

Critical Role of Functional Groups in Defect Passivation and Energy Band Modulation in Efficient and Stable Inverted Perovskite Solar Cells Exceeding 21% Efficiency

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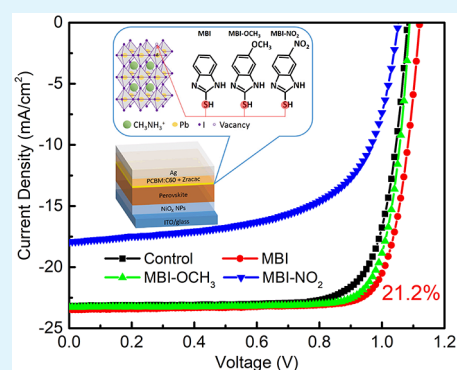
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ABSTRACT: Interfaces in perovskite solar cells (PSCs) are closely related to their power conversion efficiency (PCE) and stability. It is highly desirable to minimize the interfacial nonradiative recombination losses through rational interfacial engineering. Herein we develop an effective and easily reproducible interface engineering strategy where three mercaptobenzimidazole (MBI)-based molecules are employed to modify the perovskite/electron transport layer (ETL) interface. MBI and MBI-OCH₃ can not only passivate defects at surface and grain boundaries (GBs) of perovskite films but can also improve energy level alignment (ELA), which leads to enhanced PCE and stability. Consequently, the PCE is improved from 19.5% for the control device to 21.2% for MBI-modified device, which is among the best reported inverted MAPbI₃-based PSCs. In contrast, incorporation of MBI-NO₂ increases defect density and negligibly influences the energy level alignment. This work indicates that defect passivation and ELA modulation can be achieved simultaneously through modulating functional groups in interface modification molecules.

KEYWORDS: perovskite solar cells, NiO_x interface engineering, defect passivation, energy level alignment modulation



INTRODUCTION

Perovskite solar cells (PSCs) based on metal halide perovskite absorbers have attracted significant attention owing to their high power conversion efficiency (PCE), low cost, and solution-processable property.^{1–8} Metal halide perovskite semiconductors possess lots of unique and intriguing optoelectronic properties, such as tunable bandgap, excellent ambipolar carrier transport property, low exciton binding energy, high defect-tolerant property, high extinction coefficient, good bendability, and long carrier diffusion length and lifetimes.^{9,10} Since the first report of all-solid PSCs with an appealing PCE of 9.7%,² the PCE of PSCs has been rapidly increased to the presently certified 25.2%¹¹ within 10 years, which benefits from some critical advancements, such as device configuration engineering, development and optimization of charge transport materials (CTMs), optimization of perovskite film quality, additive engineering, interface engineering, etc. Nevertheless, this record PCE value is still much lower than the theoretical Shockley–Queisser limit value of about 30% for single-junction PSC.^{12,13} Considering the ionic nature of metal halide perovskite semiconductors, a large number of charged defects would be generated in polycrystalline perovskite films during the fast crystallization and high-temperature annealing. Meanwhile, point defects in the bulk and deep level defects mainly located at surface and grain boundaries (GBs) of

perovskite films have also been reported. It is widely demonstrated that degradation of PSCs is initially triggered by surface and GBs of perovskite films through defect- and trap-assisted nonradiative recombination.^{9,14–17} Besides the interface defects, the interfacial energy level alignment (ELA) is an important factor for interfacial nonradiative recombination.¹⁸ Consequently, minimizing the interface nonradiative recombination losses is key to achieve efficient, stable, and hysteresis-free PSCs through rational interface engineering and modulation.

It is well-known that PSC can be classified into normal n-i-p and inverted p-i-n structures. It has been reported that NiO_x-based inverted PSCs show much better stability and reduced or even free hysteresis as compared to TiO₂-based normal PSCs using Spiro-OMeTAD as hole transport material (HTM).^{19–23} However, the device performances of inverted PSCs are still much lower than that of normal PSCs,^{22–27} suggesting more serious nonradiative recombination in the

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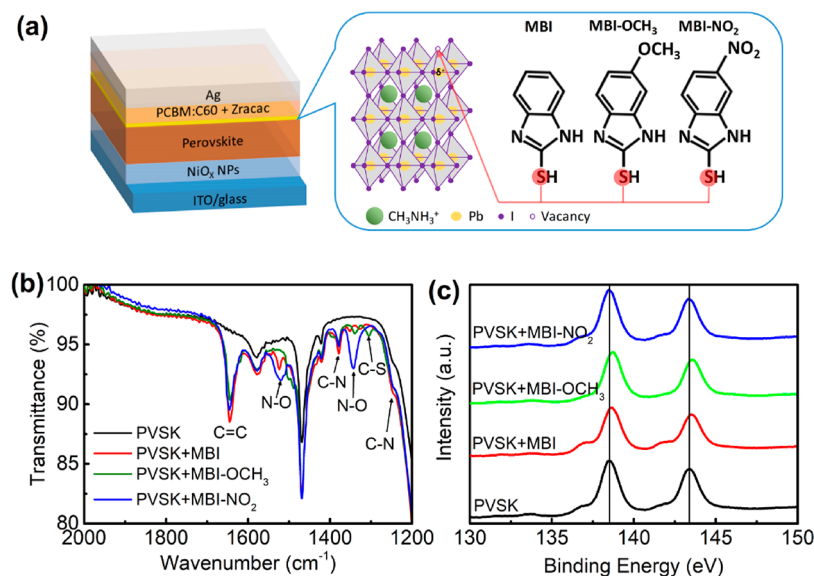


