

Imidazoanthraquinone Derivative as a Surface Passivator for Enhanced and Stable Perovskite Solar Cells

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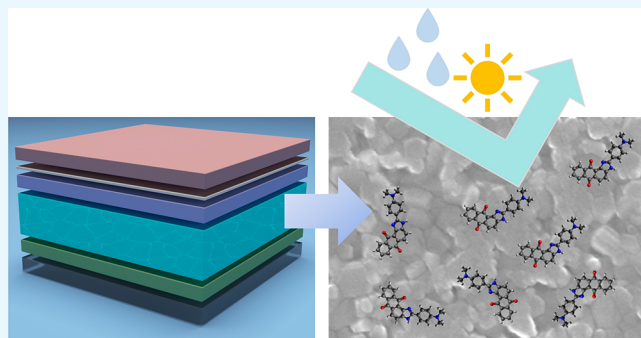


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Supporting Information

ABSTRACT: Hybrid organic–inorganic perovskites have been investigated for their potential to serve in next-generation perovskite solar cells (PSCs). While PSC technology is approaching commercialization, thermal and moisture stabilities remain a concern. Here, we describe the assembly of PSCs using an imidazoanthraquinone derivative (AQ) as a small organic additive to enhance the device performance and stability. Unlike polymer additives, AQ is easy to synthesize and is more economical. AQ was synthesized because it has both carbonyl and imidazole functional groups. The presence of C=O and N–H groups results in coordination interaction with Pb^{2+} and I^- of the perovskite. Addition of the AQ molecule to methylammonium lead iodide leads to the formation of a superior crystalline perovskite film with fewer defects and enhanced stability under humid conditions. The use of optimized perovskite films enhanced device power conversion efficiency (PCE = 17.21%) compared to pristine perovskite (PCE = 13.88%). Unencapsulated optimized devices retained 90% of the initial power conversion efficiency for 30 days at a relative humidity of nearly 35%. The optimized films also exhibited superior thermal stability to that of pristine perovskite films.



1. INTRODUCTION

Hybrid organic–inorganic perovskite-based perovskite solar cells (PSCs) have attracted considerable attention as promising candidates for next-generation solar cells due to their high absorption coefficient, extended charge carrier diffusion length, low excitation-binding energy, prominent power conversion efficiency (PCE), ease of processing, and low fabrication costs.^{1–9} In just over a decade, the PCE of PSCs has increased from 3.0% to more than 25%, and the technology is approaching the commercialization stage.^{10,11} However, long-term thermal and moisture stabilities are still major concerns and hamper practical application.^{12,13} Defects that form on the perovskite surface and in the bulk during crystallization can lead to poor film quality, which affects the performance and stability of PSCs.^{14,15} Like most ionic materials, perovskite has a large number of noncoordinated halide ions that can migrate with ease within the perovskite layer, causing various defects.¹⁶ The ions can also move off the perovskite surface and corrode electrodes,¹⁷ which leads to other defects. These defects can provide sites for nonradiative recombination, which eventually decreases the PCE.¹⁸ Perovskite degrades when it encounters moisture, oxygen, high temperatures, and ultraviolet (UV) radiation.¹⁹ To overcome these drawbacks, the development of a high-quality perovskite film with fewer defects, larger grain size, full surface coverage, and smaller grain boundaries is crucial. Several attempts have been made to produce high-quality films by retarding crystal growth, eliminating the Pb–I

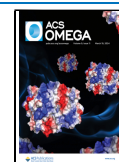
defects, and passivating the grain boundaries by solvent engineering, gas treatment, Ostwald ripening, interface engineering, and additive incorporation.^{20–27} Among these methods, incorporating an additive is a simple and widely used method to produce high-quality films.^{28,29} A variety of small organic molecules, inorganic salts, and polymers have been used to explore the possibility of high-quality films.^{30–33} Solvent additives decrease the intrinsic defect density by controlling crystallization, Lewis acid/base additives passivate the surface defects, and hydrophobic additives form a tunneling layer and suppress charge recombination.^{34–38} Recently, additives with various functional groups have been applied to perovskite.^{39–41} The functional groups interact with the lead or halide ions and change the crystallization process, resulting in a different film morphology. The halide ions of perovskite can also interact with the hydrogen attached to electronegative atoms (–OH, –NH₂, and –COOH) of the additives via hydrogen bonding, suppressing ion migration and leading to reduced hysteresis and enhanced device perform-

