

Self-Polymerization of Monomer and Induced Interactions with Perovskite for Highly Performed and Stable Perovskite Solar Cells

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While there is promising achievement in terms of the power conversion efficiency (PCE) of perovskite solar cells (PSCs), long-term stability has been considered the main obstacle for their practical application. In this work, the authors demonstrate the small monomer 2-(dimethylamino) ethyl methacrylate (DMAEMA) with unsaturated carboxylic acid ester bond in the antisolvent for perovskite formation to improve the PCE and stability. The results show that DMAEMA is self-polymerized and uniformly distributed in the film, contributing to the improved crystallinity of the perovskites. Equally important, it is found that there are newly established interactions of Pb^{2+} and DMAEMA, and iodine and ternary amine between DMAEMA and perovskites, which improves the uniformity of the lead (II) iodide vertical distribution along with the films and thus phase stability, as well as largely decreases defects density in the film. Overall, the inverted PSCs with DMAEMA exhibit a open-circuit voltage of 1.10 V, short-circuit current of 23.86 mA cm^{-2} , fill factor of 0.82, and finally PCE reaches 21.52%. Meanwhile, the PSC stability is significantly improved due to the inhibition of the formation of iodine, reduction of the uncoordinated Pb^{2+} , and suppression of phase segregation.

low-cost solution-processed method and high efficiency. In the past decade, PSCs' power conversion efficiency (PCE) has increased rapidly from 3.8% to 25.5%,^[1] which is comparable to the single-crystal silicon solar cells. The high performance of solar cells stems from high absorption coefficient, fast charge extraction, long carrier diffusion length, and facile bandgap tunability.^[2] Although PSCs show superior optoelectronic properties and attractive PCE, the easy-degradation feature originating from the intrinsic defects,^[3] ion migration,^[4] and phase segregation^[5] under ambient moisture, temperature, and light severely hinders further commercialization.^[6]

Recently, numerous approaches including additive engineering,^[7] interface engineering,^[8] and composition engineering^[8b,9] have been applied to improve the efficiency and stability of

1. Introduction

Organic–inorganic halide perovskite solar cells (PSCs) have emerged as a new type of photovoltaic material due to the

PSCs. The interface engineering including bottom and top carrier transport layer modification can reduce the trap density formed at the interface, tune band alignment, and modify perovskite crystallization (particularly for bottom carrier transport layers).^[8d,10] However, there is a concern that the trap states in the bulk perovskites originated from low temperature solution-processing and fast crystallization cannot be passivated by interface engineering. Regarding additive engineering, besides improving the band alignment and perovskite crystallization, it can directly reduce the defects both in the bulk perovskite and at the interfaces formed during the polycrystalline perovskite formation process, which are critical to suppress the film degradation.^[11]

A large number of additives, such as Lewis acid or base with different functional groups,^[12] low-dimensional perovskite,^[8b,13] and ionic liquid^[14] have been incorporated into the perovskites. For example, the metal cations such as Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Ni^{2+} , and Cu^{2+} can be doped in the lattice or grain boundary and function as a passivation agent to reduce specific defects with experimental and theoretical evidence.^[7a,15] Besides, Snaith et al. incorporated an ionic liquid named 1-butyl-3-methylimidazolium tetrafluoroborate in the perovskite active layer, which attributes to enlarged crystal size, favored NiO /perovskite interface, and suppressed defects so that more than 1800 h stability

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within 95% PCE is achieved.^[14a] Polymer additives such as poly(4-vinylpyridine),^[16] ethyl cellulose,^[17] polyethylene glycol,^[18] and polycaprolactone^[19] have been incorporated into the perovskite films to further improve the performance of the PSCs. Although polymers are stable and could be envisioned as cross-linked agents in the perovskite films, the long-chain polymers are hard to dissolve in the precursor and may affect the precursor stability by acting as nuclei centers. Recently, small functional monomers have been introduced into the perovskites and then incorporated into the perovskite films as polymer.^[20] Yang's group reports a polymerization-assisted grain growth strategy using dimethyl itaconate monomers with azobisisobutyronitrile (AIBN) to reduce defects density.^[20b] However, the film process temperature should be high, up to 150 °C, to decompose the extra AIBN by a two-step fabrication method. Also, the monomer may be polymerized in the precursor to affect the following crystallization process and thus the quality of perovskite film and the device stability.^[20,21] Furthermore, the mechanisms behind the polymerizable monomer have not been discussed in detail.

Here, we demonstrate 2-(dimethylamino) ethyl methacrylate (DMAEMA) in the perovskite film for better perovskite crystallinity and reduced defects density by a simple one-step antisolvent additive engineering (AAE). Our results show that the DMAEMA is self-polymerized in perovskite films without any initiator after annealing. Meanwhile, the Lead (II) iodide (PbI₂) distribution in the cross section becomes more uniform owing to the interactions between DMAEMA and perovskites, contributing to the improved phase stability. Furthermore, the interactions passivate the defects and thus the nonradiative recombination is significantly suppressed, promoting a longer carrier lifetime. Consequently, the inverted PSCs with DMAEMA exhibit open-circuit voltage (V_{oc}) of 1.10 V, short-circuit current (J_{sc}) of 23.86 mA cm⁻², and fill factor (FF) of 0.82, finally contributing to a PCE of 21.52%, much higher than the control device. Equally important, the PSC stability is highly improved due to the inhibition of the iodine formation, reduction of the uncoordinated Pb²⁺, and suppression of phase segregation.