Figure 1. (a) Structure of device adopted in the present work, where interface molecules are inserted between perovskite films and the PCBM:C60 layer. The halide vacancies could be passivated by introducing interface molecules. (b) FTIR spectra of the perovskite films before and after modification. (c) XPS spectra of Pb 4f of perovskite films before and after modification.

inverted PSCs, and thus more studies are needed to further enhance the PCE and stability of NiO_x -based inverted PSCs through interface engineering. Indeed, many efforts have been made for developing various interface modification strategies from the perspective of defect passivation and ELA modulation. Various materials for defect passivation have been reported such as Lewis acid^{28,29} and Lewis base,^{30,31} organic and inorganic salts,^{3,32,33} low-dimensional perovskites^{4,7,34} and other perovskite compositions,^{35,36} etc. Among them, Lewis base molecules have been demonstrated to effectively transform the undercoordinated Pb^{2+} into a Lewis acid base adduct.^{30,31} Compared with commonly reported N and O electron donors,^{30,31,37,38} the studies of S electron donor-based passivation molecules, which have the interesting properties of maximizing the potential of electron donor, are relatively limited particularly for inverted PSCs.³⁹ It is highly desirable to develop organic interface passivation molecules containing S electron donors to enhance the performances and stability of inverted PSCs. Meanwhile, various ELA modulation strategies, such as wide-bandgap perovskite compositions,^{34,40} self-assembled monolayers (SAM),⁴¹ CTMs,^{42,43} wide-bandgap insulating materials,^{44,45} and organic small molecules,^{32,46} have been investigated. Among them, small molecules exhibit great potential in the modulation of ELA because of diverse molecular structure tunability, which is suitable for modifying all kinds of CTMs. Although a large number of small molecules have been developed to passivate interface defects and modify ELA, the work on systematic and in-depth insight into the relationship between the molecular structure change induced by functional groups and the defect passivation effect and ELA is highly limited in PSCs because most of the works just focus on one kind of molecule instead of a series. Overall, it is highly expected to further improve the PCE and stability of NiO_x -based inverted PSCs through rationally modulating the properties (e.g., dipole moment and electronegativity) of functional groups and accordingly modulating the defect passivation effect as well as ELA regarding the perovskite/ETL interface.

In the present work, we propose a series of Lewis base molecules (namely 2-mercaptobenzimidazole (MBI), 5-nitro-2-mercaptobenzimidazole (MBI- NO_2), and 5-methoxy-2-mercaptobenzimidazole (MBI- OCH_3)) for modifying the perovskite/ETL interface and demonstrate that the incorporation of MBI-based molecules can be a simple and effective interface modification strategy for improving the performance and stability of PSCs. Interestingly, it is found that MBI without any functional group and its derivative MBI- OCH_3 with the electron-donating functional group OCH_3 show a positive effect on PCE improvement, but there is a negative effect for MBI- NO_2 with the electron-withdrawing functional group NO_2 . Our studies show that the defect passivation effect and ELA can be modulated via rationally modulating functional groups. This suggests that functional groups in interface molecules play a critical role in final device performance. As a result, the PCE is enhanced from 19.50% for a control device to 21.20% for an MBI-based device, and improved stability is achieved for the PSC with the modification of MBI.

RESULTS AND DISCUSSION

The device structure employed in this work is glass/ITO/ $\text{NiO}_x/\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x/\text{PC}_{61}\text{BM}:\text{C60}/\text{Zr}(\text{acac})_2/\text{Ag}$ (shown as Figure 1a). The cross-sectional scanning electron microscopy (SEM) image of the complete PSC is exhibited in Figure S1. The detailed fabrication procedure is described in Experimental Section. Herein three organic molecules based on MBI and its derivatives including MBI, MBI- NO_2 , and MBI- OCH_3 were developed to modify the perovskite/ETL interface (Figure 1a). We propose them from the expectation that the SH in passivation molecules can interact with the undercoordinated Pb^{2+} (halide vacancies) at the surface and GBs of perovskite films through forming Lewis acid adducts via coordination bonds which has been demonstrated extensively in other reported works.^{46–48} Moreover, the defect passivation effect and ELA are expected to be modulated by the incorporation of an electron-withdrawing functional group (NO_2) and electron-donating functional group (OCH_3). Finally, these interface molecules are expected to improve