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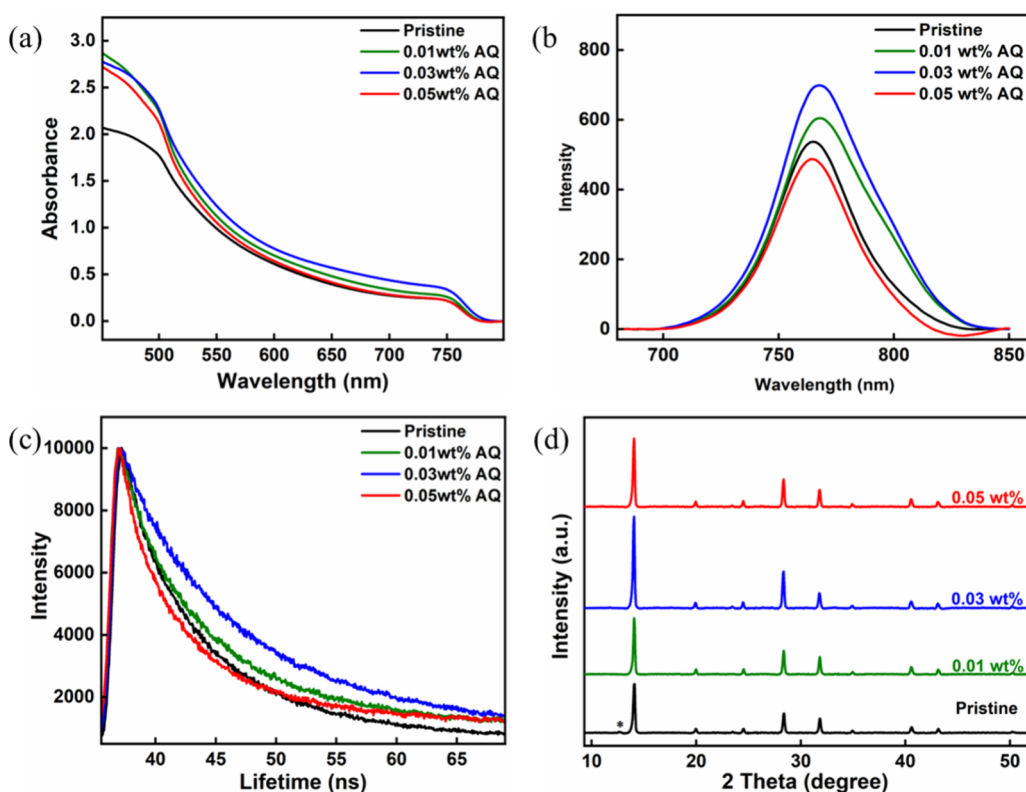


Figure 1. (a) UV, (b) PL, (c) TRPL, and (d) XRD spectra of pristine and doped perovskite with different wt % of AQ.

ance and stability. Yang and co-workers exploited the C=O group interaction with a methylammonium-based perovskite layer by introducing caffeine, which resulted in slow crystal growth and greater activation energy, producing a high-quality perovskite layer.⁴² Chen et al. and Hou et al. used additives to bridge and interconnect perovskite grains, successfully producing high-quality perovskite films with fewer defects.^{43,44} Moreover, the additive covering the surface of the perovskite offered shielding against atmospheric oxygen and moisture.

Here, we introduce a small imidazoanthraquinone derivative (AQ) into a methylammonium lead iodide (MAPbI₃) perovskite layer to passivate the surface and produce high-quality films with fewer defects. The AQ has a C=O group that interacts with lead ions and an N–H group that interacts with iodide ions, leading to high-quality films with fewer defects and greater surface coverage. The AQ covered the surface of the perovskite and may provide shielding from atmospheric moisture due to the increase in the contact angle of the surfaces. Devices that incorporated AQ maintained an external quantum efficiency (EQE) of 90% without encapsulation for 30 days at a relative humidity of approximately 35%.

2. RESULTS AND DISCUSSION

AQ was synthesized by the condensation reaction of 1,2-diaminoanthraquinone with 4-(dimethylamino)benzaldehyde using a previously described method (Scheme S1).⁴⁵ After purification, AQ was characterized by NMR (Figures S1 and S2). Perovskite cells were synthesized by mixing MAI and PbI₂ in a 1:1 ratio in a DMSO:DMF (1:4) solution at 70 °C for 4 h. The resulting mixture was filtered using a 0.45 μ m filter and used for fabrication of thin films and devices. A desired quantity of AQ was added to the precursor solution for obtaining optimized perovskite films.

