structures of the (a) thin FAPbI₃ slab and (b) FAPbI₃/TiO₂ heterojunction. (c) Relative energy differences for different FA orientations of the FAPbI₃/TiO₂ heterojunction. The inset shows the schematic diagram of θ , which is defined as the dihedral angle between the surface where the FA moiety resides and the XY plane.

structures that eight FA moieties in the supercell have an orientation of $\varphi_0 = 0^\circ$ (FA moieties are parallel to the XY plane). After structural optimization, in contrast to that in the MAPbI₃ slab, the eight FA groups of the FAPbI₃ slab show similar orientations with $\varphi \approx 10^\circ$. When the FAPbI₃ slab has been put onto the TiO₂ substrate, the FA ions in the top layer and those in the interface layer are all randomly aligned (Figure 5b). The presence of the TiO₂ substrate does not influence the orientation of FA ions because of the weak FA/TiO₂ interactions and in turn the rather shallow surface confinement potential. This is in sharp contrast to the case for the MAPbI₃/TiO₂ heterostructure.

To be prudent, we assume that the FAPbI₃ perovskite also has orientation selectivity as that for MAPbI₃, induced by the interactions with TiO₂. We sweep the PES of the FAPbI₃/TiO₂ heterojunction as a function of φ , with φ ranging from 0° to 90° by fixing the C and N atoms of the FA ions while keeping other atoms relaxed. As shown in Figure 5c, there are two local minima on the PES: $\varphi = 0^\circ$ and $\varphi = 60^\circ$. The energy difference

between the two local minima, however, is very small, only 31 meV per FA moiety, which approaches the thermal energy at 300 K. Thus, we infer that this assumed orientation selectivity of FA cations in FAPbI₃ might not be stable against thermal fluctuations at device operation conditions.

For verifying this point, we have implemented MD simulations starting from the initially relaxed structures of the two conformations to test the stability of the orientation selectivity at room temperature. Figure 6 shows the time

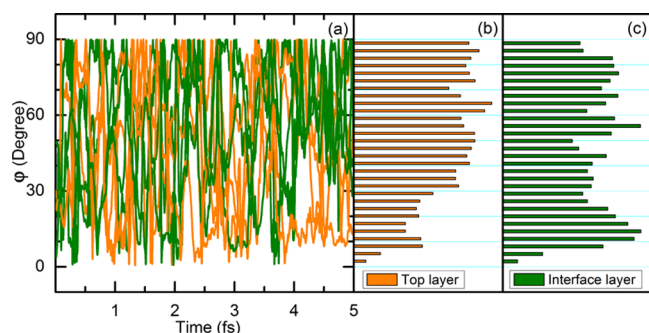


Figure 6. (a) Time evolution of ϕ of the top layer and interface layer FA moieties in the FAPbI₃/TiO₂ heterojunction during MD simulations with the initial structure of $\phi_0 = 0^\circ$. (b,c) Occurrence frequency of ϕ of the top layer and interface layer FA moieties in the FAPbI₃/TiO₂ heterojunction during 5 ps MD simulations with the initial structure of $\phi_0 = 0^\circ$.

evolution of ϕ for FA moieties in the top layer and in the interface layer in the FAPbI₃/TiO₂ heterojunction during the 5 ps MD simulations. It is clearly shown that both conformations do not have an orientation preference of the FA moieties, where FA can freely rotate at 300 K with ϕ in a uniform distribution ranging from 0° to 90° . Therefore, as a result of its symmetric molecular structure, FA groups in both the bulk FAPbI₃ perovskite and the FAPbI₃ layer on TiO₂ can rotate freely at room temperature, giving rise to a random alignment of FA ions, thus leading to the absence of ferroelectric polarization in the FAPbI₃ perovskite at room temperature.

Interestingly, Jeon et al. have observed the improvement of efficiency and stability of the current–voltage curve of PSCs by doping FA moieties in the MAPbI₃ perovskite, as compared to pure MAPbI₃ devices.⁶⁸ Moreover, Lee et al. observed that high-efficiency photovoltaic devices were almost free of hysteresis using pure FAPbI₃.⁶⁹ Here, we infer that the fact that no ferroelectricity exists for FAPbI₃/TiO₂ might be the intrinsic reason for the hysteresis-free phenomenon of FAPbI₃-based PSCs. As the FA ions are randomly oriented under the external electric field during J – V curve scanning, the interfacial electronic dynamics between FAPbI₃ and TiO₂ is irrelevant to the influence of the direction and scan rate of the voltage sweep. Our results suggest that using FA to substitute all or a part of MA in the perovskite lattice is an effective way to reduce the interface-induced FE and the associated current–voltage hysteresis, thus improving the stability and overall efficiency of PSCs.