2. Results and Discussion

The perovskite film was fabricated by the simple one-step low-temperature AAE method. Briefly, the DMAEMA was dissolved in the chlorobenzene (CB) and applied as an antisolvent for film formation. DMAEMA molecule has unsaturated carboxylic acid ester and a tertiary amino group as shown in Figure S1, Supporting Information. The molecule can be polymerized simultaneously due to the C=C bond, and the C=O bond and tertiary amino group can interact with lead ions and iodine, respectively. **Figure 1a** shows the scheme of the fabrication process; the CB including different DMAEMA concentration functions as the antisolvent. **Figure 1b** shows the scanning electron microscope (SEM) of control perovskite film after annealing at 100 °C with the composition of Cs_{0.05}(MA_{0.1}FA_{0.9})_{0.95}Pb(I_{0.9}Br_{0.1})₃ (FA = formamidinium and MA = methylammonium), while **Figure 1c** shows the perovskite film with AAE method. Compared with **Figure 1b,c**, the size of perovskite grains is almost unchanged but many small grains existed surrounding the large perovskite grains. During the film fabrication process, the DMAEMA is incorporated into the perovskite film by the antisolvent dropping at the 20th second based on existed nucleation sites in the intermediate phases. Therefore, the grains formed from nuclei via the nucleation induced by the monomer are smaller as shown in **Figure 1c** so that larger grains and smaller grains are formed after annealing process.^[22]

The chemical interactions between DMAEMA and perovskites are investigated by Fourier transform infrared spectroscopy (FTIR) as shown in **Figure 1d,e**. The characteristic vibration peaks of C=O at 1717 cm⁻¹ and C–N stretch peak at 1157 cm⁻¹ are the typical peaks of DMAEMA. The DMAEMA is liquid, so the PbI₂ and DMAEMA are mixed directly and heated at 100 °C. The FTIR results show that the C=C stretch peak at 1637 cm⁻¹ and bend peak at 940 cm⁻¹ are almost disappeared, demonstrating that the DMAEMA is polymerized in the PbI₂, and indicating that the DMAEMA is also polymerized in the films after heating with the AAE fabrication process. Besides, the C–N stretch peak shifts to a lower value and the C=O

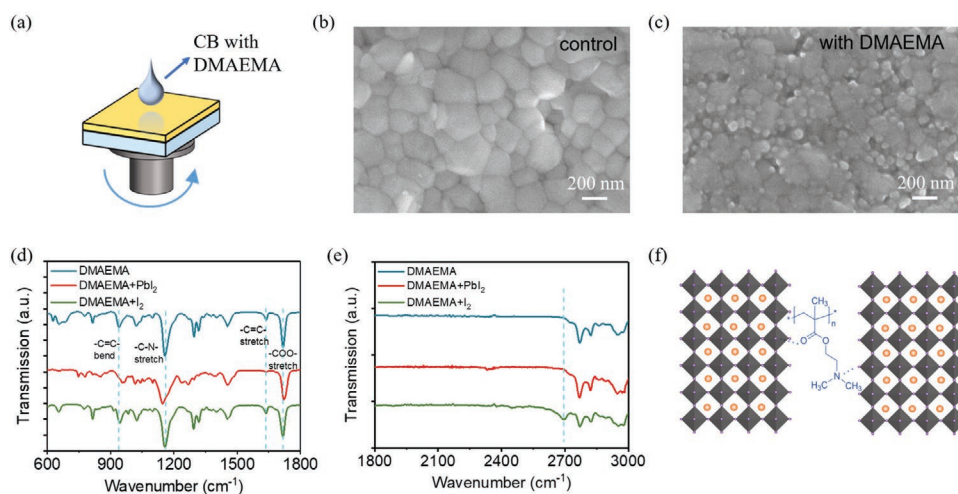


Figure 1. a) Scheme of the AAE fabrication process. b) SEM of control perovskite film. c) SEM of DMAEMA-incorporated perovskite film fabricated by AAE method. d,e) FTIR of DMAEMA and DMAEMA with iodine and PbI₂, respectively. f) Schematic illustration of interactions between DMAEMA and perovskite crystals.