The absorption spectra of the AQ were observed in chloroform with a maximum of 490 nm, and emission maxima were observed at 690 nm (Figure S3). Figure 1a depicts the UV-visible light absorption spectra of MAPbI₃ without and with the AQ. The AQ-incorporated perovskite exhibited enhanced absorption as the concentration of the AQ increased to 0.03 wt % and then decreased. The superior absorbance of perovskite with 0.03 wt % AQ suggests improved crystallinity of the films. The absence of change in the absorption edges of the perovskite with and without the AQ indicated that the band gap of perovskite was not affected. Figure 1b displays the PL spectra of perovskite with and without the AQ. The PL intensity of MAPbI₃ with additives also increased with an additive concentration of up to 0.03 wt % AQ and then decreased. A slight red shift is observed in the peak position for the samples containing AQ, which is believed to be arising due to the modification of the perovskite surface by the AQ additive. A shift is observed depending on the experimental conditions, molecular nature, or surface modification. Additionally, it also depends upon the quantum confinement and ligand passivation.^{46–48} The PL decay lifetime also increased from 6.3 ns for pristine perovskite to 9.8 ns for 0.03 wt % AQ optimized perovskite, as shown in Figure 1c and Table S1. The increments in PL intensity and decay lifetime suggest reductions in trap states and suppression of nonradiative recombination. Photophysical studies revealed that the perovskite film was optimized when 0.03 wt % AQ was added to MAPbI₃. To further confirm that 0.03 wt % achieved optimized conditions and to analyze the effect of the AQ on the crystallinity of the perovskite films, we recorded the XRD spectra of pristine and AQ-incorporated perovskite films. Figure 1d shows that the signature diffraction peaks of MAPbI₃ occurred at 14.19, 28.52, and 31.98°, which correspond to the

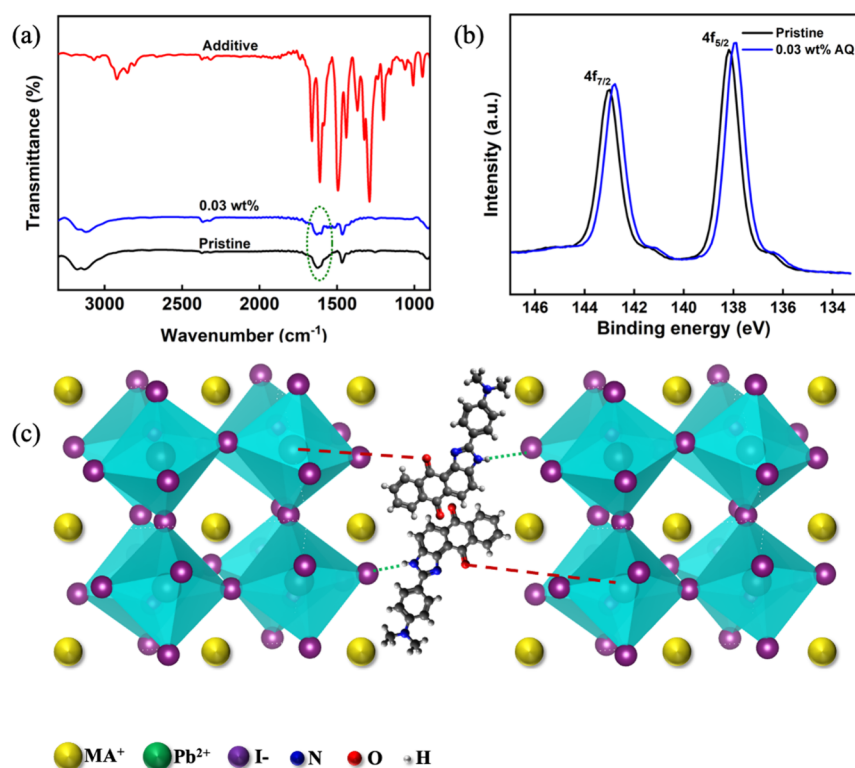


Figure 2. (a) FTIR spectra of the AQ and pristine and 0.03 wt % AQ optimized perovskite, (b) XPS spectra of Pb 4f for pristine and 0.03 wt % AQ perovskite films, and (c) schematic of the interaction between perovskite and AQ.