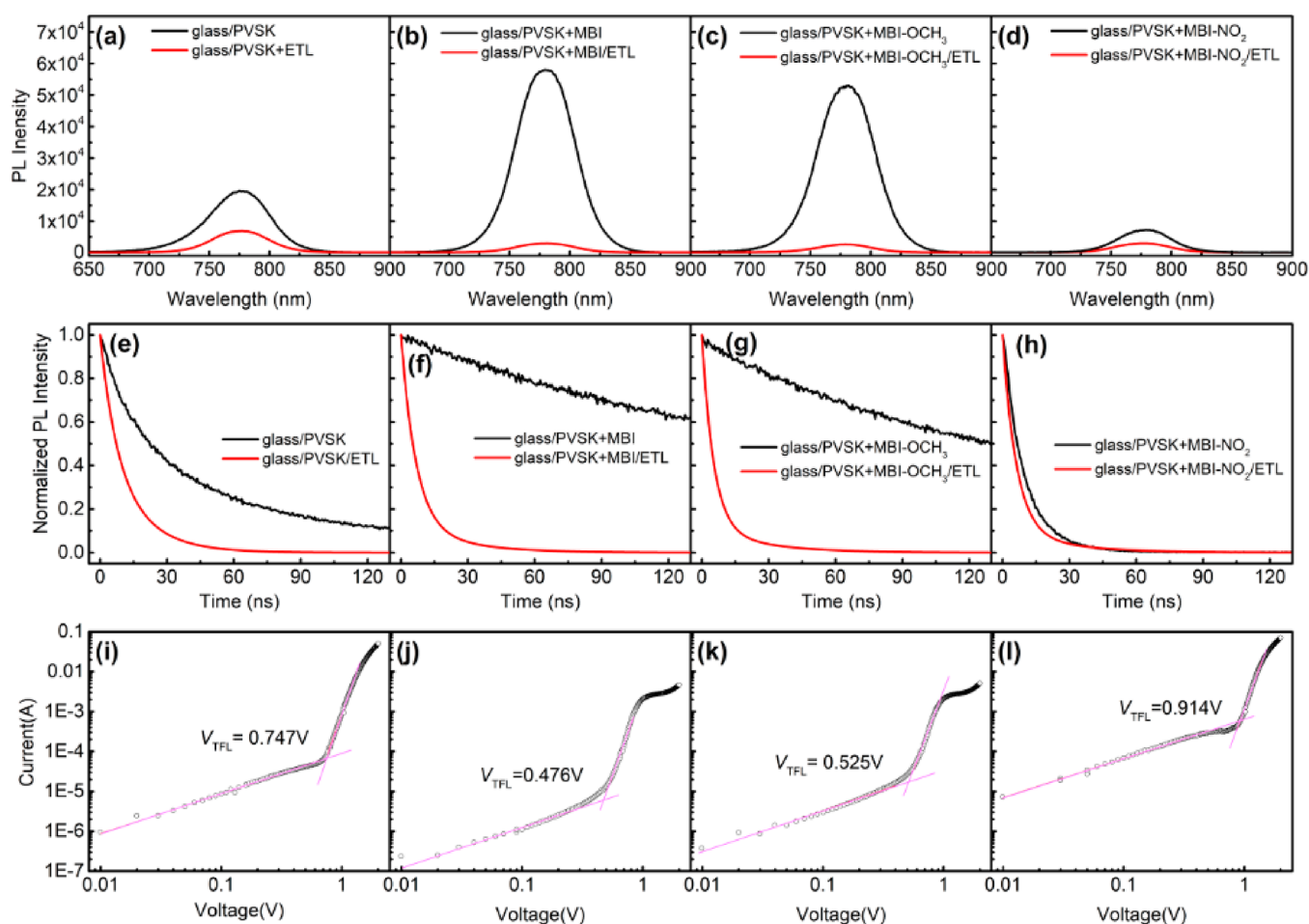


Figure 2. PL spectra of (a) glass/perovskite and glass/perovskite/ETL, (b) glass/perovskite/MBI and glass/perovskite/MBI/ETL, (c) glass/perovskite/MBI-OCH₃ and glass/perovskite/MBI-OCH₃/ETL, and (d) glass/perovskite/MBI-NO₂ and glass/perovskite/MBI-NO₂/ETL. TRPL spectra of (e) glass/perovskite and glass/perovskite/ETL, (f) glass/perovskite/MBI and glass/perovskite/MBI/ETL, (g) glass/perovskite/MBI-OCH₃ and glass/perovskite/MBI-OCH₃/ETL, and (h) glass/perovskite/MBI-NO₂ and glass/perovskite/MBI-NO₂/ETL. Dark *J*-*V* curves of the devices with ITO/perovskite/Au structure, (i) control perovskite film, (j) MBI-modified perovskite film, (k) MBI-OCH₃-modified perovskite film, and (l) MBI-NO₂-modified perovskite film.

stability due to the protection effect and defect passivation effect for perovskite films. Figure S2 shows the electrostatic potential (ESP) map of MBI, MBI-NO₂, and MBI-OCH₃ molecules. Apparently, high but different dipole moments are observed for the three molecules, suggesting that they can serve as interface modifiers. The dipole moments of these molecules can be tuned via the electronegative functional groups. The perovskite/ETL interface is modified by directly spin-coating the molecules dissolved in 2-propanol (IPA) onto the as-prepared perovskite films. Figure 1b presents Fourier transform infrared (FTIR) spectra of perovskite films before and after the treatment. Characteristic peaks ($\sim 1645\text{ cm}^{-1}$) from C=C of the benzene ring are found in the perovskite films modified by MBI, MBI-NO₂, and MBI-OCH₃ but not the control film. To investigate the chemical interaction between the molecules and perovskite, X-ray photoelectron spectra (XPS) measurements were performed for unmodified and modified films. Figure 1c shows that the peaks of Pb 4f_{7/2} and Pb 4f_{5/2} are located at 138.5 and 143.3 eV for the pristine and MBI-NO₂ modified perovskite, respectively. Meanwhile, the binding energy (138.7 and 143.5 eV) of the MBI- and MBI-OCH₃-modified perovskite shifts to higher energy. That implies that strong chemical interaction exists between MBI

