

**Blading Phase-Pure Formamidinium-Alloyed Perovskites for High-Efficiency Solar Cells with Low Photovoltage Deficit and Improved Stability**

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**Abstract:** Currently, blade-coated perovskite solar cells (PSCs) with high power conversion efficiencies (PCEs), i.e. greater than 20%, normally employ methylammonium lead tri-iodide with a sub-optimal bandgap. Alloyed perovskites with formamidinium (FA) cation have narrower bandgap and thus enhance device photocurrent. However, FA-alloyed perovskites show low phase stability and high moisture sensitivity. Here, we report that incorporating 0.83 molar percent organic halide salts (OHs) into the perovskite inks enables phase-pure, highly crystalline FA-alloyed perovskites with extraordinary optoelectronic properties. The OH molecules modulate the crystal growth, enhance the phase stability, passivate ionic defects at the surface and/or grain boundaries, and enhance the moisture stability of the perovskite film. We demonstrate a record efficiency of 22.0% under 1 sun illumination for blade-coated PSCs with an open-circuit voltage of 1.18 V, corresponding to a very small open-circuit voltage deficit of 0.33 V, and significantly improved operational stability with 96% of the initial efficiency retained under one sun illumination for 500 hours.

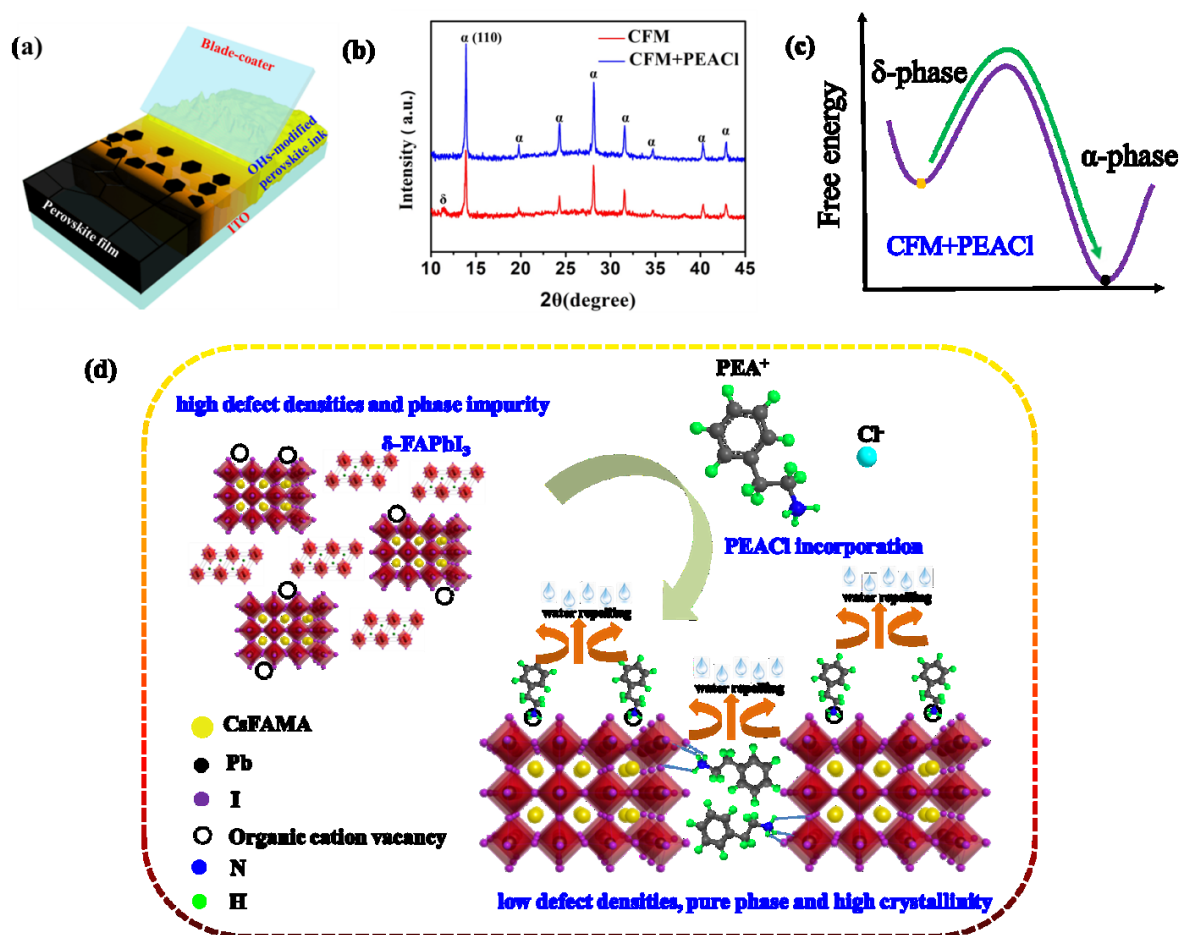
The power conversion efficiencies (PCEs) of perovskite solar cells (PSCs) are already higher than other well-established, commercial, thin-film photovoltaic technologies.<sup>[1]</sup> The most impressive task for commercializing PSC technology is to translate the high efficiency achieved in small-area devices into perovskite modules fabricated via scalable processes, such as the blade-coating and ink-jet printing.<sup>[2-4]</sup> By rational designing ink composition, the device performances of bladed PSCs are on par with spun ones, while blading can make large-area modules at unprecedented speed.<sup>[3, 4]</sup> However, almost all bladed PSCs with PCEs over 20% still employed methylammonium lead iodide (MAPbI<sub>3</sub>) as the light absorbing material, which has a bandgap of 1.55 eV, too large for maximum efficiency.<sup>[4, 5]</sup> By comparison, cubic-phase formamidinium lead iodide (FAPbI<sub>3</sub>) has a smaller bandgap of 1.48 eV which potentially can achieve higher device efficiency.<sup>[6, 7]</sup> However, FAPbI<sub>3</sub> inherently suffers from poor phase stability at room temperature. It can easily convert from cubic perovskite phase to a thermodynamically more stable  $\delta$ -phase (yellow-phase).<sup>[8]</sup> Several approaches have been reported to stabilize the photoactive black-phase of FAPbI<sub>3</sub> by effectively manipulating the material surface energy, including 2D/3D mixture engineering,<sup>[9,10]</sup> surface functionalization,<sup>[11]</sup> or compositional engineering with alloying of multiple cations or halide ions,<sup>[12,13]</sup> where all the perovskite films were made by spin-coating process. It is noted alloying with 60% of MA did stabilize the perovskite phase, but also increased the bandgap. Producing a high-quality, phase-pure, FA-dominant perovskite films via blade-coating has not been achieved in the past, due to less controlled nucleation and/or crystal growth. Moreover, the device efficiency of bladed, triple-cation cesium formamidinium methylammonium (CsFAMA) perovskite-based PSCs is still below 20%, which is much lower than those MAPbI<sub>3</sub> PSCs with an even larger bandgap.<sup>[4, 12, 13]</sup>