3.5. Reducing Interfacial FE via Interface Passivation by PCBM. Interface passivation is another most usually used and effective strategy to reduce hysteresis and optimize the photovoltaic devices. Researchers have found that inserting PCBM^{25,26,41,42,70} or another fullerene/graphene derivative^{71–74} as a passivation layer between the perovskite active

layer and ETL can significantly reduce hysteresis as well as enhance the photostability of PSCs. We speculate that the additional PCBM or fullerene/graphene derivative layer may destroy the interfacial electric field between TiO₂ and the perovskite, causing disappearance of orientation selectivity of MA cations, leading to identical interfacial electronic dynamics in the reverse and forward scans, thus effectively eliminating hysteresis and enhancing the photovoltaic performance of PSCs. To test our hypothesis, we have examined the orientation selectivity of MA ions in the MAPbI₃/PCBM heterojunction.

We first optimize the geometric structure of MAPbI₃/PCBM starting from an artificial structure with all MA ions orienting at $\theta = 90^\circ$ (Figure 7a). Optimized stable geometry of MAPbI₃/

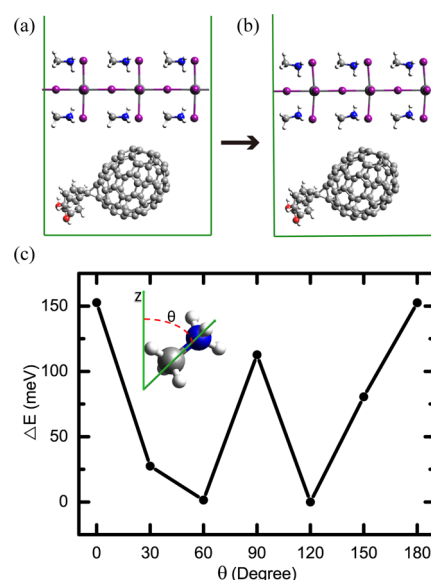


Figure 7. (a) Structures of the MAPbI₃/PCBM heterojunction (a) before and (b) after structural optimization. (c) Relative energy differences for different MA orientations of the MAPbI₃/PCBM heterojunction.

PCBM is shown in Figure 7b, in which the MA moieties of the top layer and interface layer show distinct orientation. The MA ions in the top layer orient at $\theta = 102^\circ$ and the MA groups in the interface layer orient at $\theta = 78^\circ$. The arrangement of MA ions in the MAPbI₃/PCBM heterojunction is similar to that in the MAPbI₃ slab, which stands in stark contrast to the case of the MAPbI₃/TiO₂ heterostructure. We assume that MA moieties have orientation selectivity in MAPbI₃/PCBM as that for MAPbI₃/TiO₂, by way of precaution, and sweep the PES of the MAPbI₃/PCBM heterostructure as a function of θ with all MA ions fixed in identical direction. As shown in Figure 7c, there are two local minima on the PES: $\theta = 60^\circ$ and $\theta = 120^\circ$. The energy difference between the two local minima is 1 meV per MA moiety, and the estimated energy barrier for structural transformation between these two conformations is 113 meV per MA ion.

We have also performed MD simulations of the two conformations to check whether the kind of orientation selectivity of MA ions in MAPbI₃/TiO₂ also exists in MAPbI₃/PCBM at room temperature. From Figure 8, regardless of the initial structures, the thermodynamic equilibrium structures at 300 K are the same after enough time of thermal motion, where the MA groups in the interface layer tend to stabilize at