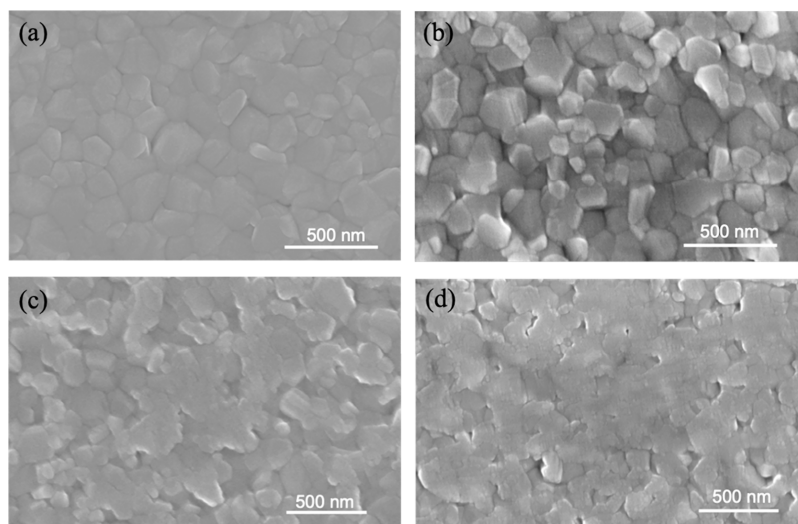


Figure 3. FE-SEM surface images of (a) pristine and perovskite with (b) 0.01 wt % AQ, (c) 0.03 wt % AQ, and (d) 0.05 wt % AQ additives.

(110), (220), and (310) planes, respectively. The intensities of the diffraction peaks were enhanced after the addition of AQ, which suggests that the crystallinity of the optimized films increased compared with pristine films. The presence of diffraction peaks at the same 2θ degrees indicated that AQ only increased the crystallinity of the perovskite films without affecting their structures. The intensity of the diffraction peaks increased for optimized films with up to 0.03 wt % AQ in perovskite and then decreased.

The full width at half-maximum (fwhm) of the (110) peak decreased from 0.184 to 0.167° in 0.03 wt % AQ optimized films (Figure S4). We estimated the size of the crystallite using Scherrer's equation and the fwhm value of the (110) peak

(Table S2). The crystallite size increased from 45.44 to 50.06 nm in the 0.03 wt % AQ optimized perovskite films compared with pristine perovskite. The narrow fwhm indicated that the addition of AQ can improve the charge transport in PSCs by enhancing the growth of perovskite grains toward the in-plane direction, which could increase the charge transport in PSC devices.^{42,49} Thus, we concluded that 0.03 wt % AQ in perovskite leads to an optimized state and can improve device performance.

The organic additive AQ contains a carbonyl group whose lone pair of electrons can be delocalized to the empty orbitals of Pb²⁺, leading to the formation of coordination bonds.^{50–52} The unshared electrons or C=O group activates and cross-