or MBI-OCH₃ and perovskite films but no or extremely weak interaction between MBI-NO₂ and perovskite films. The introduction of strong electron-withdrawing NO₂ was not beneficial for defect passivation because of the reduced electron density of SH. The small peaks at around 137 and 142 eV can be identified as metallic Pb, which are generally caused by sample degradation during the measurements. Subsequently, we measured the UV-vis absorption spectra to investigate the effect of modification molecules on light-harvesting ability (Figure S3). It is found that these molecules do not influence the UV absorption of perovskite films. Meanwhile, the modification molecules seem to be observed at the surface of perovskite films as shown in the SEM images in Figure S4a-d. This indicates that the thicknesses of modification molecules are extremely thin but good enough for carrier transport across the perovskite/ETL interface as will be discussed below. The roughness of perovskite films with and without modification was evaluated through atomic force microscopy (AFM) measurement (Figure S4e-h). The root-mean-square (RMS) is determined to be 16.6 nm for the control film, 15.9 nm for the MBI-modified film, 15.7 nm for the MBI-OCH₃-modified film, and 16.6 nm for the MBI-NO₂-modified film, which is indicative of a negligible change of

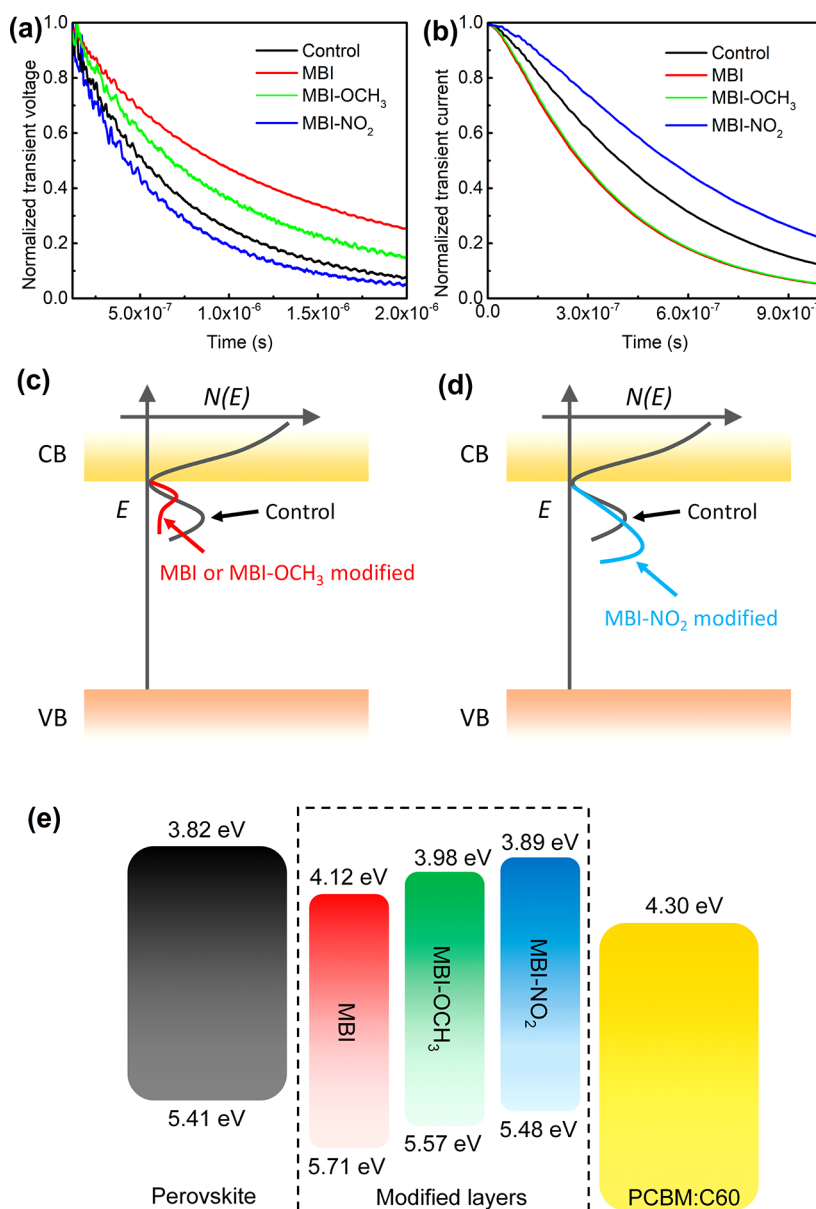


Figure 3. (a) TPV and (b) decay curves of devices with and without interface modification. Defect profile diagram of perovskite films modified by (c) MBI and MBI-OCH₃ and (d) MBI-NO₂. (e) Energy level diagram of the control perovskite film, the MBI-based modification layers, and PCBM:C60.

RMS before and after modification. To gain insights into the effect of interface modification on electronic properties of the surface and GBs, conductive AFM measurement was performed, as illustrated in Figure S4i–l. It is seen that the surface becomes more conductive after MBI and MBI-OCH₃ modification and more significant for MBI as compared to the control perovskite film but almost similar to the control for MBI-NO₂-modified film. This indicates that MBI and MBI-OCH₃ modification, but not MBI-NO₂ modification, can improve the carrier transport pathways at the surface and GB of perovskite films. These results show that the modification of interface molecules is highly dependent on their molecular structures.