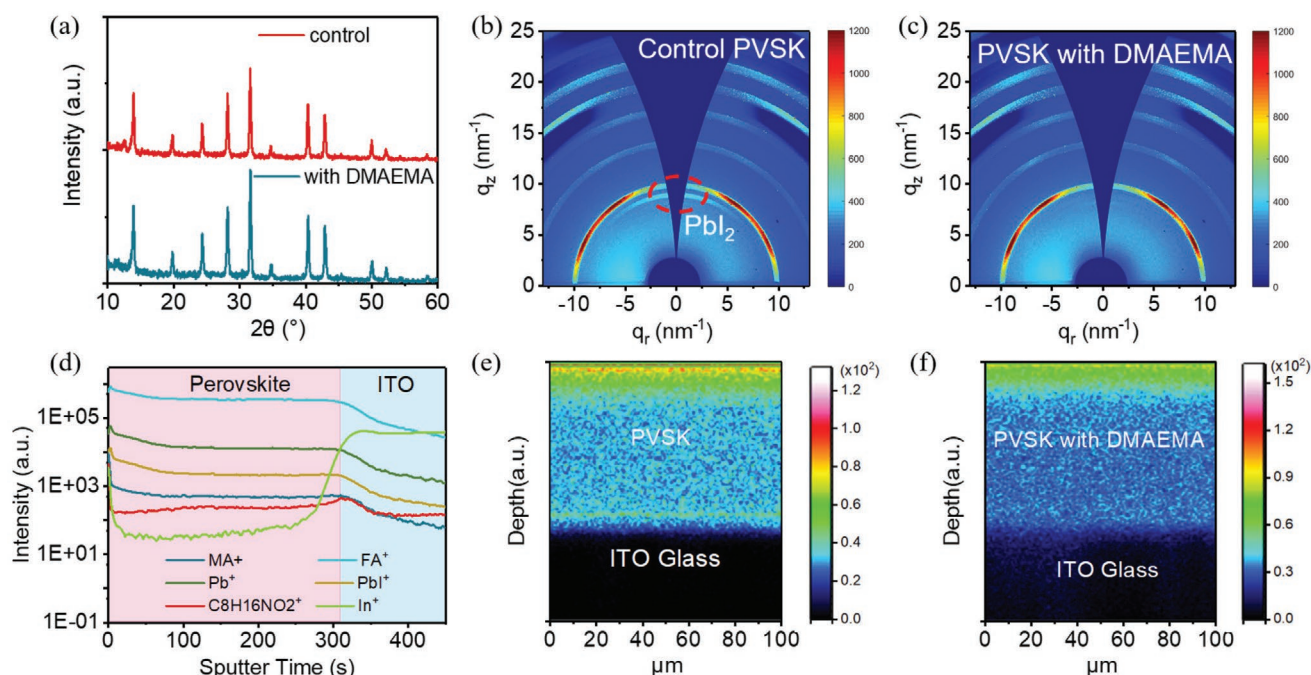


Figure 2. a) GIXRD with an incident angle at 1° of control and DMAEMA-treated perovskite films. b) 2D-GIXRD of control perovskite film. c) 2D-GIXRD of DMAEMA-incorporated perovskite film. d) TOF-SIMS spectrum of DMAEMA-incorporated perovskite film on ITO glass. e) Pbl^+ cross-sectional distribution of control perovskite film. f) Pbl^+ cross-sectional distribution of DMAEMA-incorporated perovskite film.

stretch peak shifts to a higher value due to the interaction between DMAEMA and Pb^{2+} . Also, the picture in Figure S2, Supporting Information, shows that the liquid mixture becomes solid, further proving the polymerization process straightforwardly. The schematic illustration of interactions between DMAEMA and perovskite crystals is presented in Figure 1f.

We also mixed iodine (I_2) and DMAEMA to explore the possible interaction of I_2 and DMAEMA. The as-prepared I_2 -DMAEMA solution has a dark brown color, as shown in Figure S3a, Supporting Information. After storing this solution for 1 day, the color of the I_2 -DMAEMA becomes light ochre as presented in Figure S3b, Supporting Information. Besides, at the bottom of the stored solution, the transparent crystal appeared, indicating I_2 -DMAEMA complex is formed. The absorbance of the fresh and aged solutions is measured to show the possible reactions. The result indicates that a new absorbance peak of the aged solution at around 500 nm existed compared to the fresh solution. According to the FTIR result shown in Figure 1e, the peak of tertiary amine salt formed at 2693 cm^{-1} .^[23] Thus, the DMAEMA can reduce the trace amount of iodine that presents as defects in the perovskites.

To investigate the perovskite crystallinity of DMAEMA-incorporated films, the grazing incidence X-ray diffraction (GIXRD) with an incident angle of 1° is measured as shown in Figure 2a. The DMAEMA-incorporated perovskite film has the same orthorhombic crystal structure as the control perovskite film. The peaks at 13.95° , 24.33° , 28.17° , 31.59° , and 40.32° are assigned to (001), (111), (002), (012), and (022) crystal planes, respectively. Compared to the reference film, the GIXRD peak intensity is improved due to the DMAEMA monomers via

