

Origin of Open-Circuit Voltage Enhancements in Planar Perovskite Solar Cells Induced by Addition of Bulky Organic Cations

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The origin of performance enhancements in p-i-n perovskite solar cells (PSCs) when incorporating low concentrations of the bulky cation 1-naphthylmethylamine (NMA) are discussed. A 0.25 vol % addition of NMA increases the open circuit voltage (V_{oc}) of methylammonium lead iodide (MAPbI₃) PSCs from 1.06 to 1.16 V and their power conversion efficiency (PCE) from 18.7% to 20.1%. X-ray photoelectron spectroscopy and low energy ion scattering data show NMA is located at grain surfaces, not the bulk. Scanning electron microscopy shows combining NMA addition with solvent assisted annealing creates large grains that span the active layer. Steady state and transient photoluminescence data show NMA suppresses non-radiative recombination resulting from charge trapping, consistent with passivation of grain surfaces. Increasing the NMA concentration reduces device short-circuit current density and PCE, also suppressing photoluminescence quenching at charge transport layers. Both V_{oc} and PCE enhancements are observed when bulky cations (phenyl(ethyl/methyl)ammonium) are incorporated, but not smaller cations (Cs/MA)—indicating size is a key parameter. Finally, it demonstrates that NMA also enhances mixed iodide/bromide wide bandgap PSCs (V_{oc} of 1.22 V with a 1.68 eV bandgap). The results demonstrate a facile approach to maximizing V_{oc} and provide insights into morphological control and charge carrier dynamics induced by bulky cations in PSCs.

1. Introduction

Recently, organometal halide perovskites have demonstrated great potential in photovoltaic (PV) devices, attributed to their high charge carrier mobility, long carrier lifetimes, and tunable bandgaps.^[1–5] Over recent years, the power conversion efficiency (PCE) of single junction perovskite solar cells (PSCs) has increased from 3.8% to 23.7%, enabled by a diverse range of strategies including interface passivation, compositional engineering, and energy level tuning.^[6–12] Moreover, organometal halide perovskites show promise in tandem solar cells, coupled with incumbent PV materials, i.e., silicon and copper indium gallium diselenide.^[13,14] This versatility is due, in-part, to the ready tunability of the perovskite bandgap—achieved by facile cation, e.g., methylammonium (MA), formamidinium (FA); metal, e.g., Pb²⁺, Sn²⁺, and halide, e.g., I[−], Br[−], Cl[−] substitution.^[3,5,15–17] Whilst advances in performance enhancement have been impressive, PSCs still suffer from significant

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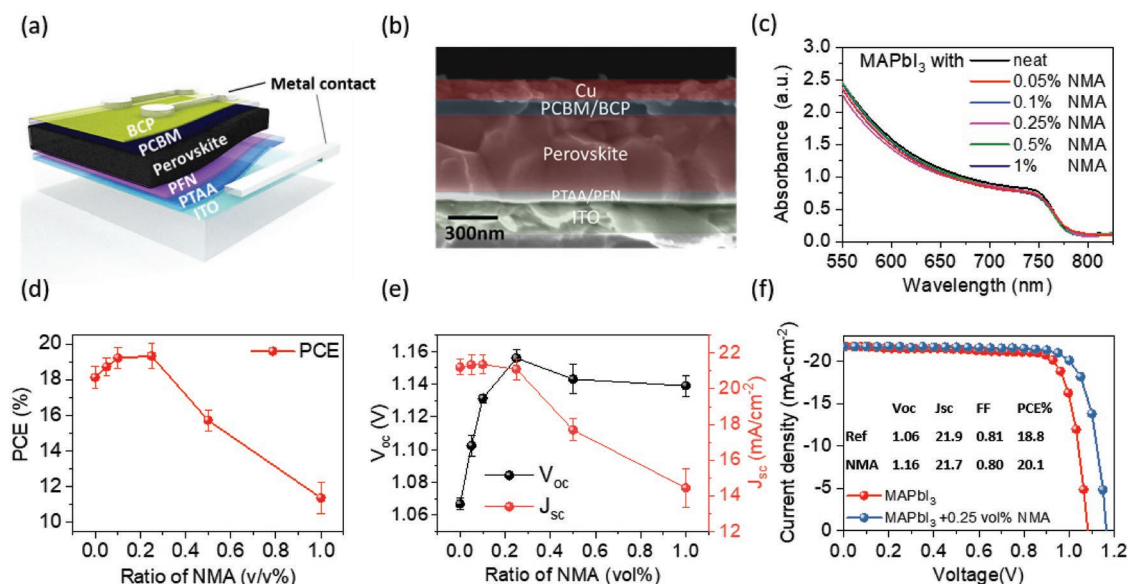