Here, we report that incorporating a small amount of organic halide (OH) molecules, namely, phenylethylammonium chloride (PEACl), in FA-alloyed perovskite thin films enhances phase

purity and stability. The Cl anion could modulate the crystal growth to obtain perovskite films with high crystallinity, large grains and low trap densities. Meanwhile, the positively charged PEA cations passivate the charged defects at the perovskite surface and/or grain boundaries (GBs) via electrostatic interactions with A site vacancies or forming hydrogen bonds with undercoordinated I<sup>-</sup> ions, while the hydrophobic conjugated rings are capable of enhancing the moisture resistance. PEACl addition also assist in facilitating the charge collection. As a result, we have demonstrated an optimized, phase-pure cesium formamidinium methylammonium lead iodide (CsFAMAPbI<sub>3</sub>) perovskite with a bandgap of 1.51 eV. A high PCE of 22.0% (stabilized PCE of 21.8%) has been achieved, which is a record value for blade-coated PSCs. Notably, the PSCs show a very small  $V_{oc}$  loss of 0.33 V. In addition, the ambient and operational stabilities of the devices based on PEACl-modified perovskite films have been dramatically enhanced.

**Figure 1a** depicts the fabrication of the FA-alloyed perovskite films via a blade-coating method. In order to reduce the perovskite bandgap, it is necessary to incorporate a high ratio of FA cations in the perovskite composition. We employed a triple-cation Cs<sub>0.05</sub>FA<sub>0.70</sub>MA<sub>0.25</sub>PbI<sub>3</sub> perovskite compound (denoted as CFM) as an initial study objective. A series of OHs featuring functionalized aromatic rings or long alkyl chains terminating with an ammonium group and various halide counterions (Cl, Br or I) were added into perovskite inks for suppressing the formation of  $\delta$ -phase non-perovskite impurities. The representative OHs were PEACl, phenylethylammonium bromide (PEABr), phenylethylammonium iodide (PEAI), butylammonium chloride (BACl), butylammonium bromide (BABr) or butylammonium iodide (BAI). Among the various OHs, PEACl was shown to be most effective, and the optimal additive amount was determined to be 0.83 mol% (relative to Pb) based on the intensive study of photovoltaic performances, which are summarized in Tables S1-S2. X-ray diffraction patterns (XRD) of pristine CFM and targeted CFM modified with 0.83 mol% PEACl are shown

in Figure 1b. The pristine CFM perovskite film contains a notable non-perovskite  $\delta$ -phase. In contrast, adding a small amount of PEACl has effectively suppressed the formation of  $\delta$ -phase and improved the crystallinity of the black-phase perovskite, which is beneficial to decrease the structural disorders in grain interiors and/or at GBs.<sup>[14, 15]</sup> Specifically, the intensity enhancement of the characteristic (110) peak suggests the grains of the PEACl-modified film are more oriented, possibly by influencing the surface energy (Figure 1c).<sup>[16]</sup> In addition to the electrostatic interaction between  $\text{PEA}^+$  and perovskite crystals, the  $\pi$ - $\pi$  interactions between conjugated rings of  $\text{PEA}^+$  molecules staying at grain surface could add compressive strain that inhibits the tilting of  $[\text{PbI}_6]^{4-}$  octahedras and stabilizes black-phase perovskite.<sup>[17]</sup>



**Figure 1.** Fabrication process, crystallographic properties and functions of OH additives. (a) Scheme showing the blade-coating process of the perovskite film; (b) XRD patterns of pristine CFM and CFM modified with 0.83 mol% PEACl; (c) Schematic diagram of free energy versus

$\alpha$ -phase CFM perovskite and  $\delta$ -phase non-perovskite upon PEACl modification; (d) Schematic illustration of  $\delta$ -phase non-perovskite suppression, defect passivation and water repellence induced by PEACl modification.