slowing down the crystallization process as shown in Figure S4, Supporting Information, and improved composition uniformity which will be discussed later.^[24] Besides, the control film has a small peak at 12.55° which is the PbI_2 peak. However, this peak disappeared in the DMAEMA-incorporated perovskite films. However, the crystallization information is mainly from the film surface (about 150 nm) at an incident angle of 1° , so we also measured GIXRD at an incident angle of 3° which enables the bulk of perovskite film that can be measured.^[25] As shown in Figure S5a, Supporting Information, the DMAEMA-incorporated film shows an apparently improved intensity. Moreover, the full width at half maximum of the GIXRD peak fitted by Voigt function at 28.2° is decreased from 0.29° to 0.26° , demonstrating an improved perovskite film crystallinity. To further explore the crystallinity of perovskite films, the 2D-GIXRD is performed to investigate the film crystallinity comprehensively and the results are presented in Figure 2b,c. The deep color of the diffraction rings indicated the improved crystallinity with the AAE process by DMAEMA. The diffraction ring located at about 10 nm^{-1} is assigned to (110) diffraction of tetragonal perovskite crystal. It should be noted the light color at 9 nm^{-1} is assigned to PbI_2 , which is in accordance with the 1D-GIXRD spectrum shown in Figure 2a. In addition, the radially integrated intensity plots along (001) crystal plane are presented in Figure S6, Supporting Information, indicating that the preferred orientation is stronger after the AAE process, and the crystal distributions are much regular, which is favorable for charge transfer.^[26]

To clarify the mechanism of the improved crystallinity benefiting from DMAEMA monomer, the time-of flight secondary ion mass spectrometry (ToF-SIMS) depth profiling on

perovskite film is conducted to study the molecular fragments distributions. The ToF-SIMS depth profiling spectra of control perovskite film and DMAEMA-incorporated film are presented in Figure 2d and Figure S7, Supporting Information, respectively. We can distinguish the composition of perovskite film and ITO glass by the distribution of indium (In) from ITO clearly. The results show that the DMAEMA molecules distribute uniformly with a low concentration. The bottom interface is a little bit higher, suggesting the complete infiltration of DMAEMA. ToF-SIMS 3D and 2D of DMAEMA distribution in perovskite film are presented in Figure S8, Supporting Information, further confirming the uniform distribution of DMAEMA on the surface and bulk. The cross-sectional 2D ToF-SIMS distributions of MA^+ , FA^+ , Cs^+ , and In^+ with and without DMAEMA are shown in Figure S9, Supporting Information, where In^+ is for the reference of the perovskite location, indicating the uniform perovskite composition. Figure 2e,f shows the information of secondary ion PbI^+ from the degraded or unreacted PbI_2 and pure perovskites. Since the perovskite composition is the same according to MA^+ , FA^+ , and Cs^+ distribution with and without DMAEMA in Figure S9, Supporting Information, the PbI^+ can be an indicator of PbI_2 . There is a large amount of PbI_2 at the top and bottom interface in the control film according to the cross-sectional 2D ToF-SIMS distribution of PbI^+ as shown in Figure 2e, which is in accordance with the small PbI_2 peak in the GIXRD. Besides, the PbI_2 in DMAEMA-incorporated film which can be indicated from Figure 2f distributes more uniformly compared to the control film, indicating a better perovskite composition distribution with the DMAEMA-incorporated AAE treatment. Therefore, after incorporating DMAEMA, our results show that the composition distribution is more uniform, which can contribute to better perovskite crystallinity as compared to the control film where the more PbI_2 phase is located on the surface instead of forming perovskites. In addition, we have conducted cross-sectional SEM as presented in Figure S10, Supporting Information, and the result shows that the thickness is the same after incorporating DMAEMA, which can exclude the influence of thickness on XRD intensity. Also, the cross-sectional crystallization is slightly improved compared to the control film. Furthermore, the AAE treatment contributes to a higher absorbance for the perovskite film containing DMAEMA as shown in Figure S11, Supporting Information, which can be a result of the improved crystallinity and uniformity of the perovskite. Consequently, the enhanced XRD crystallinity and disappeared PbI_2 phase could be supported from much more uniform perovskite composition as discussed from TOF-SIMS results and improved absorption properties.

To clarify the mechanism of DMAEMA and perovskites, X-ray photoemission spectroscopy (XPS) is conducted to analyze the chemical interactions in the perovskite films after incorporating DMAEMA in antisolvent. The result of Pb 4f is presented in Figure 3a, and no metallic Pb^0 small peak exists, confirming good film quality in both films. Besides, the binding energy of DMAEMA-incorporated perovskite film shifts to a higher value, indicating the interactions between Pb and DMAEMA, which is consistent with FTIR results. Figure 3b shows the I 3d peaks of perovskite incorporated with and without DMAEMA. The I 3d peaks of the film incorporated with DMAEMA shift

toward higher binding energies in contrast to the control film. This shift derives from the interaction between iodine and ternary amine as discussed before, which can reduce the iodine vacancy defects. The full XPS spectra of perovskite film with and without DMAEMA are presented in Figure S12, Supporting Information.