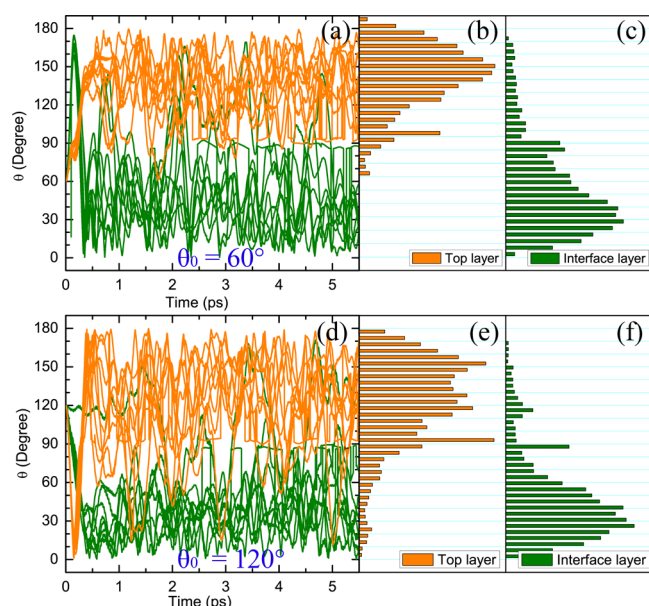


Figure 8. (a) Time evolution of θ of the top layer and interface layer MA moieties in the MAPbI₃/PCBM heterojunction during MD simulations with the initial structure with an MA orientation of $\theta_0 = 60^\circ$. (b,c) Occurrence frequency of θ of the top layer and interface layer MA moieties in the MAPbI₃/PCBM heterojunction during 5 ps MD simulations with the initial structure of $\theta_0 = 60^\circ$. (d) Time evolution of θ of the top layer and interface layer MA moieties in the MAPbI₃/PCBM heterojunction during MD simulations with the initial structure of $\theta_0 = 120^\circ$. (e,f) Occurrence frequency of θ of the top layer and interface layer MA moieties in the MAPbI₃/PCBM heterojunction during 5 ps MD simulations with the initial structure of $\theta_0 = 120^\circ$.

the orientation of $\theta = 30^\circ$, while the MA groups in the top layer reach equilibrium at the orientation of $\theta = 150^\circ$. The same kind of orientation selectivity of MA ions in MAPbI₃/TiO₂ does no longer exist in MAPbI₃/PCBM. To be prudent, we have further examined the orientation preference of MA ions in MAPbI₃/PCBM under external electric fields with opposite directions. Figure S7 shows the time evolution of θ of the top layer and interface layer MA moieties in the MAPbI₃/PCBM heterojunction under external electric fields of $E = \pm 0.1$ V/Å. A positive electric field indicates that the electric field is pointing from the perovskite to PCBM. Apparently, the orientation preferences of MA ions in MAPbI₃/PCBM are almost the same under electric fields with opposite directions, where the MA groups in the interface layer tend to align with the orientation of $\theta = 45^\circ$, while the MA groups in the top layer array with the orientation of $\theta = 135^\circ$. The identical conformations of the MAPbI₃ perovskite in the MAPbI₃/PCBM heterojunction under opposite electric field directions indicate identical interfacial electronic dynamics in forward and backward voltage sweep of PSCs passivated via PCBM. Because of the large size of PCBM, the PCBM layer can separate MAPbI₃ and TiO₂ by ~ 10 Å in space, which efficiently eliminates the interfacial electric field between MAPbI₃ and TiO₂. Therefore, inserting PCBM between MAPbI₃ and the electrode can effectively eliminate the electric field at the MAPbI₃/TiO₂ interface, reducing the interfacial FE-induced photocurrent–photovoltage hysteresis and enhancing the overall performance of PSCs. Our results agree well with the experimental observations that inserting a thicker

PCBM at the TiO₂/MAPbI₃ interface as a passivation layer can alleviate the electrode polarization efficiently.²⁶

4. CONCLUSIONS

The interface structures and nonadiabatic electron dynamics of MAPbI₃ (FAPbI₃)/TiO₂ and MAPbI₃/PCBM heterojunctions have been investigated by NAMD simulations combined with time-domain DFT (TDDFT). The polar organic cations in the MAPbI₃ perovskite show orientation selectivity at room temperature with two preferred MA orientations: $\theta = 60^\circ$ and $\theta = 150^\circ$, induced by the interfacial electric field. The orientation of MA ions could switch under the applied gate field, resulting in significantly different photoelectron injection and electron–hole recombination timescales at the interface, thus leading to unfavorable hysteresis during current–voltage scan. While the FA cations can rotate freely in the FAPbI₃ perovskite at room temperature, which results in identical interfacial electron dynamics, leading to the absence of hysteresis accordingly. Insertion of the PCBM layer between MAPbI₃ and TiO₂ is another efficient way to reduce the interface FE induced by the interface electric field, thus eliminating hysteresis. The present study on the relationship between interface ferroelectric polarization and photovoltaic performance of the perovskite emphasizes the interfacial orientation of the organic moiety as a new degree of freedom for controlling polarization-related hysteresis and puts forward novel insights into a comprehensive understanding of working mechanisms of PSCs at the microscopic scale and further optimization in the performance of PSC devices.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.9b20988>.

Linear response TDDFT method used to compute the exciton charge density; band structure of the bulk MAPbI₃ perovskite calculated with PBE and PBE + SOC; atomic and electronic structure of the thin MAPbI₃(001) film; adiabatic and nonadiabatic ET during electron injection for different MA orientations at the MAPbI₃/TiO₂ interface; PDOS and electron injection and electron–hole recombination dynamics for different FA orientations at the FAPbI₃/TiO₂ interface; adiabatic and nonadiabatic ET during electron injection for different FA orientations at the FAPbI₃/TiO₂ interface; exciton charge density of the FAPbI₃/TiO₂ heterojunction; kinetic stability of the orientation selectivity of MA ions at the MAPbI₃/PCBM interface under different external electric fields; and estimation of driving forces ΔG^0 , coupling strength $|S_{DA}|$, charge-transfer distances d and rates k^{-1} for electron injection and charge recombination of different FA orientations (PDF)

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