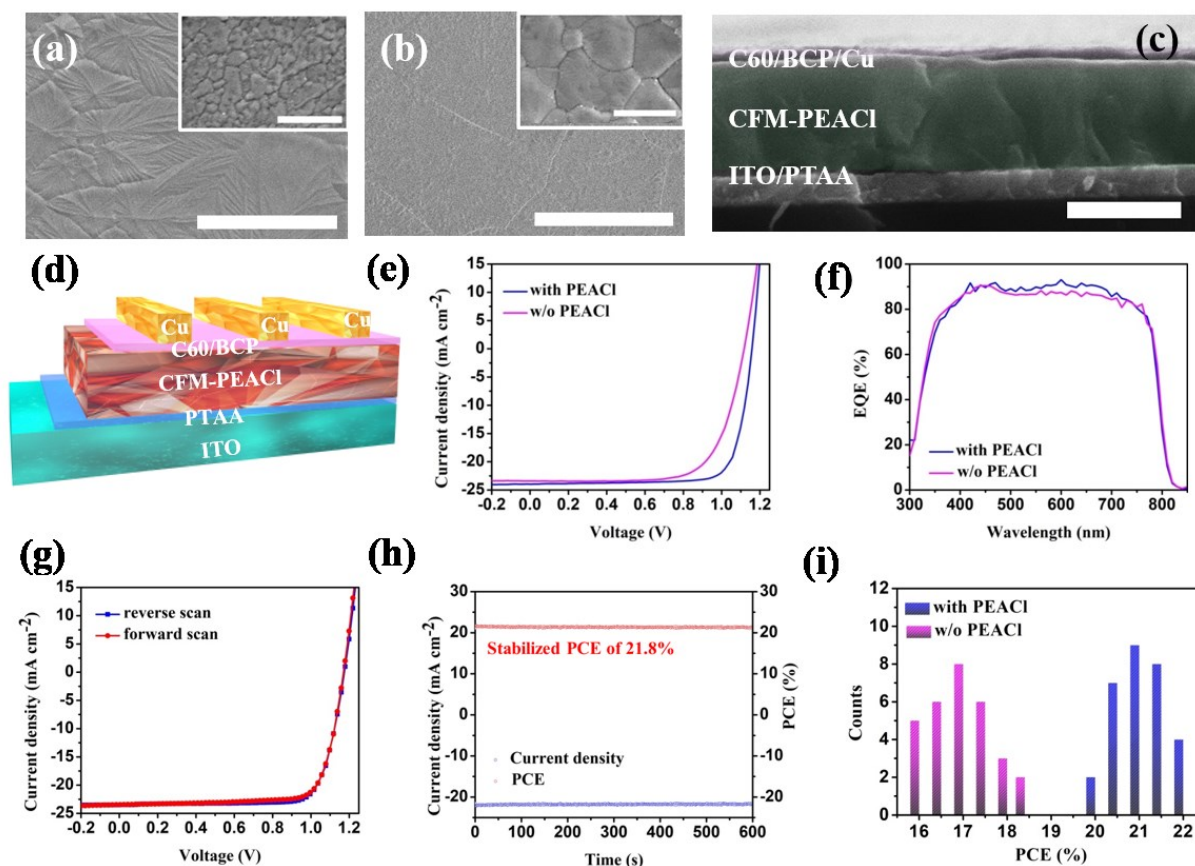
There was no noticeable shift of XRD peaks towards lower angles, indicating no significant unit cell expansion in the perovskite lattice or incorporation of PEACl into the perovskite crystal structure.<sup>[4, 18]</sup> Notably, addition of 6.7 mol% PEACl resulted in the formation of a 2D/3D mixed perovskite (Figure S1), which in some cases would inhibit charge transport.<sup>[9, 18, 19]</sup> Compared to the pristine CFM film, the phase-pure CFM-PEACl film exhibited improved absorption over all wavelength regions (Figure S2), which can be ascribed to enhanced phase purity and improved crystallinity. In addition, the absorption onset was barely changed, suggesting the bandgap was maintained upon addition of a small amount (0.83 mol%) of PEACl.

PEACl consists of a PEA cation and Cl anion. Cl anions have been broadly shown to enhance crystal growth and crystallization of perovskite, while they might evaporate during annealing stage.<sup>[12, 20]</sup> We previously demonstrated that amines could stay within perovskite films even after annealing at relatively high temperatures owing to a strong chemical interaction between the amine groups and perovskites.<sup>4</sup> Fourier transform infrared (FTIR) spectra in Figure S3 indicate the PEA<sup>+</sup> cation still presented within the layered CFM perovskite films after thermal annealing at 100 °C for 10 min, as is evident by observable characteristic spectral features, e.g., aromatic C-H bending at ~680-860 cm<sup>-1</sup> and aromatic C=C bending at ~1560 cm<sup>-1</sup>. Owing to the larger molecular size of PEA cation than the interstitial sites in perovskite structure, the PEA cation would prefer to either occupy A-site vacancies at perovskite grain surfaces or passivate crystallographic defects at the perovskite GBs by forming ionic interactions with under-coordinated I<sup>-</sup> ions, as schematically illustrated in Figure 1d. An X-ray photoelectron spectroscopy (XPS) study revealed that the I 3d<sup>5</sup> signal peak shifted to a higher binding energy after PEACl modification (Figure S4), suggesting the possibility of reduced electronic cloud

density surrounding the iodine atom, and thus indicating potential interaction via ionic bonding between  $\text{PEA}^+$  cations and under-coordinated I<sup>-</sup> ions for passivating negative charged defects.<sup>[21,22]</sup> The interaction between the ammonium group of PEA and the perovskite surface or GBs leaves the bulky hydrophobic aromatic ring exposed, which enhances moisture tolerance of the CFM perovskite films.