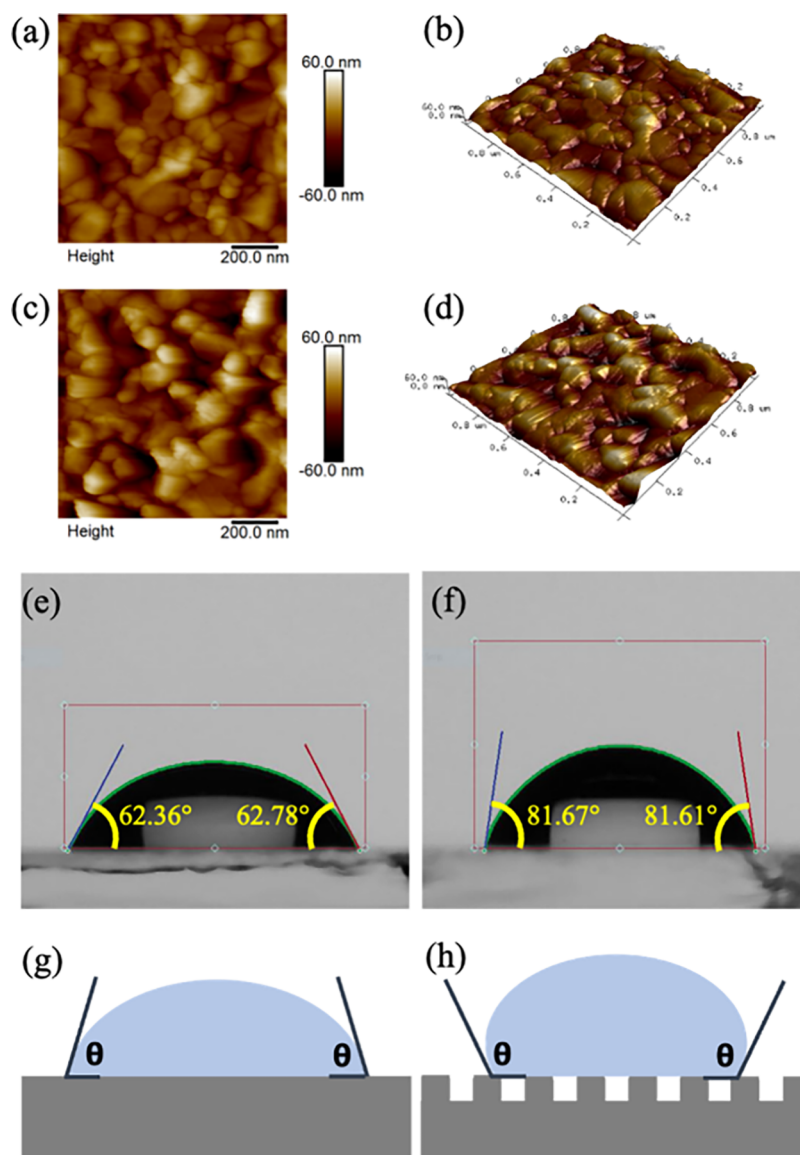


Figure 4. 2D and 3D AFM images of pristine perovskite (a, b) and optimized perovskite (c, d), the contact angle of pristine (e) and optimized perovskite (f), and a schematic representation of the Cassie–Baxter contact angle for pristine (g) and optimized (h) perovskite films.

links with lead ions to form complexes at the perovskite surface and grain boundaries. The resulting complex leads to a decrease in defect density and decreases nonradiative recombination.⁵³ To verify the interaction between perovskite and functional groups of the AQ, the FTIR transmission spectra of the AQ, pristine (MAPbI₃) and optimized (MAPbI₃ + 0.03 wt % AQ) thin films were recorded. In Figure 2a, the C=O vibration band of the AQ is shifted from 1608 to 1600 cm⁻¹, which can be attributed to the interaction between the lone pairs of the carbonyl group and lead ions of the perovskite. This suggests that the AQ molecules strongly interacted with the perovskite grains, possibly affecting the crystallization and morphology of the perovskite films. This interaction was further confirmed by XPS measurements of pristine and 0.03 wt % AQ optimized perovskite films. A shift in the binding energy of the 4f orbitals of lead, as seen in Figure 2b, and the 3d orbitals of iodine (Figure S5) was observed and is indicative of the interaction between the perovskite and the AQ molecule. Figure 2c shows a schematic of the interaction between perovskite and the additive

molecule AQ. Due to its lone pair of electrons, the oxygen of the carbonyl group present in the AQ molecule interacts with the lead ions of the perovskite, whereas the iodide of perovskite is believed to interact with the hydrogen attached to the electronegative nitrogen atom of the imidazole group. ¹H NMR is generally used to confirm the presence of the additive in perovskite and to verify the interaction experimentally.^{54,55} We scratched the perovskite films with and without AQ, recorded the ¹H NMR spectra in DMSO, and found the presence of AQ in the samples (Figure S6). To verify the interaction, we recorded the ¹H NMR spectra of AQ + PbI₂ (1:1) and found a considerable shift in the NH peak along with the other hydrogen peaks of the additive (Figure S7).

To further investigate the film morphology of the perovskite layer, FE-SEM images were recorded for pristine and doped perovskite films. The pristine films of MAPbI₃, as shown in Figure 3a, include grain sizes of approximately 200–300 nm with clear boundaries, which agrees with previous reports. However, perovskite films with additives show different surface morphologies that depend on the concentration of the

additive. Because heterogeneous nucleation reduces the free-energy barrier and promotes crystal nucleation, the number of crystals increases and the size decreases.⁵⁶ Initially, at low concentrations of the additive, the size of the perovskite grains decreased slightly, which suggests that AQ increased the number of nucleation sites along the grain boundaries, as shown in Figure 3b.

As the concentration of AQ increased, the number of nucleation sites increased, and sheet-like features began to appear on the surface of the perovskite film, as seen in Figure 3c. The formation of these structures over the perovskite film surface suggests that AQ passivates the perovskite surface and also starts to bridge the perovskite grains.⁴⁴ When the concentration of AQ was further increased, the sheet-like structures began to spread across the entire surface of the perovskite, as shown in Figure 3d. Because the conductivity of organic compounds is low, it is believed that the thick layer of AQ over the perovskite film reduced electron tunneling and obstructed charge transfer.