Figure 1. a) Schematic diagram showing the device architectures investigated. b) Cross-section SEM image of a typical operational device. c) UV-vis spectrum of MAPbI₃ with NMA from 0.05 to 1 vol% and d) representative PCE data, e) typical J_{sc} and V_{oc} data. f) Standard and NMA modified J - V curves for champion devices with inset table showing device characteristics.

bulk nonradiative recombination losses that prevent device performance reaching the Shockley–Queisser limit. In this study, we focus on reducing open-circuit voltage (V_{oc}) losses in PSCs though the passivation of defect states in the perovskite active layer associated with this undesired nonradiative recombination pathway.^[18]

The development of PSCs has focused on the classical three-dimensional (3D) perovskite structure, i.e., ABX₃, although more recently there have been developments in devices employing mixed 2D/3D perovskite structures—motivated in particular by the promising stabilities observed for devices employing such mixed structures.^[19,20] These are typically formed by combining bulky organic cations (R) into the ABX₃ structure to drive the formation the 2D phases, generally represented as R₂A_{n-2}B_nX_{3n+1}, where n is the number of layers between bulky cation layers. When $n < 5$, the properties of the perovskite can be easily tuned by varying the number of Pb-X layers sandwiched by the bulky organic spacer layers.^[21] This class of perovskite films with the formation of a mixed 2D/3D phase, often referred to as quasi-2D Ruddlesden–Popper (RP) hybrid perovskites, has shown a rapid increase in PCE from 4% to 13.7% in only four years.^[22,23] However, this is still far lower than 3D systems, most probably owing to the organic spacer layer impeding charge transport in the material. When $n > 5$, the optical absorption properties, i.e., bandgap, are dominated by the properties of the 3D perovskite. This class of perovskite films were termed quasi 3D perovskites by Hu et al., with there being little evidence of 2D structure formation.^[24] Studies of such perovskite devices, where a low concentration of bulky organic spacer cation is incorporated into the 3D structure, have reported both high performance and enhanced stability.^[6,25–29] The enhanced performance of these devices has primarily been due to improved V_{oc} ,^[6,26–29] whereas a reduced current density (J_{sc}) has also been observed in several studies.^[26,29] Despite interest in these devices, the underlying origins of this

enhanced performance in terms of charge carrier dynamics and structural analysis remains relatively unexplored.^[30]

Here, we demonstrate that 1-naphthylmethylamine (NMA), previously used as a bulky organic cation in quasi-2D RP perovskite light-emitting diodes (LEDs), can, at low concentrations, terminate grain surfaces and effectively passivate defects in MAPbI₃. As such, PSCs using an NMA-MAPbI₃ light absorbing layer yield improvements in PCE from 18.7% to 20.1 %, with an observed increase in V_{oc} from 1.06 to 1.16 V. Detailed structural and photophysical analyses are employed to elucidate the origin of this enhancement. We go on to extend this study to related bulky cations and from MAPbI₃ to the wider bandgap MAPb(I_{1-x}Br_x)₃ demonstrating the broad applicability and versatility of this approach.