As shown in **Figure 2a**, the bladed CFM film still has a rough surface and some big gaps between GBs. The grain sizes of the control CFM film were 100-200 nm with an averaged grain size of ~150 nm (inset in Figure 2a). The FA-alloyed perovskites have a very fast crystallization, making it difficult to obtain uniform films compared to bladed  $\text{MAPbI}_3$ .<sup>13</sup> In contrast, the CFM-PEACl film (0.83 mol% PEACl) showed a relatively smoother surface and larger grains of 300-800 nm with larger averaged sizes of ~500 nm (Figure 2b). The enlarged grain sizes and improved crystallinity for CFM-PEACl film can be ascribed to that the Cl ions lower the crystallization rate and induce the preferred grain orientation.<sup>[20, 23-25]</sup> In addition, the smooth CFM-PEACl film enables conformal coating of the electron transport layer (ETL) and the cathode during device fabrication. Figure 2c presents the cross-sectional SEM image of a completed PSC device. The PEACl-modified perovskite film shows a columnar character with the grains monolithic throughout the film. The completed PSC device is based on a layer-by-layer stacking of indium doped tin oxide (ITO) substrate, poly(triaryl amine) (PTAA) hole transport layer (HTL), perovskite layer,  $\text{C}_{60}$ / bathocuproine (BCP) ETL and copper (Cu) electrode (denoted as ITO/HTL/perovskite/ETL/Cu), with a *p-i-n* planar heterojunction architecture (Figure 2d). The current density-voltage (*J-V*) curves for the best-performing PSCs based on CFM perovskite films with or without PEACl modification are shown in Figure 2e. Specifically, the champion PCE for the CFM-PEACl device reached 22.0% (Table 1), which was significantly higher than the pristine CFM counterpart (18.2%). The enhanced device performance with PEACl modification was mainly due to the enhanced  $V_{oc}$  and fill factor (*FF*). As is clearly observed in the external quantum efficiency (EQE) measurement in Figure 2f, the

optical bandgap of both CFM and CFM-PEACl perovskite films was determined to be  $\sim 1.51$  eV based on the onset (821 nm) of the EQE spectra. Compared with the control CFM device, the  $V_{oc}$  of the CFM-PEACl device increased significantly by 60 mV, which yields a very small  $V_{oc}$  deficit of 0.33 V.



**Figure 2.** (a) Surface SEM images of (a) CFM and (b) CFM-PEACl (the scale bars in (a) and (b) are 100  $\mu\text{m}$ , and 500 nm in the insets); (c) Cross-sectional SEM image of a completed PSC device (the scale bar is 500 nm); (d) Schematic illustration of an inverted p-i-n device structure; (e) J-V curves and (f) EQE spectra of PSCs based on CFM perovskite in the absence or presence of PEACl additive; (g) J-V curves of the champion PSC with PEACl passivation measured under forward and reverse scanning directions; (h) Stabilized current density and PCE at the maximum power point (0.98 V) of the champion device ( $0.08 \text{ cm}^2$ ) based on the CFM-PEACl thin film; (i) PCE histogram of the PSCs based on CFM and CFM-PEACl films.

A high short-circuit current density ( $J_{sc}$ ) larger than  $23 \text{ mA cm}^{-2}$  has been achieved for the CFM-PEACl based PSCs. The calculated  $J_{sc}$  values from the EQE spectra are 22.9 and 22.3  $\text{mA cm}^{-2}$  for the CFM-PEACl and CFM devices, respectively, agreeing well with the  $J$ - $V$  results with <3% discrepancy. The hysteresis in the best-performing CFM-PEACl device was negligible, with only a 0.9% absolute PCE discrepancy between the forward and reverse scans (Figure 2g and Table S3). The champion device was held at a maximum power point of 0.98 V, and the  $J_{sc}$  was steadied within seconds, giving a stabilized power output of 21.8% under AM 1.5G illumination (Figure 2h). This high stabilized PCE outperforms the previously demonstrated MAPbI<sub>3</sub>-based PSCs owing to the beneficially higher component of FA cations,<sup>[4]</sup> which hitherto represented the record efficiency for PSCs fabricated via a blade-coating method. The PCE histogram of CFM and CFM-PEACl based PSCs were constructed from data collected from a batch of 30 devices for each condition (Figure 2i). The CFM-PEACl devices consistently showed higher PCEs, with better reproducibility than the CFM-based counterparts. Exceptionally, in this work, more than 93% of CFM-PEACl devices had PCEs above 20.5%, while only 36% of the control CFM devices had efficiencies over 17% under 1 sun illumination. This result highlights the effectiveness of PEACl modification on improving film compactness and uniformity, and thus improving the reproducibility of device performances.

Steady-state and time-resolved photoluminescence (PL) measurements were carried out to identify the passivation effect of PEACl molecules on perovskite films. In general, spontaneous radiative recombination via trap states normally leads to a red-shifted emission, and passivation of these trap states can blue-shift the PL emission peak.<sup>[26-28]</sup> As shown in **Figure 3a** and Table S4, the steady-state PL intensity was enhanced, accompanied by a  $\sim 3 \text{ nm}$  blue-shift upon addition of 0.83 mol% PEACl, irrespective of whether the PL was emitted from the top or bottom of the perovskite film. This indicates an efficient defect passivation effect induced by PEACl. The spatial distribution of PEACl molecules in the perovskite films is largely dependent on the fabrication process, which would consequently affect the PL peak positions and