The photoluminescence and time-resolved photoluminescence (TRPL) are measured to study the defects in the films as shown in Figure 3c,d. The photoluminescence spectra demonstrate a considerably increased intensity after DMAEMA-incorporated antisolvent fabrication process, indicating that the trap-assisted recombination is highly reduced. TRPL curves are presented in Figure 3d and the fitting parameters are summarized in Table S1, Supporting Information, by the following bi-exponential decay model function:

$$I(t) = A_1 \exp\left(-\frac{t-t_0}{\tau_1}\right) + A_2 \exp\left(-\frac{t-t_0}{\tau_2}\right) \quad (1)$$

The average carrier lifetime (τ_{avg}) is 284.56 and 1088.45 ns for control film and DMAEMA-incorporated film. The largely enhanced τ_{avg} confirms that the nonradiative recombination is effectively suppressed by the interactions between the DMAEMA and perovskites. Ultraviolet photoelectron spectroscopy (UPS) is also conducted to study the energy levels after the AAE method with DMAEMA. The Fermi edge and cut-off edge of control and DMAEMA-incorporated perovskite film are presented in Figure 3e,f, and the calculated parameters are summarized in Table S2, Supporting Information. The Tauc plot of perovskite film with and without DMAEMA incorporation is presented in Figure S13, Supporting Information. The conduction band energy (E_{CB}) of the DMAEMA-incorporated film is -4.18 eV while the control film is -4.08 eV so that the E_{CB} of the treated film is much close to the E_{CB} of [6,6]-phenyl-C61-butyric acid methyl ester (PCBM).^[27] The reduced energy offset of the conduction band between perovskite film and PCBM favors the carrier extraction to the electron transportation layer.

The device structure is presented in Figure 4a with the band alignment discussed above, and the corresponding cross-sectional SEM with AAE process is presented in Figure 4b. The bottom interface layer is NiO_x for hole extraction and the top interface layer is PCBM for electron extraction. The concentration of DMAEMA additive in CB during the fabrication process is first optimized and the corresponding $J-V$ curves are presented in Figure S14, Supporting Information. The result shows that 6 mM is the best concentration for the best device performance. The $J-V$ curves of control and DMAEMA-treated PSCs are shown in Figure 4c. The corresponding photovoltaic parameters of the control device are PCE of 19.76%, J_{sc} of 23.58 mA cm^{-2} , V_{oc} of 1.06 V, and FF of 0.79. Differently, the DMAEMA-treated PSCs exhibited a V_{oc} of 1.10 V, J_{sc} of 23.86 mA cm^{-2} , and FF of 0.82, finally contributing to a PCE of 21.52%. The improved V_{oc} and FF are attributed to the enhanced perovskite crystallinity, composition uniformity, and defects termination effects after incorporating DMAEMA. Steady-state current output at the maximum PCE point is measured as shown in Figure 4d and a stabilized PCE of 21% is achieved at 0.95 V. The external quantum efficiency (EQE)