Photoluminescence (PL) and time-resolved PL (TRPL) measurements were performed to investigate the effect of interface modification on carrier lifetimes and charge extraction (Figure 2a–h). The structures of PL and TRPL samples are

glass/perovskite and glass/perovskite/ETL before and after modifications. More details about the fabrication process can be found in Experimental Section. TRPL spectra were fitted according to a biexponential decay equation of $I(t) = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where τ_1 and τ_2 stand for fast and slow decay time constant, respectively.^{32,35} Average lifetimes were calculated by the equation $\tau_{ave} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$.³² Fitted results and τ_{ave} are presented in Table S1. The PL intensity increases remarkably after MBI and MBI-OCH₃ modification compared with the control film but decreases significantly for the MBI-NO₂-modified film. At the same time, the lifetime (130.96 ns) of the control film increases significantly to 319.64 ns for the MBI-modified film and 285.40 ns for the MBI-OCH₃-modified film while markedly decreases to 11.96 ns for the MBI-NO₂-modified film, which indicates that MBI and MBI-OCH₃ interface molecules can effectively passivate defects at the surface and GB of perovskite

films but that MBI-NO₂ can act as recombination centers and thus lead to serious trap-assisted nonradiative recombination. As reflected by the electron lifetimes when perovskite films are contacted with ETL, electron extraction is significantly improved after MBI and MBI-OCH₃ modification compared to the unmodified sample while is suppressed remarkably after MBI-NO₂ modification. This suggests that MBI and MBI-OCH₃ could modulate ELA toward a beneficial direction for electron transport and extraction whereas MBI-NO₂ can modulate ELA toward the opposite direction, which will be discussed later in detail.

Space-charge-limited current (SCLC) measurement was carried out to determine the defect density of perovskite films. Figure 2i–l shows the dark current density (*J*)–voltage (*V*) characteristics of ITO/perovskite with or without modification/Au. Typically, three regions can be found in as-measured *J*–*V* curves, including the ohmic region at low bias, the trap-filled limited region at the intermediate bias region, and the trap-free SCLC region at high bias. In the trap-filled limited region, the traps are filled continuously as bias increases and all traps are filled until the trap-filled limited voltage (*V*_{TFL}). *V*_{TFL} can be used for calculating the trap density according to the equation $n_t = (2\epsilon\epsilon_0 V_{TFL})/(eL^2)$, where ϵ is the dielectric constant of perovskite, ϵ_0 is the vacuum permittivity, *L* is the thickness of the perovskite film, and *e* is the elementary charge. The dielectric constant of the perovskite is calculated by the formula of $\epsilon = (C_g L)/(\epsilon_0 A)$, where *C_g* is the geometrical capacitance of the perovskite layer.³² In light of the similar *C_g*, *L*, and *A*, ϵ values are almost the same. In this case, *n_t* is proportional to *V*_{TFL}. In other words, *V*_{TFL} can directly reflect the amount of trap density. *V*_{TFL} is determined to be 0.747 V for the control device, 0.476 V for the MBI-treated device, 0.525 V for the MBI-OCH₃-treated device, and 0.914 V for the MBI-NO₂-treated device. On top of the PL results, the results reconfirm that MBI and MBI-OCH₃ effectively passivate the defects of the surface and GB of perovskite films.

Transient photovoltage (TPV) and transient photocurrent (TPC) measurements were also performed to investigate the interfacial carrier dynamics of real devices with and without interface modification as shown in Figure 3a. The devices modified by MBI and MBI-OCH₃ decay much slower than the control device but much faster for the MBI-NO₂-modified device, which is indicative of much suppressed trap-assisted nonradiative recombination in MBI and MBI-OCH₃-modified devices and increased trap-assisted nonradiative recombination in the MBI-NO₂-modified device. As a result, interfacial electron extraction is facilitated after MBI and MBI-OCH₃ modification while it is inhibited for the MBI-NO₂-modified device (Figure 3b), which is in good accordance with TRPL results on evaluating electron extraction.

Figure 3c,d shows the schematically illustrated defect passivation diagram after interface modification. The number of trap states is reduced, and the energy level of trap states becomes shallower after MBI and MBI-OCH₃ modification. In contrast, MBI-NO₂ modification increases the number of traps and makes the energy level of traps deeper relative to control film. To gain insights into the effect of interface modification on interfacial energy band alignment, ultraviolet photoelectron spectroscopy (UPS) measurements were used to determine the energy levels of perovskite films before and after modification (Figure S5). The work function (WF) was determined to be −4.18 eV for bare perovskite film, −4.21 eV for the MBI-