intensities. Upon PEACl addition, the top surface exhibited a nearly one-fold enhancement of PL intensity, while only a 40% increase of PL intensity was observed for bottom side of the film, suggesting that the top surface was more effectively passivated by PEACl. Time-resolved photoluminescence (TRPL) lifetimes were measured for CFM perovskite films with and without PEACl modification, and the profiles were fitted with bi-exponential decays. The relatively fast decay component ( $\tau_1$ ) was assigned to the charge trapping process, while the much slower decay components ( $\tau_2$ ) were assigned to de-trapping or carrier recombination processes.<sup>[29]</sup> Although the  $\tau_1$  increased from 1.2 ns to 4.2 ns upon PEACl passivation, in the CFM-PEACl film the TRPL decay is largely dominated by the long decay process and  $\tau_2$  was significantly elongated from 0.69  $\mu$ s to 1.58  $\mu$ s (Figure S5 and Table S5). These results implied that charge trapping and carrier recombination in PEACl-modified perovskite films was largely suppressed, suggesting reduced trap densities. The device was then irradiated under AM 1.5 G illumination and a small transient photovoltaic signal was triggered by a laser pulse (337 nm, 4 ns) to measure the transient photovoltage (TPV) decay.<sup>[30]</sup> The carrier recombination lifetime increased from 0.47  $\mu$ s in the CFM device to 0.92  $\mu$ s for the PEACl-modified device (Figure 3b). We also conducted electrochemical impedance spectroscopy (EIS) characterization and analysis to understand the charge recombination dynamics within the devices (Figure S6a and S6b). Accordingly, the recombination resistance ( $R_{\text{rec}}$ ) and carrier lifetime ( $\tau_e$ ) of the PSCs were calculated by fitting the EIS spectra with an equivalent circuit model (Figure S6e). The PSC modified with PEACl showed both larger recombination resistance and longer carrier lifetime (Figure S6c, S6d and Table S6) than the control device without PEACl modification. These results suggest the passivation by PEACl suppresses charge recombination, which enhanced  $V_{\text{oc}}$  of the CFM-PEACl device.

**Table 1.** Photovoltaic parameters of PSCs based on CFM perovskite (with a bandgap of 1.51 eV) with or without PEACl modification under 1 sun illumination (AM 1.5G, 100 mW cm<sup>-2</sup>).

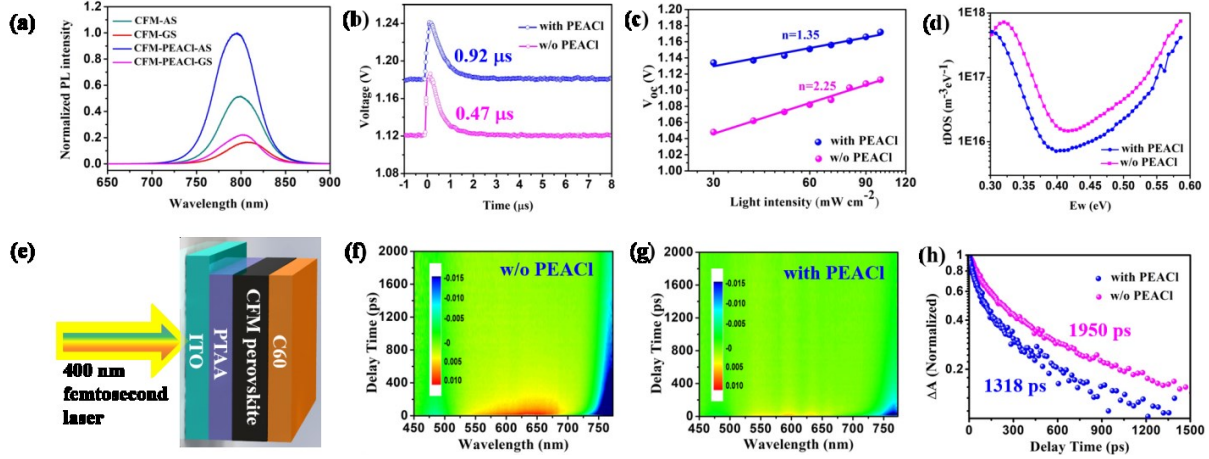
| PSCs      | $J_{sc}/$     | $V_{oc}$ | $\eta$ | Average $\eta$ | FF   | $V_{oc}$ deficit |
|-----------|---------------|----------|--------|----------------|------|------------------|
|           | $mA\ cm^{-2}$ | V        | %      | %              | %    | V                |
| CFM       | 23.0          | 1.12     | 18.2   | 16.88±1.32     | 70.8 | 0.39             |
| CFM-PEACl | 23.6          | 1.18     | 22.0   | 21.25±0.75     | 79.0 | 0.33             |

[\*] data for average PCE ( $\eta$ ) were calculated from at least 30 devices.

The light-intensity dependent  $V_{oc}$  was also measured to provide more information on charge recombination process in PSCs. By fitting the results to the equation,  $n = kT/q\Delta V_{oc}/\Delta \ln J_L$  (where  $k$ ,  $T$ ,  $q$  and  $J_L$  are the Boltzmann constant, absolute temperature, elementary charge and photogenerated current density, respectively), the diode ideal factor ( $n$ ) can be obtained.<sup>[31]</sup> In general,  $n$  can vary between 1 and 3 for PSCs depending on trap-assisted recombination.<sup>[32, 33]</sup> The CFM-PEACl device exhibited a larger  $V_{oc}$  than the control CFM device under all light intensities. The  $n$  decreased from 2.25 for the control CFM device to 1.35 for the CFM-PEACl device (Figure 3c), which is much closer to that of an ideal diode, indicating the non-radiative recombination process was effectively suppressed by PEACl passivation.<sup>[34]</sup> The prolonged carrier lifetime and suppressed non-radiative recombination of PSCs with PEACl passivation can be attributed to an effective reduction of trap densities within the perovskite films. Thermal admittance spectroscopy (TAS), a well-established characterization technique in thin-film photovoltaics,<sup>[35]</sup> was performed to quantify the trap density of states (tDOS) of the control and PEACl-modified devices. Figure 3d shows that the CFM-PEACl device had lower tDOS over the whole trap depth region compared to the pristine CFM counterpart. We inferred that surface defects/trap states at grain surfaces and/or GBs were effectively passivated upon PEACl

modification, which resulted in reduced charge recombination loss, and thus higher  $V_{oc}$ ,  $FF$  and, ultimately, a record PCE for blade-coated PSCs.