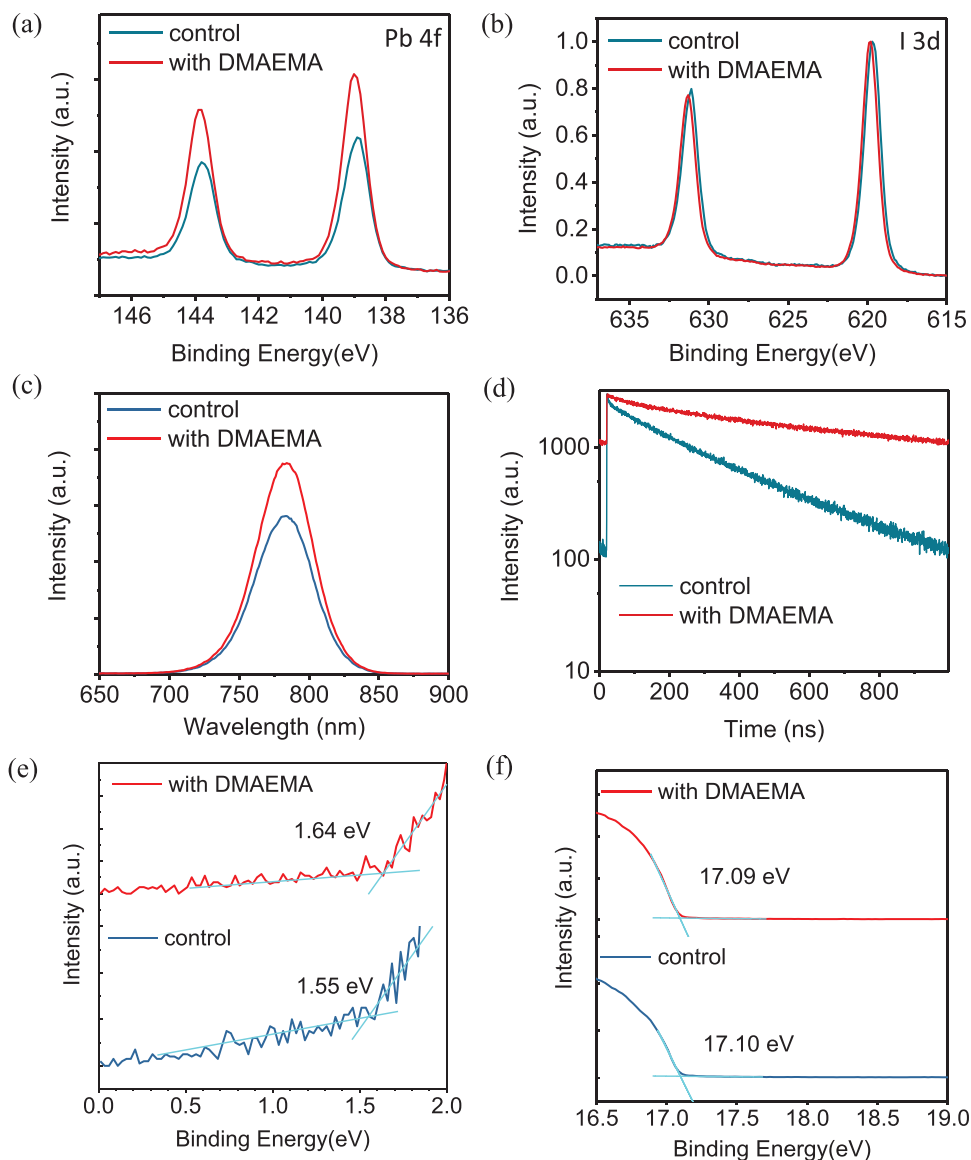


Figure 3. a) Pb 4f of control and DMAEMA-incorporated perovskite film. b) I 3d of control and DMAEMA-incorporated perovskite film. c) PL of control and DMAEMA-incorporated perovskite film. d) TRPL of control and DMAEMA-incorporated perovskite film. e) UPS of Fermi edge of control and DMAEMA-incorporated perovskite film. f) UPS of cut-off edge of control and DMAEMA-incorporated perovskite film.

of the best performance device is measured and the integral current density is 23.6 mA cm^{-2} , consistent with the device J_{sc} . Besides, to investigate the reproducibility of the device, statistical PCE distributions of 15 devices are presented in Figure 4f. And, other photovoltaic parameters' statistic distributions are presented in Figure S15, Supporting Information. It is clearly seen that the improved device performance is mainly attributed to the increased FF and V_{oc} due to the reduced nonradiative recombination and good film uniformity.

The space-charge-limited current (SCLC) is a general method to study the defects in the perovskite films quantitatively. The electron-only device was fabricated with the configuration of ITO/SnO₂/perovskites (with and without DMAEMA additive)/PCBM/Zr(acac)₄/Ag.^[28] The dark current–voltage (I – V) curves are shown in Figure S16a, Supporting Information. The curves

are fitted into three parts named Ohmic region, trap-filled limited region, and trap-free SCLC region. The defects density (N_{d}) can be calculated by the following formula,

$$N_{\text{d}} = \frac{2\varepsilon_0\varepsilon_r V_{\text{TFL}}}{qL^2} \quad (2)$$

where L is the thickness of perovskite, ε_0 is the vacuum permittivity, and ε_r is the relative dielectric constant of perovskite. Finally, the defect density of the DMAEMA-incorporated perovskite device is calculated to be $9.96 \times 10^{14} \text{ cm}^{-3}$, which is significantly lower than that of the control device with a value of $1.49 \times 10^{15} \text{ cm}^{-3}$. The result proves that the defect density decreases which can be explained by the reduced unbonded Pb²⁺ and undesired I₂ in the films. To further investigate the

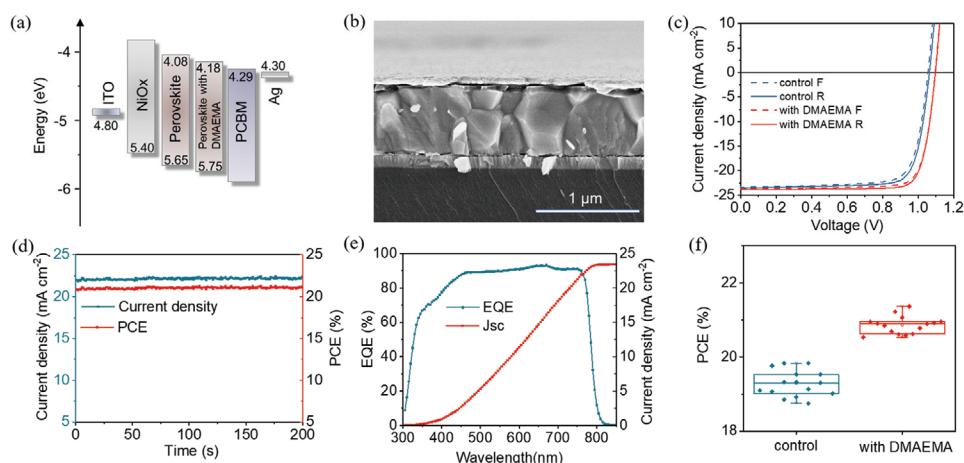


Figure 4. a) Structure and energy diagram of the device. b) Cross-sectional SEM of DMAEMA-incorporated device. c) J - V curves of control and DMAEMA-incorporated device. d) Steady-state current density output. e) EQE of the best DMAEMA-incorporated device and the integrated current density. f) Statistical PCE distributions of 15 devices with and without DMAEMA.

charge carrier recombination process in perovskite devices, electrochemical impedance spectroscopy (EIS) was conducted to measure the perovskite device with and without DMAEMA in CB during the fabrication process. Figure S17, Supporting Information, shows the Nyquist plots of the perovskite with and without DMAEMA under 1 V bias. The improved recombination resistance of the perovskite devices with DMAEMA-based AAE method confirms that the reduction of recombination in the PSCs which attributes to lower V_{oc} loss.