Atomic force microscopy (AFM) was used to study the surface morphology of the thin films. Figure 4a–d provides two- and three-dimensional AFM images of pristine and 0.03 wt % AQ optimized perovskite films, respectively. The roughness of the 0.03 wt % AQ optimized film was greater than that of the pristine film. The root-mean-square value (RMS) for the pristine film was 12.1 nm, whereas that for the 0.03 wt % AQ optimized film increased to 17.4 nm. The increase in roughness is believed to be the result of the AQ occupying the surface of the perovskite grains. The roughness of the perovskite film surfaces is expected to increase the contact angle and increase stability toward moisture.^{57,58} The measurements of the contact angles over the perovskite surface for both pristine and optimized films are presented in Figure 4e and Figure 4f, respectively. The pristine films had a contact angle of 62.5° with water, whereas that of 0.03 wt % AQ optimized films increased to 81.6°, suggesting that the optimized films were more stable toward moisture. According to the Cassie–Baxter theory, when the contact surface is not smooth, air is trapped between the protrusions, and the droplets of water come into contact with the complex interface of vapor and solid.⁵⁸ The Cassie–Baxter contact angle equation is

$$\cos \theta_r = f_1 \cos \theta_1 + f_2 \cos \theta_2$$

where θ_r denotes the apparent contact angle of the composite contact surface, θ_1 and θ_2 are the intrinsic contact angles of the two media, f_1 and f_2 are the proportions of the two media at the composite interface, and $f_1 + f_2 = 1$. Because the contact angle of air and liquid is 180°, the above equation can be modified to

$$\cos \theta_r = f_1(1 + \cos \theta_1) - 1$$

Figure 4g,h includes a schematic of the contact angles observed for smooth and rough surfaces according to the Cassie–Baxter theory. Because the perovskite surface in devices is covered with PCBM, we also measured the contact angle for the perovskite films covered with PCBM. The contact angle for the pristine PCBM film was 88.15°, but that for the 0.03 wt % AQ optimized perovskite PCBM film was 102.8°, indicating that the surface had become hydrophobic. Also, after 5 min, an intact drop of water remained over the surface without spreading along 0.03 wt % AQ optimized films (Figure S8). The contact angle results suggest that 0.03 wt % AQ

optimized films are more tolerant of moisture. We performed Hall effect measurements to obtain insights into the charge carrier of the perovskite films. Table 1 summarizes the findings.

Table 1. Summary of Hall Measurements for Pristine and Optimized Perovskite

devices	type	Hall coefficient (cm ³ C ^{−1})	carrier density (cm ^{−3})	carrier mobility (cm ² V ^{−1} s ^{−1})
pristine	p	2.4×10^{-2}	2.55×10^{20}	45.4
0.03 wt % AQ	n	-3.01×10^{-2}	2.06×10^{20}	55.3

Pristine perovskite had a positive Hall coefficient (R_H) of $2.4 \text{ cm}^3 \text{ C}^{-1}$, whereas the 0.03 wt % AQ optimized films had a negative R_H of $-3.01 \text{ cm}^3 \text{ C}^{-1}$. The change from positive to negative R_H suggests a change from the p- to n-type in the perovskite surface.

The change in the surface of the perovskite from a p-type to an n-type matched a top electron-transporting layer in p-i-n-type inverted solar cells. This could play a crucial role in charge collection at the electron-collecting interface and improve device performance.⁵⁹ Carrier mobility increased for the 0.03 wt % AQ optimized films, from 45.4 to 55.3 cm² V^{−1} s^{−1}.

Inverted solar cells with a p-i-n structure were fabricated with a device geometry of ITO/PEDOT:PSS/perovskite/PCBM/BCP/Ag. ITO was used as the cathode, and silver was used as the anode. PEDOT:PSS and PCBM were viewed as hole-transporting and electron-transporting layers, respectively (Figure S9). MAPbI₃ without and with an additive was used as the active layer. We observed enhanced device performance during current density–voltage (J – V) measurements for the devices based on different wt % of AQ in perovskite. Figure S11 represents the J – V curves of the best devices for different wt % AQ, and Table S5 summarizes photovoltaic parameters. It was observed that the devices based on 0.03 wt % AQ in perovskite showed the best device performance as compared to both pristine and other wt % of AQ. Figure 5a presents the J – V curves for pristine and 0.03 wt % AQ in a perovskite-optimized solar cell. For solar cell devices based on pristine MAPbI₃, an open-circuit voltage (V_{OC}) of 0.94 V, a fill factor of 0.74, and a short-circuit current density (J_{SC}) of 18.42 mA/cm² were obtained, leading to a maximum yield of 13.88%. However, all parameters showed improvement in devices based on 0.03 wt % AQ optimized perovskite, and our champion device achieved a V_{OC} of 0.98, a J_{SC} of 23.12 mA/cm², and a fill factor of 0.76, yielding an efficiency of 17.21%, which is nearly 24% greater than that of pristine perovskite solar cells. Table 2 summarizes the device data obtained for both pristine and 0.03 wt % AQ optimized devices. Table S6 compares the devices based on MAPbI₃ and additives containing oxygen and nitrogen functional groups (Lewis bases), which are similar to the AQ additive used in the present work. The incident photon-to-electron conversion efficiency (IPCE) spectra of 0.03 wt % AQ optimized and pristine perovskite-based solar cells were recorded. Figure 5b shows the enhancement in IPCE for 0.03 wt % AQ optimized devices compared with pristine perovskite devices, which can be attributed to the superior absorption and film quality of the 0.03 wt % AQ optimized films. The integrated J_{SC} values calculated from IPCE spectra were 18.42 and 21.39 mA/cm² for pristine and 0.03 wt % AQ optimized devices, respectively, which agrees with the values from the J – V curves. The optimized device shows almost identical J – V hysteresis