**Figure 3.** Photoluminescence, carrier recombination lifetime, ideal factor, trap densities and



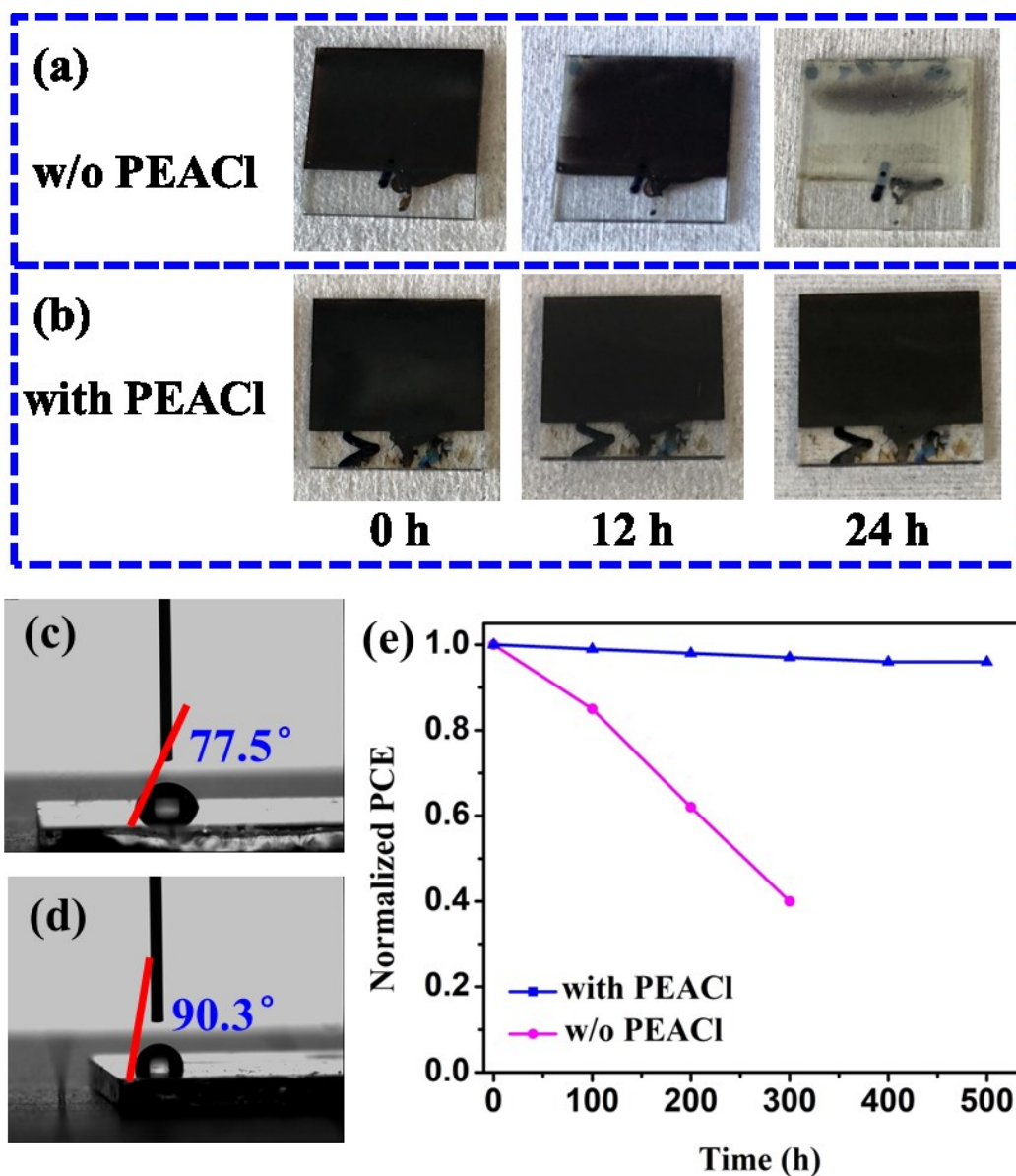
transient absorption. (a) PL spectra of perovskite films with or without PEACl emitted from either the air side (AS, top) or glass side (GS, bottom); (b) Carrier recombination lifetime measured by TPV, (c)  $V_{oc}$  dependence as a function of light intensities and (d) trap density of states (tDOS) obtained from TAS measurement of perovskite devices with or without PEACl passivation; (e) Schematic of the layer-stacking structure for TA measurement, where a 400 nm pump pulse generated by a fs laser was used to probe the TA signal; (f, g) Contour plot TA spectra and (h) dynamic TA decay probed at the GSB peak for CFM perovskite films with or without PEACl modification.

It is reported that the photo-excited charge transfer process at interfaces within PSCs occurs on a timescale of picoseconds, which significantly affects charge extraction and collection.<sup>[36]</sup> We used femtosecond (fs) transient absorption (TA) spectroscopy to characterize the ultrafast carrier dynamic of the perovskite film, which is sandwiched between the PTAA HTL and C<sub>60</sub> ETL contacts (Figure 3e). As shown in Figure 3f and 3g, the contour plots of the TA spectra for both CFM and CFM-PEACl samples exhibit a distinct ground-state bleaching (GSB) peak at ~750 nm. The GSB peak intensity reflects the photoinduced carrier population in the

conduction and valence bands of perovskite.<sup>[37, 38]</sup> In contrast to the control CFM sample, a promptly fading signal in the contour plot for the CFM-PEACl sample suggested that photo-induced electrons and holes were more efficiently extracted out to the ETL and HTL. Accordingly, the decay kinetics of the GSB were analyzed, revealing a much faster decay for the sample with PEACl modification than that of the control CFM sample (i.e., 1318 ps versus 1950 ps, Figure 3h and Table S7). This result verified the beneficial role of PEACl modification on accelerating charge extraction and collection from perovskite to the respective carrier transport layers, which could be ascribed to the improved quality of the CFM-PEACl perovskite film with enhanced phase purity, crystallinity and reduced defect densities.<sup>[39, 40]</sup>