Besides the high efficiency of the PSCs, the stability attracts more attention recently for future commercialization. First, we study the film phase stability by measuring the film absorbance. The absorbance of the control and DMAEMA-incorporated perovskite films under continuous light illumination in ambient environment after 0, 24, and 72 h was measured as shown in Figure 5a,b. The absorbance intensity of the control film reduces after a long-time illumination. Besides, the absorbance edge of control film extends from 780 to 805 nm

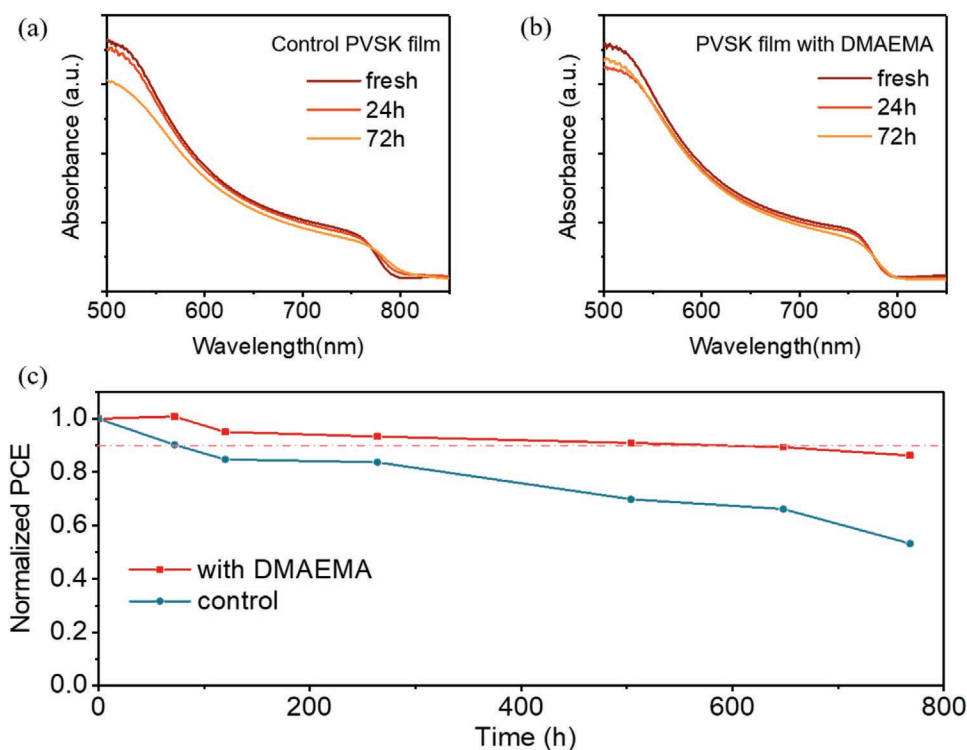


Figure 5. Absorbance of a) control film and b) DMAEMA-incorporated film under continuous light illumination under 0, 24, and 72 h. c) Device stability under continuous light illumination.

after illuminating for 72 h. Interestingly, the DMAEMA-incorporated perovskite film has a negligible absorbance edge shift. The large redshift of the control film may originate from the phase segregation of generated unstable FAPbI₃ perovskites. As a result, the self-polymerized DMAEMA can effectively improve the film phase stability by inhibiting ion migrations at the grain boundaries and reducing the defects density. Finally, the encapsulated PSC is measured under continuous light illumination (white LED equals to 1-sun illumination intensity) in the ambient environment at 60 °C and 50–60% relative humidity. The DMAEMA-incorporated perovskite device retains 90% efficiency after more than 600 h of continuous light illumination, further proving the improved stability by the DMAEMA-based AAE method.

3. Conclusion

In summary, we demonstrate a novel strategy of incorporating DMAEMA monomer in the antisolvent for the one-step film process. We find that the DMAEMA is self-polymerized after incorporating in the film and located at the grain boundaries, improving the crystallinity of perovskite. Our results also confirm the newly established interactions of Pb and DMAEMA, and iodine and ternary amine between the DMEMA and perovskites which help reduce defects density. Furthermore, the composition distribution in the cross section becomes more uniform, contributing to improved crystallinity and phase stability. Finally, a high PCE over 21% of DMAEMA-incorporated inverted PSCs was achieved with a V_{oc} of 1.10 V, J_{sc} of 23.86 mA cm⁻², and FF of 0.82. Meanwhile, the stability of the PSCs was greatly improved due to inhibiting the formation of iodine, reducing the uncoordinated Pb²⁺, and suppressing phase segregation. Consequently, our work offers an insight into the self-polymerized monomer engineering for high performance and stable PSCs and other optoelectronic devices.