treated film, −4.20 eV for the MBI-OCH₃-treated film, and −4.48 eV for MBI-NO₂-treated film. It can be evidently found that MBI-NO₂ lowers the WF, which may influence the electron extraction. To define the valence band maximum (VBM) of these samples exactly, logarithmic detection modes are also shown in Figure S5b to avoid the probably erroneous VBM position caused by the low density of states at the VBM.^{49,50} The top of the valence band was estimated to be 1.23 eV for bare perovskite film, 1.50 eV for the MBI-treated film, 1.37 eV for the MBI-OCH₃-treated film, and 1.00 eV for the MBI-NO₂-treated film, respectively. The valence band maximum (VBM) was calculated to be −5.41 eV for the pristine, −5.71 eV for the MBI-treated, −5.57 eV for the MBI-OCH₃-treated, and −5.48 eV for the MBI-NO₂-treated perovskite films. According to UV–vis spectra, the bandgap of the perovskite film was estimated to be 1.59 eV. Therefore, the conduction band minimum (CBM) was calculated to be −3.82 eV for the bare perovskite film, −4.12 eV for the MBI-treated film, −3.98 eV for the MBI-OCH₃-treated film, and −3.89 eV for the MBI-NO₂-treated film, respectively. This suggests that band bending takes place due to the introduction of interfacial dipole molecules and that the bending volume is greatly affected by the substituent groups on the benzene ring. As illustrated in Figure 3e, the CBM (−3.82 eV) of the bare perovskite film has an energy offset of about 480 meV concerning PCBM:C60, which is much higher than the ideal energy offset (200 meV). After modification with MBI-based layers, the offsets of the interfaces of the perovskite/modified layer and modified layer/PCBM:C60 demonstrate 300 and 180 meV for MBI, 160 and 320 meV for MBI-OCH₃ and 70 and 410 meV for MBI-NO₂. This indicates that MBI has the best energy alignment and contributes to the least voltage loss. Also, MBI-OCH₃ has a capability similar to that of MBI. Consequently, MBI and MBI-OCH₃ modification effectively passivates interfacial defects and improves band alignment while MBI-NO₂ modification increases interfacial defects and shows negligible influence over VBM.

Because the thicknesses of these insulating organic modification molecules are very important to achieve high PCE, the effect of concentrations of these molecules on device performance was compared systematically and the corresponding photovoltaic parameters are given in Tables S2–S4. It should be stressed that we used the low transmission ITO glass to preliminarily optimize the concentrations of modification molecules (Tables S2–S4) while high transmission ITO glass was utilized when we compared the effect of different modification molecules on device performance (Table 1). As

Table 1. Photovoltaic Parameters of Control Device and Devices Based on Different Interface Modification Molecules^a

device		<i>J</i> _{SC} (mA/cm ²)	<i>V</i> _{OC} (V)	FF	PCE (%)
control	best	23.19	1.080	0.78	19.50
	average	22.72	1.066	0.78	18.85
MBI	best	23.50	1.120	0.81	21.20
	average	22.97	1.108	0.79	20.07
MBI-OCH ₃	best	23.28	1.090	0.81	20.55
	average	22.58	1.095	0.79	19.41
MBI-NO ₂	best	17.96	1.050	0.62	11.77
	average	15.38	1.063	0.58	9.58

^a*J*–*V* curves were measured.