The FA-alloyed perovskite is liable to undergo a phase transformation from cubic black-phase perovskite to yellow-phase non-perovskite under ambient conditions, especially in high relative humidity (RH).<sup>[8, 41]</sup> To evaluate the effects of PEACl modification on phase stability, we traced the degradation of the perovskite films under RH of  $80 \pm 5\%$ . **Figure 4a** and **4b** show photographs of perovskite films stored for different durations. The control CFM was almost completely bleached after 24 h owing to its transformation to the  $\delta$ -phase (Figure 4a, Figure S7), while no obvious change in color was observed for the CFM-PEACl film (Figure 4b), suggesting that PEACl addition enhanced phase stability in a high humidity environment. The defective surface and GBs of perovskite film are vulnerable to moisture invasion.<sup>[42]</sup> As aforementioned, the large, hydrophobic  $\text{PEA}^+$  cation strongly bonds with the perovskite, and thus self-assembles a moisture-repelling barrier at the boundaries and surface of perovskite grains (Figure 1d). As shown in Figure 4c and 4d, the surface contact angle of water droplets increased from  $77.5^\circ$  on the CFM film to  $90.3^\circ$  on the PEACl-modified CFM film, which implied that possible ingress pathways of moisture into the perovskite film were largely prohibited, and decomposition of perovskite under atmospheric condition would be retarded. Besides the high initial PCE performance, the operational stability of PSCs under realistic

conditions should be considered.<sup>[43]</sup> The stability of encapsulated PSCs based on CFM and CFM-PEACl films were compared under continuous 1 sun illumination. The CFM-PEACl device retained 96% of its initial PCE after 500 h, while the CFM device degraded to about 40% of its original PCE after 300 h (Figure 4e), indicating the significantly improved stability with the addition of PEACl. Only a very minor drop in photovoltaic parameters (i.e.  $J_{sc}$ ,  $V_{oc}$ , FF and PCE) has been recorded for the CFM-PEACl devices (Figure S8), which can be attributed to an increase in temperature up to 60 °C during device operation.<sup>[44]</sup> Under operational conditions with abundant photo-generated charges and a built-in electric field, the degradation of device performance is normally caused by the presence of high concentrations of mobile charged or neutralized ions/defects that can lead to undesirable recombination loss.<sup>[45]</sup> In this work, the charged defects and/or undercoordinated ions at grain surfaces and/or GBs are effectively passivated by the addition of a robust passivation agent like PEACl. The enhanced phase purity of the CFM-PEACl film may also partially contribute to the enhanced operational stability, because the secondary, heterogeneous  $\delta$ -phase non-perovskite can generate numerous active defect sites for charge recombination.



**Figure 4.** (a, b) Photographs of CFM perovskite films modified with or without PEACl after prolonged exposure to 80±5% RH environment for 24 hours; Contact angle of a water droplet on the surface of a CFM perovskite film (c) without or (d) with PEACl modification; (e) Operational stability of encapsulated PSCs based on CFM and CFM-PEACl films under continuous 1 sun illumination.

## Conclusions

In summary, we have demonstrated the beneficial roles of organic halide molecules, particularly PEACl, in improving optoelectronic properties by improving the phase purity,

reducing trap-state density and facilitating charge collection. The PEACl modification strategy enabled us to demonstrate FA-dominant blade-coated devices with a record efficiency up to 22% and a good operational stability. We anticipate the chemical-modification via a combination of composition engineering and additive engineering is a promising strategy to stabilize perovskite with improved quality and optimal bandgap for prosperous optoelectronic applications.

### Experimental Section

*Materials:* Unless stated otherwise, all materials and solvents were purchased from Sigma-Aldrich. Lead iodide ( $\text{PbI}_2$ , 99.999%) and cesium iodide (CsI) were purchased from Alfa Aesar. Formamidinium iodide (FAI) and methylammonium iodide (MAI) were purchased from GreatCell Solar.

*Device Fabrication:* The ITO glass substrates were cleaned ultrasonically in deionized water, acetone, and isopropanol baths for 30 min successively, followed by a UV-ozone (UVO) treatment for 15 min. A ~20 nm thick poly(triaryl amine) (PTAA) layer was blade-coated onto the ITO glass according to our previous report.<sup>[4]</sup> The perovskite layers were also fabricated via a blade-coating method.<sup>[4]</sup> The  $\text{Cs}_{0.05}\text{FA}_{0.70}\text{MA}_{0.25}\text{PbI}_3$  perovskite ink (1.2 M) was prepared by dissolving  $\text{PbI}_2$ , FAI, MAI and CsI in dimethylformamide (DMF). Before use, small amounts of additives, i.e. methylammonium hypophosphite (MHP, 0.15 wt%) and L- $\alpha$ -phosphatidylcholine (LP, 0.05 wt%), were added to achieve uniform perovskite film coating with good surface coverage.<sup>[3,46]</sup> A series of organic halide salts, i.e. phenylethylammonium chloride (PEACl), phenylethylammonium bromide (PEABr), phenylethylammonium iodide (PEAI), butylammonium chloride (BACl), butylammonium bromide (BABr) and butylammonium iodide (BAI), were dissolved in DMF separately, then added to the as-prepared perovskite ink at an optimized concentration of 0.83 mol%. 5-10  $\mu\text{L}$  of perovskite ink was used for each blade-coating on a pre-heated 1.5 cm $\times$ 1.5 cm ITO substrate, and the film applicator

was swiped linearly at a speed of  $7.5 \text{ mm s}^{-1}$ . After coating, the perovskite films were annealed at  $100 \text{ }^\circ\text{C}$  for 10 min. Finally, 25 nm of  $\text{C}_{60}$  (Nano-C), 8 nm of bathocuproine (BCP), and 80 nm of Cu electrode were sequentially deposited by thermal evaporation to assemble a complete PSC device.