2. Results and Discussion

2.1. Solar Cell Performance

A schematic illustration of the inverted p–i–n planar architectures employed in this study is shown in **Figure 1a**, accompanied by a representative scanning electron microscope (SEM) image of a device stack (Figure 1b). The device composition utilized, with layer thicknesses in parenthesis, was ITO (150 nm)/PTAA (10 nm)/poly[(9,9-bis(3'-(N,N-dimethylamino) propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene) (PFN) (<10 nm)/perovskite (≈300 nm)/PCBM (60 nm)/BCP (<10 nm)/Cu (100 nm). PFN is used as surface modifier to enhance the wettability of the perovskite solution on the hole transport material poly(triarylamine) (PTAA).^[31] Here, NMA was chosen as a bulky cation to drive the formation of “quasi-3D” structures.^[32] The perovskite absorber layers were prepared from MAI/PbI₂ in DMSO/DMF solutions with and without the addition of 0.05–1 vol% NMA and were deposited using antisolvent

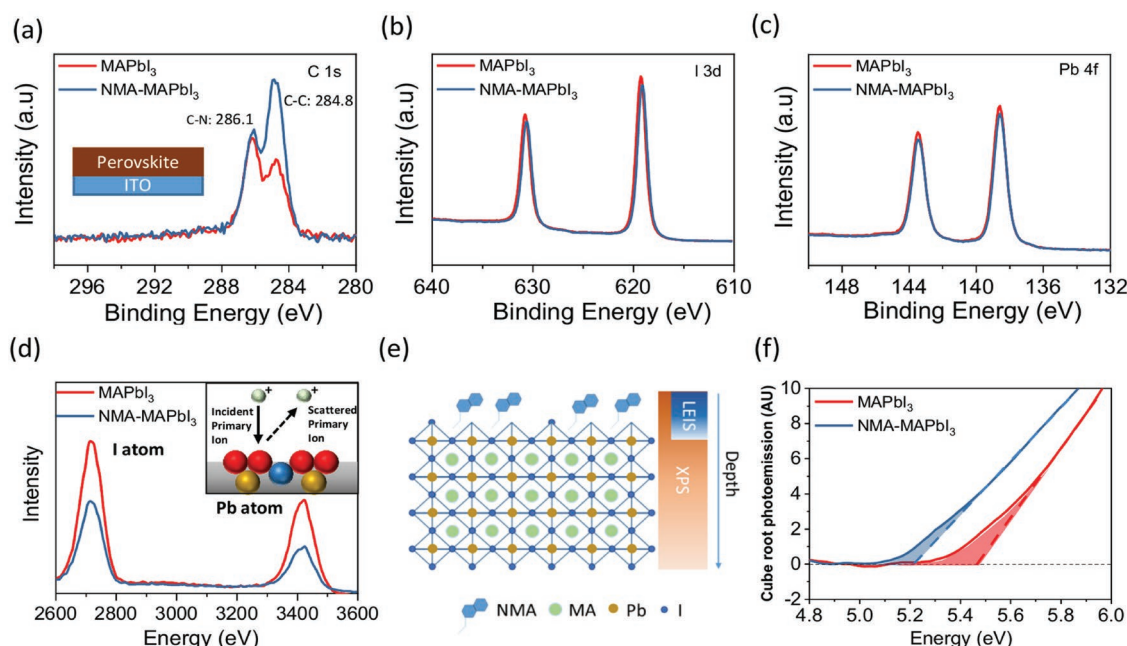


Figure 2. XPS spectra of a) C 1s, b) I 3d, c) Pb 4f, and d) low-energy ion scattering (LEIS) spectra of the MAPbI₃ and NMA-MAPbI₃ films. The inset figure is an illustration of the LEIS measurement technique. e) Schematic diagram of the sensitivity of the XPS and the LEIS measurement. f) Ambient pressure photoemission spectroscopy (APPS) spectra of the MAPbI₃ and NMA-MAPbI₃ films.

engineering with solvent-assisted thermal annealing to form a compact layer (details in the Supporting Information). Figure 1c shows typical absorption spectra of perovskite thin films prepared over a range of NMA concentrations, there is a consistent onset of absorption around 780 nm, indicating that the optical bandgap is insensitive to the addition of NMA over the conditions investigated.