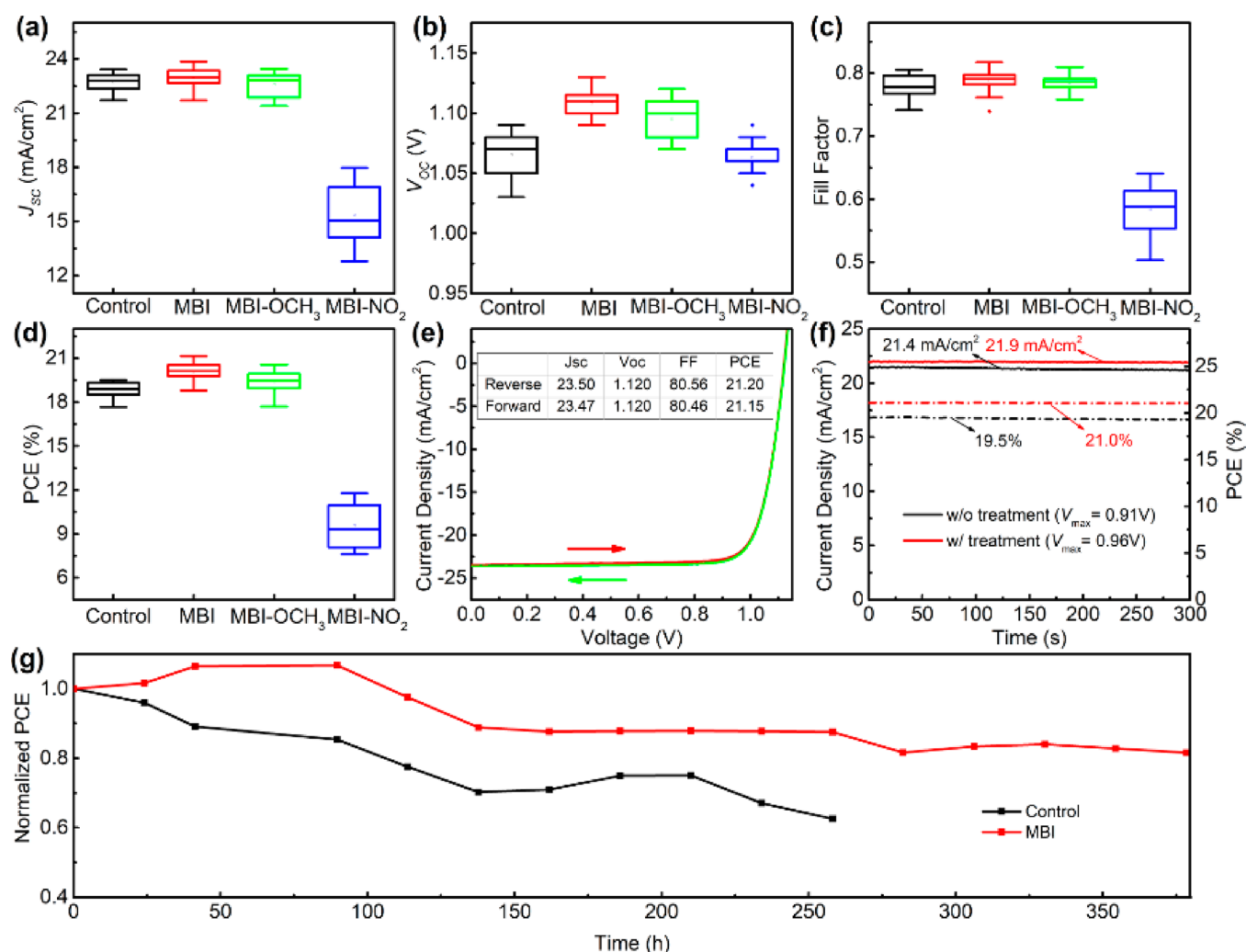


Figure 4. Statistical distribution of (a) J_{sc} , (b) V_{oc} , (c) FF, and (d) PCE of devices with and without interface modification. The statistical data are analyzed from over 20 cells for each condition. (e) J - V curves of the champion device modified by MBI. (f) Steady-state current density and PCE as a function of time for the control device and MBI-modified devices holding the voltage at the maximum power point. (g) Stability of devices with and without MBI modification exposed to continuous one-sun illumination. The stability was tracked at maximum power points.

displayed in Tables S2–S4, the optimal concentration is found to be 0.2 mg/mL for MBI and MBI- OCH_3 , but MBI- NO_2 modified devices show significant reduction even if the extremely low concentration of 0.05 mg/mL is employed. Therefore, the concentration of 0.2 mg/mL is adopted for all the molecules for proper performance comparison of PSCs with different molecule modifications. The statistical distribution diagrams of photovoltaic parameters of the devices with/without interface modification are shown in Figure 4a–d, and corresponding data are given in Table 1. The average PCE increases from 18.85% for the control PSC to 20.07% for the MBI-based device and 19.41% for the MBI- OCH_3 -based device because of improved V_{oc} and fill factor (FF). In contrast, the average PCE is reduced from 18.85% for the control device to 9.58% for the MBI-based device or 19.41% for the MBI- NO_2 -based device as a result of all parameters being reduced, especially for short circuit current (J_{sc}) and FF. The improved V_{oc} and FF of devices based on MBI and MBI- OCH_3 modification are attributed to effective defect passivation and improved energy band alignment as discussed above. Meanwhile, the performance reduction of MBI- NO_2 -modified PSCs is ascribed to increased defects and worse energy band

alignment. The above results highlight the importance of functional group modulation in passivating defects and modulating ELA. The best-performing control device exhibits 23.19 mA/cm^2 (23.13 mA/cm^2), 1.080 V (1.080 V), 0.78 (0.78 V), and 19.50% (19.41%) for J_{sc} , V_{oc} , FF, and PCE in reverse scan (RS) (forward scan (FS)), respectively. Interestingly, the champion device with MBI modification yields 23.50 mA/cm^2 (23.47 mA/cm^2), 1.120 V (1.120 V), 0.805 (0.805), and 21.20% (21.15%) for J_{sc} , V_{oc} , FF, and PCE in RS (FS), respectively (Figure 4e). Importantly, almost no hysteresis is observed in all the PSCs with and without the modifications. The integrated current density of the device based on MBI modification is 22.25 mA/cm^2 from incident photon-to-current conversion efficiency (IPCE) as shown in Figure S6, which is in good agreement with J_{sc} from the J - V curve. The stabilized PCE was measured to evaluate the device performances at maximum power point (V_{max}) (Figure 4f). The target device with MBI modification produces a stabilized PCE of 21% at $V_{max} = 0.96\text{ V}$ as compared to 19.5% at $V_{max} = 0.91\text{ V}$ of the control device. The current density and PCE of both kinds of devices immediately reach their maximum values, which again confirms no hysteresis.

While the operational stability is a critical issue for the large-scale commercial application of PSCs, the photostability of devices with and without MBI interface modification measured at maximum power point under one standard sun illumination at room temperature is shown in Figure 4g. It is easily observed that the MBI-modified PSCs show significantly improved stability as compared to the control. This implies that the reduced interface defects and thus interfacial trap-assisted nonradiative recombination also offer improved stability for the MBI-modified device, which agrees well with other studies.^{9,16,35}

CONCLUSIONS

In summary, we developed an effective and reproducible interface engineering strategy where three molecules containing SH at one side and functional groups with different electronegativities at the other side (at the benzene ring) are introduced to modify the perovskite/ETL interface. It is found that MBI and MBI-OCH₃ modification can enhance the PCE and stability of devices whereas a significantly negative effect on device performance is observed for MBI-NO₂ modification. It is demonstrated that the improved PCE and stability of MBI- and MBI-OCH₃-based devices are ascribed to suppressed interfacial nonradiative recombination induced by reduced defect density and improved energy band alignment induced by ideal energy offsets near 200 meV. The device with MBI modification yields a PCE of 21.2% and is among the highest efficiency of the NiO_x-based PSCs reported recently. The present work suggests that modulation of functional groups in interface molecules plays a key role in defect passivation and energy band alignment modulation to realize efficient and stable PSCs simultaneously.