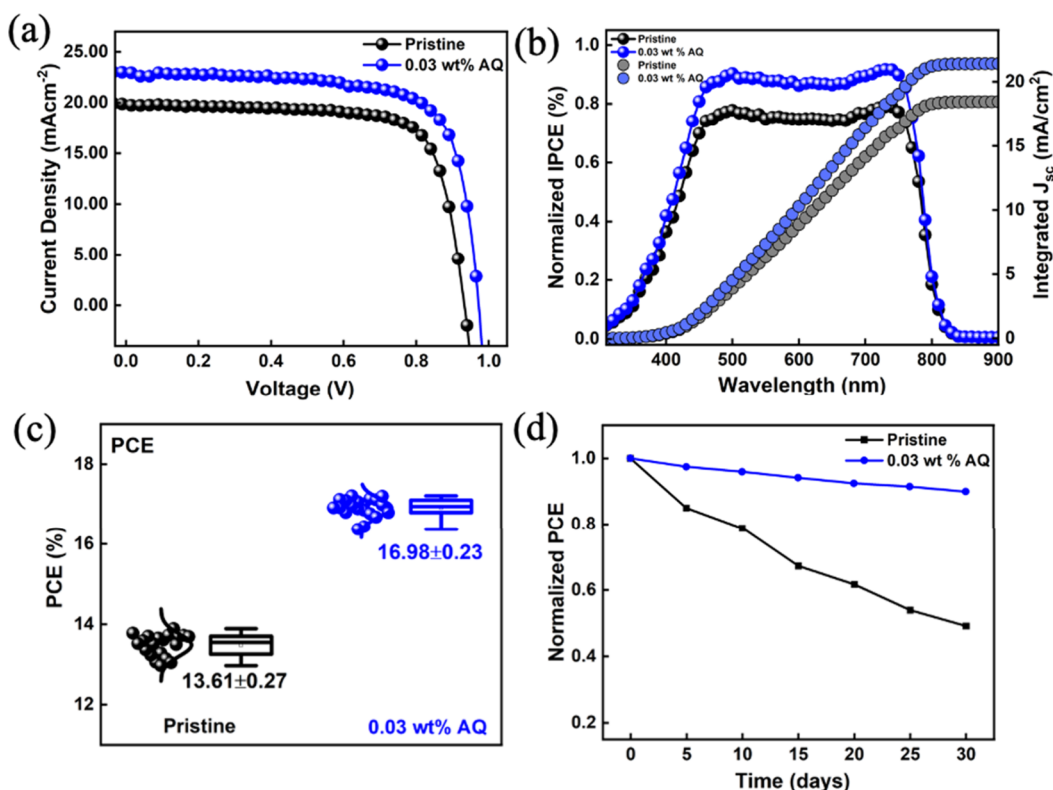


Figure 5. (a) J – V curves, (b) normalized IPCE and integrated J_{sc} , (c) average PCE distribution of 20 devices, and (d) normalized PCE for pristine and optimized perovskite devices.

Table 2. Photovoltaic Parameters of the Devices

samples (%)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η (%)	IPCE J_{sc} (mA/cm ²)
pristine	0.94	19.96	0.74	13.88	18.42
0.03 wt % AQ	0.98	23.12	0.76	17.21	21.39

compared with the control device. The hysteresis index (HI) is calculated together with photovoltaic parameters and is presented in Table S3, Supporting Information.