The PCEs of devices prepared with a variety of NMA volume ratios are shown in Figure 1d, with the corresponding V_{oc} and short-circuit current density (J_{sc}) values plotted in Figure 1e. The PCE is observed to rise steadily from 18.1 ($\pm 0.6\%$) to 19.5 ($\pm 0.5\%$) as the NMA concentration is increased to 0.25 vol%, above this concentration the PCE falls sharply to well below the value observed with no NMA added. Analysis of the V_{oc} and J_{sc} data show the improvements in PCE are driven by an increase in V_{oc} as NMA, up to 0.25 vol%, is added. Above this NMA concentration, there is a slight reduction in V_{oc} but a rather more drastic reduction in J_{sc} ; analogous J_{sc} reductions have been reported with different additives in PSCs with the behavior attributed to impeded charge transport across passivated grain boundaries.^[33] The current–voltage (J – V) characteristics of the champion devices are plotted in Figure 1f. In the absence of NMA our best devices show a stabilized PCE (Figure S1a, Supporting Information) of 18.6% (18.8% in reverse scan), which are comparable to the best performing planar p–i–n MAPbI₃ devices reported in the current literature.^[31] With the addition of 0.25 vol% NMA the champion device has a stabilized PCE of 20.0% (20.1% in reverse scan) and a measured V_{oc} of 1.16 V in addition to exhibiting minimal hysteresis, Figure 3. The external quantum efficiency values of these devices are shown in Figure S1b of the Supporting Information, the integrated J_{sc} of MAPbI₃ and 0.25 vol% NMA in MAPbI₃ are 21.5 and 21.1 mA cm^{−2}, respectively, in reasonable

agreement with the directly measured values. Representative J – V characteristics are given in Table S1 of the Supporting Information. As an NMA concentration of 0.25 vol% was determined to be optimum we focus on this composition, referred to as NMA-MAPbI₃.

2.2. Location of NMA within the Absorber Layer

In the existing literature, where alternative bulky cation additives have been incorporated into various perovskite devices, the location of the additive remains poorly defined. Grancini et al. proposed that the addition of 3 mol% of 5-aminovaleric acid (5-AVA) into MAPbI₃ based n–i–p devices resulted in a 2D/3D interface at the perovskite–metal oxide interface.^[34] In planar devices, several reports suggest bulky cations are possibly located at grain surfaces or boundaries, however in the literature no direct evidence to support these claims has been presented.^[7,26,28,35] Given the size of NMA we consider the molecule is too large to be incorporated into the bulk of MAPbI₃, without at least causing significant structural distortion (XRD data shown in Figure S2a, Supporting Information). To explore this, we employed X-ray photoelectron spectroscopy (XPS) to probe the surface composition of our NMA-MAPbI₃. Core level spectra for C 1s, I 3d, and Pb 4f are shown in Figure 2a–c with a survey-spectra provided in Figure S2b of the Supporting Information. The C 1s signal shows a significant variation in the relative intensity and ratio of the peaks associated with C–C and C–N, centered around 284.8 and 286.1 eV, respectively. In particular, there is a distinct increase in the C–C signal, which we attribute to the presence of NMA at/near the film surface. No significant changes are seen in the I 3d or Pb 4f signals although a subtle reduction in signal intensities