EXPERIMENTAL SECTION

Materials. All chemicals were commercially available and used as purchased unless noted otherwise, including methylammonium iodide MAI (MA: CH₃NH₃) (99%, Greatcell Solar Materials Co., Australia), lead(II) iodide PbI₂ (99%, Sigma-Aldrich), methylammonium chloride MACl (98%, Dyesol), [6,6]-phenyl C61 butyric acid methyl ester PC₆₁BM, and fullerene C60 (99%, Xi'an Polymer Light Technology Co.). NiO_x nanoparticles (NPs) were synthesized according to our previous works.^{51,52}

Device Fabrication. Normal ITO-coated glasses (maximum transmittance = 88%) and highly transparent ITO-coated glasses (maximum transmittance = 93%) were both used as the substrates in this work. They were cleaned sequentially with detergent, acetone, ethanol, and deionized water with ultrasonic cleaning. The substrates were kept in clean deionized water and dried with nitrogen purging before use. Fifteen milligrams of NiO_x nanoparticles were dispersed in 1 mL of deionized water–2-propanol (4:1) mixtures. After 20 min of ultraviolet–ozone treatment, the substrates were ready for spin-coating NiO_x NPs to obtain 20 nm NiO_x films. The products were annealed at 120 °C for 10 min in the ambient environment and then transferred into a nitrogen-filled glovebox for another 10 min annealing process at 120 °C. The perovskite precursor was prepared by dissolving 190 mg of MAI, 500 mg of PbI₂, and 30 mg of MACl in 1 mL of *N,N*-dimethylformamide (DMF) solvent with vigorous stirring for 2 h. To fabricate the perovskite film, the precursor (50 μ L) was dropped on the ITO/NiO_x substrates and spin-coated at 5000 rpm. After 6 s, 200 μ L of anhydrous chlorobenzene was softly dropped at the center of the substrates. The spin-coating process took 16 s. The products were annealed at 80 °C for 5 min and 100 °C for 10 min gradually. The modification process needs to deposit a thin film on the surface of the perovskite. MBI, MBI-OCH₃, and MBI-NO₂ 2-propanol solutions at different concentrations are prepared in advance. These solutions are spin-coated at 4000 rpm for 40 s and

annealed at 80 °C for 5 min sequentially. The PL and TRPL samples are prepared under the same conditions on the glasses. The electron transporting layer was fabricated via spin-coating PC₆₁BM:C60 solution (8 mg of PC₆₁BM + 12 mg of C60 in 1 mL of dichlorobenzene) at 1500 rpm for 40 s and 4000 rpm for 20 s. Subsequently, zirconium(IV) acetylacetonate (Zracac) (2 mg/mL in anhydrous ethanol) was spin-coated at 4000 rpm for 40 s. Finally, the resulting samples were transferred into the interconnected high-vacuum evaporation chamber to deposit 100 nm silver as the top electrode. The area of electrodes defined by shadow masks is 0.06 cm².

Measurement and Characterization. X-ray photoelectron spectroscopy (XPS) of the perovskite films was measured in the ultrahigh vacuum environment using a Physical Electronics PHI 5802 with a monochromatic Al K α X-ray source. Ultraviolet photoelectron spectroscopy (UPS) was measured by a He discharge lamp (He I 21.22 eV, Kratos Analytical). A bias of 5 V was applied to the sample during UPS measurement. Surface morphology of the perovskite films was characterized by atomic force microscopy (AFM) in tapping mode and SEM (Hitachi S4800 FEG). The *J*–*V* curves were recorded from –0.1 to 1.15 V using a Keithley 2635 apparatus with scan rate of 0.1 V/s. The simulated light source was Newport AM 1.5G irradiation (100 mW/cm²) and calibrated with an ISO 17025-certified KG3-filtered silicon reference cell. To ensure the device area, a shadow mask with an area of 0.0336 cm² was used for *J*–*V* measurement. During maximum power point tracking measurement, the devices are simply encapsulated by torr seal epoxy resin leak sealant. The measurement proceeds under the relative humidity range of 30–50% at room temperature. The samples for storage stability measurement are not encapsulated and are stored in a nitrogen-filled glovebox. The steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) characterization was performed with a PicoQuant FluoTime 300. A picosecond 375 nm pulse laser (LDH–P-C-375) with a pulse width of <40 ps was employed to excite the perovskite. The time-resolved single was measured by a time-corrected single photon counting (TCSPC, PicoHarp 300E) module with a photomultiplier (PMA-C 192-M) detector. The obtained data were fitted with the below biexponential function:

$$I(t) = A1 \exp\left(-\frac{t}{\tau_1}\right) + A2 \exp\left(-\frac{t}{\tau_2}\right) \quad (1)$$

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.0c18862>.

SEM, ESP map, UV–vis spectra, AFM and conductive-AFM, energy level measurement, IPCE and integrated current density, fitted result of TRPL, and photovoltaic parameters (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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