4. Experimental Section

Materials: PbI₂ (99%), lead (II) bromide (PbBr₂, 99%), cesium iodide (CsI, 99%) were purchased from TCI. Methylammonium bromide (MABr) and formamidinium iodide (FAI) were purchased from Dyesol. Dimethyl sulfoxide (DMSO, extra dry, 99%), *N,N*-dimethylformamide (DMF, extra dry, 99%), isopropyl alcohol, and CB (extra dry, 99.8%) were purchased from Acros. PCBM was purchased from Solarmer Energy, Inc. Zirconium (IV) acetylacetonate (Zr(acac)₄, 98%) was purchased from Sigma-Aldrich. DMAEMA (99%) was purchased from J&K. NiO_x nanoparticles inks were prepared according to the authors' previous reports.^[29]

Device Fabrication: For Cs_{0.05}(MA_{0.1}FA_{0.9})_{0.95}Pb(I_{0.9}Br_{0.1})₃ perovskite precursor solution, MABr (14.9 mg), PbI₂ (580.9 mg), PbBr₂ (51.4 mg), CsI (18.2 mg), and FAI (206.8 mg) were dissolved in the mixed solvent of DMF and DMSO with a volume ratio of 4:1. The precursors were then filtered by 0.2 μm PTFE syringe filter before use. Patterned ITO-coated glasses were washed with detergent, deionized water, acetone, and ethanol with ultrasonication for 15 min each and dried by a nitrogen gas flow. Then, the ITO glasses were ultraviolet–ozone-treated for 20 min. Next, 50 μL NiO_x (20 mg mL⁻¹ in deionized water) was spin-coated on ITO glass by 2500 rpm for 50 s. After transferring substrates with NiO_x film into the nitrogen-filled glovebox, the mixed perovskite precursor was spin-coated on top of NiO_x layer at 1000 rpm for 6 s and 4000 rpm for

30 s, and 120 μL of CB with different DMAEMA concentration was dropped onto the spinning samples at the 20th second of the second step to form a brown film. Then, the film was annealed at 100 °C for 60 min. Next, 20 mg mL⁻¹ PC₆₁BM in CB was spin-coated on perovskite surface at 2000 rpm for 40 s, followed by spin-coating Zr(acac)₄ (2 mg mL⁻¹ in isopropanol) at 4000 rpm for 40 s. Finally, 120 nm Ag electrode was thermally evaporated on top of the device under a vacuum of 2×10^{-6} Torr in the high-vacuum deposition system with a device area of 0.0725 cm².

Measurement and Characterization: Simulated AM 1.5 sunlight was generated by an Abet Class AAB AM 1.5G solar simulator. The light intensity (100 mW cm⁻²) was calibrated by an ISO 17025-certified KG3-filtered silicon reference cell. The *J*–*V* curve was recorded by a Keithley 2635 source meter. UV–vis absorption spectra were obtained from a UV–vis spectrometer (Perkin Elmer Lambda 750). The EQE spectra were collected with a photomodulation spectroscopic setup (Enlitech QE-R). The photoluminescence and TRPL were investigated using PicoQuant FluoroTime 300. The perovskite film was excited by a picosecond 510 nm pulse laser (LDH-P-C-510) with a pulse width of <40 ps and a repetition rate of 5 MHz. The continuous light illumination stability characterization was measured with Keithley 2635 with white LED as the light source. A field-emission SEM (G500, Zeiss Co.) was used to characterize the morphologies of the perovskite films. 2D-GIXRD measurements were performed at the BL 14B1 beamline of the Shanghai Synchrotron Radiation Facility using an X-ray beam with a wavelength of 1.2398 Å. GIXRD patterns were obtained by a MarCCD 225 detector at a grazing incidence angle of 0.3° from the sample with an exposure time of 50 s. The x-axis of GIXRD patterns was represented by the diffraction vector with $q = 4\pi\sin(\theta)/\lambda$, where θ was half of the diffraction angle and λ was the wavelength of incident X-ray. XPS and UPS were performed with a Kratos AXIS UltraDLD ultrahigh vacuum surface analysis system. XPS measurements were performed to characterize the elemental constituents and chemical reactions using a monochromatic Al K α X-ray gun (1486.6 eV) with a total instrumental energy resolution of 500 meV. UPS analysis was used to determine the position of valence states, which was conducted using an unfiltered He I (21.2 eV) gas discharge lamp with a total instrumental energy resolution of 100 meV. TOF-SIMS was performed by TOF.SIMS 5 IONTOF, Germany. The sputtering beam for depth profiling was Cs⁺ ion beam with 1 keV energy and 70.52 nA current. The primary ion beam for depth profiling was Bi³⁺ with 30 keV energy and 0.75 pA current. The sputtering area was 300 × 300 μm² and the probe area was 100 × 100 μm². Besides, the primary ion beam for 2D mapping was the same with depth profiling and the probe area was 10 × 10 μm². The EIS of devices in the dark at room temperature was measured by an electrochemical analyzer (Agilent 4294A).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

crystallinity, efficiency, monomer self-polymerization, perovskite solar cells, stability

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