*Device Characterization:* Scanning electron microscopy (SEM) images were investigated by a Quanta 200 FEG environmental scanning electron microscope. X-ray diffraction (XRD) patterns were recorded with a Bruker D8 Discover Diffractometer with Cu  $K\alpha$  radiation ( $1.5406 \text{ \AA}$ ). The FTIR spectra ( $4000$  to  $500 \text{ cm}^{-1}$ ) were recorded on a PerkinElmer FTIR spectrometer with powders scratched from several pieces of samples. The  $J$ - $V$  measurement of the devices (voltage scanning rate  $0.1 \text{ V s}^{-1}$ ) and the steady photocurrent under maximum power output bias ( $0.98 \text{ V}$ ) were recorded with a Keithley 2400 source-meter under simulated AM 1.5G irradiation produced by a Xenon lamp based solar simulator (Oriel Sol3A, Class AAA Solar Simulator). The light intensity was calibrated by a silicon reference cell equipped with a Schott visible color KG5 glass filter (Newport 91150V). A non-reflective shadow mask was used to define a  $0.08 \text{ cm}^2$  active area of the PSCs. External quantum efficiency (EQE) spectra were measured by a Newport QE measurement kit by focusing a monochromatic light beam with wavelength from 300 nm to 900 nm onto the devices. Photoluminescence (PL) spectrum was measured with a Horiba iHR320 Imaging Spectrometer at room temperature. A 532 nm green laser (Laserglow Technologies) with an intensity of  $100 \text{ mW cm}^{-2}$  was used as the excitation source. Time-resolved photoluminescence (TRPL) was obtained using a DeltaPro TCSPC Filter Fluorometer with a pulsed laser source at 406 nm (Horiba NanoLED 402-LH; pulse width below 200 ps, 20 pJ per pulse, approximately  $1 \text{ mm}^2$  spot size), and the signal was recorded using time-correlated single photon counting (TCSPC). The tDOS measurement was performed by using an Agilent E4980A precision LCR meter. The DC bias was fixed at 0 V and the amplitude of the AC bias was 20 mV. The scanning range of the AC frequency was 0.02 – 2000



kHz. The tDOS ( $N_T(E_\omega)$ ) is calculated by using an equation:  $N_T(E_\omega) = -\frac{1}{qkT} \frac{\omega dC}{d\omega} \frac{V_{bi}}{W}$ , where  $W$  and  $V_{bi}$  are the depletion width and built-in potential, respectively, which were derived from the Mott-Schottky analysis of the  $C$ - $V$  measurement.  $q$ ,  $k$ ,  $T$ ,  $\omega$  and  $C$  are elementary charge, Boltzmann's constant, temperature, angular frequency and specific capacitance, respectively. The demarcation energy  $E_\omega = kT \ln\left(\frac{\omega_0}{\omega}\right)$  (where  $\omega_0$  is the attempt-to-escape angular frequency that equals to  $2\pi\nu_0 T^2$  ( $\nu_0$  is the temperature-independent attempt-to-escape frequency)) is derived from the temperature-dependent  $C$ - $f$  measurements which were carried out in a Lake Shore Cryotronics probe stage with a Lake Shore Cryotronics temperature controller model 336. Transient photovoltage (TPV) decay was measured under one sun illumination and recorded by a 1 GHz Agilent digital oscilloscope. The EIS measurements were carried out by using an electrochemical workstation (Zahner Zennium) with the frequency range from 1 Hz to 1 MHz under dark and different applied biases from -0.9 V to -1.1 V. Transient absorption (TA) measurement was conducted by using a regeneratively amplified Ti:Sapphire laser source (Coherent Legend, 800 nm, 150 fs, 5 mJ per pulse, and 1 kHz repetition rate) and Helios spectrometers (Ultrafast Systems LLC). A portion of the 800 nm output (75%) pulse was frequency doubled in a BaB<sub>2</sub>O<sub>4</sub> (BBO) crystal, which could generate 400 nm pump light; the remaining portion of the output was concentrated into a sapphire window to produce a white light continuum (420–780 nm) probe light. The 400 nm pump beam was generated as part of the 800 nm output pulse from the amplifier and its power was adjusted by using a range of neutral-density filters. The pump beam was focused at the sample with a beam waist of about ~360 nm and the power intensity was fixed at 14  $\mu\text{J cm}^{-2}$  in this experiment. With the aid of a mechanical chopper, the pump repetition frequency was synchronized to 500 Hz. The probe and reference beams could be split from the white light continuum and sent into a fiber optics-coupled multichannel spectrometer by using complementary metal-oxide-semiconductor sensors with a frequency of 1 kHz.

**Supporting Information**

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

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## ToC

A multifunctional conjugated benzene ammonium halide was introduced to enhance phase purity, reduce trap-state density and suppress non-radiative charge recombination. Blade-coated solar cells based on stabilized formamidinium-dominant perovskite compositions deliver a record efficiency of 22.0% and an improved operational stability.

**Keyword:** perovskite solar cells, light harvesting, charge recombination, passivation, charge collection

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**Blading Phase-Pure Formamidinium-Alloyed Perovskites for High-Efficiency Solar Cells with Low Photovoltage Deficit and Improved Stability**