Figure 5c presents the average PCE of 20 devices for both pristine and optimized PSCs. Other device parameters and a summary for 20 devices are shown in Figure S10 and Table S4. 0.03 wt % AQ optimized devices stored over 30 days at a relative humidity of approximately 35% retained nearly 90% of the initial PCE compared with pristine perovskite, which held

up to only 50% of its PCE, as shown in Figure 5d. We also recorded the XRD spectra for pristine and 0.03 wt % AQ optimized thin films after 30 days at a relative humidity of approximately 35% and discovered an intense peak of lead iodide at 12.8° in pristine perovskite films compared with 0.03 wt % AQ optimized films corresponding to the (001) planes of hexagonal PbI₂. As shown in Figure 6a, the appearance of the PbI₂ peak at 12.8° indicates degradation of perovskite films, which is greater than in pristine films compared with 0.03 wt % AQ optimized perovskite. This suggests a possible explanation for the poor retention capacity of PCE for pristine compared with 0.03 wt % AQ optimized PSCs after 30 days.

To assess the thermal stability of the perovskite films, we performed TGA experiments on pristine and 0.03 wt % AQ optimized perovskite. Figure 6b depicts the weight loss of

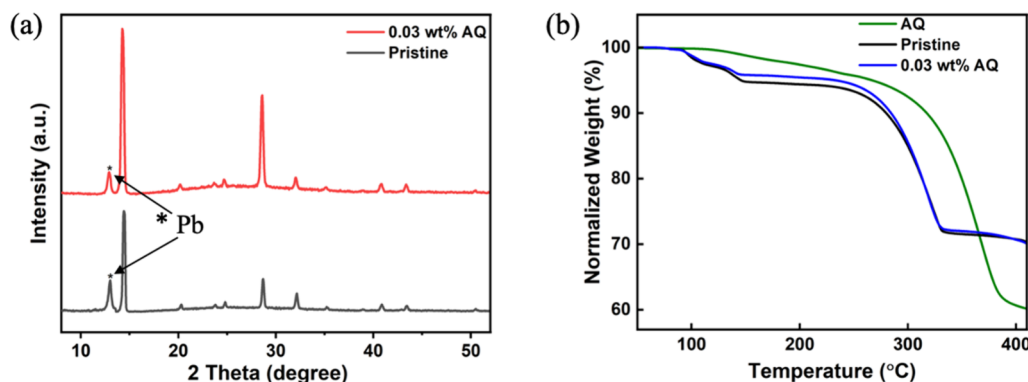


Figure 6. (a) XRD spectra after 30 days for pristine and optimized films and (b) TGA plots for additive-only and perovskite films without and with additives.

additive AQ and perovskite without and with additives. The AQ produced superior thermal stability below 200 °C and a major weight loss at temperatures higher than 300 °C. There are three major weight loss steps for pristine perovskite, at nearly 70, 340, and 460 °C, which can be attributed to the respective sublimation of DMSO, MAI, and PbI₂, respectively.^{42,60} As shown in Figure 6b, perovskites with additives had higher sublimation temperatures for MAI and PbI₂, indicating that extra energy is needed to overcome the interaction between the AQ additive and perovskite. This suggests that the interaction between AQ and perovskite could increase the activation energy for the degradation of perovskite and lead to greater thermal stability.

3. CONCLUSIONS

Anthraquinone derivative AQ was synthesized and characterized using NMR spectroscopy and used as an additive in MAPbI₃ perovskite films and devices. Photophysical studies and XRD analysis suggest that 0.03 wt % AQ in MAPbI₃ was optimal for producing high-quality films. The interaction between AQ and perovskite was confirmed using FTIR, XPS, and ¹H NMR. FE-SEM images revealed the surface morphology of pristine and 0.03 wt % AQ optimized films. With an increase in the concentration, the AQ material tended to passivate the surface and appear over the perovskite layer to bind the perovskite grains and shield the surface from atmospheric moisture. This was further confirmed by the large contact angle for 0.03 wt % AQ optimized films, which is believed to be due to the increase in surface roughness. PSCs based on 0.03 wt % AQ optimized perovskite achieved superior device performance, and a PCE of 17.21% was obtained compared with 13.88% for pristine perovskite devices. The 0.03 wt % AQ optimized devices retained nearly 90% of their initial PCE compared with 50% for pristine devices. The superior performance of 0.03 wt % AQ optimized devices can be attributed to the formation of high-quality films with greater moisture and thermal stability. Our findings suggest that an AQ molecule can effectively control the crystal formation of perovskites with fewer defects and will bind and cover the perovskite grains, leading to greater moisture tolerance. This approach to incorporating AQ in perovskites can be beneficial for the development of economical and stable next-generation PSCs.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c10373>.

Experimental section, synthesis scheme of AQ, ¹H and ¹³C NMR, UV, PL, fwhm, XPS, contact angle, device parameters and J–V curves (PDF)

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Author Contributions

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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