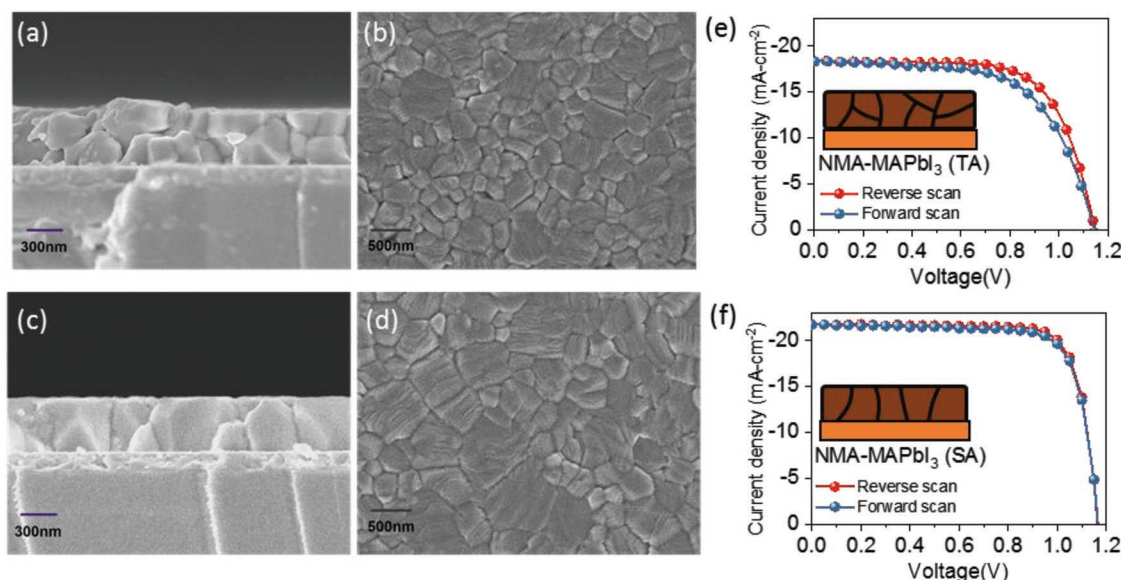


Figure 3. The cross-section and surface SEM images of NMA-MAPbI₃ films fabricated by a,b) thermal annealing and c,d) solvent annealing. The *J*–*V* characteristics of device fabricated by e) thermal annealing and f) solvent annealing. The forward and reverse scans are measured from –0.2 to 1.2 V at a scan rate of 100 mV s^{–1}.

are observed, which can be attributed to the surface NMA attenuating the signal.

To investigate further the surface termination of these films, we implemented low-energy ion scattering (LEIS). Relatively unexplored in this research field, LEIS operates on the principle of low-energy primary ion (He⁺, Ne⁺, Ar⁺) bombardment on a surface resulting in surface scattering from the top atomic layer, producing characteristic backscattered ions, Figure 2d. Subsurface atoms do not produce scattering peaks under static conditions (nondestructive) contributing only to the overall background signal. Thus, LEIS provides an incredibly sensitive surface probe, which provides greater surface sensitivity than XPS alone.^[36] Figure 2e, capable of detecting subtle modulations in surface composition and termination. Comparison of scattering data obtained for MAPbI₃ and NMA-MAPbI₃ films, Figure 2d, show a reduction of ≈40–50% in the yield of backscattered peaks attributed to I and Pb, which we can explain as being due to the NMA being present as a partial covering on the grain surface, rather than being located within the bulk of the perovskite. Given that the NMA-MAPbI₃ films are prepared by direct addition of NMA to the precursor solution we can speculate that NMA may also reside in the grain boundary regions, however the low ratio of grain boundary to bulk MAPbI₃ means that signal attenuation, by XPS or LEIS, is not observed (Figure S2c, Supporting Information).

The surface energetics were studied using ambient pressure photoemission spectroscopy and Kelvin probe analyses. The valence band edge (VBE) and work function (*W*_F) data for MAPbI₃ and NMA-MAPbI₃ are plotted in Figure 2f and Figure S3 (Supporting Information). MAPbI₃ has a measured VBE of 5.42 eV and *W*_F of 4.90 eV, compared with NMA-MAPbI₃ having a VBE of 5.13 eV and *W*_F of 4.56 eV. It has been reported that the outermost layer of MAPbI₃ can significantly shift the frontier electronic levels, where MAI terminated films have been shown to exhibit ≈1 eV higher VBE than PbI ter-

minated films, ascribed to their different dipole directions.^[37] Here, the significant (0.3–0.4 eV) shift in both the VBE and work function of NMA-MAPbI₃ compared to MAPbI₃ indicates the presence of a thin interfacial dipole layer at the surface, further supporting the results of XPS and LEIS indicating NMA being located at the grain surface.

2.3. Morphological Analysis

There is a growing body of literature suggesting that perovskite active layers composed of large, continuous grains are beneficial for device performance.^[38–40] However, the correlation between morphology and device performance when bulky organic cations are incorporated into active layers remains inconclusive.

To investigate how film morphology impacts device performance in PSCs employing NMA, we investigated two processing routes, namely thermal annealing (TA) and solvent-assisted thermal annealing (SA). In the former films are heated after spin-coating and in the latter case the films annealed in a solvent rich atmosphere. The SA method has been reported to promote the formation of single grains orientated along the charge-transport direction (i.e., perpendicular to the substrate).^[40,41] Figure 3a,b shows typical cross-section and top-view SEM images of the NMA-MAPbI₃ film prepared by TA. A polycrystalline structure can be seen both across and through the films. By contrast, films prepared using SA, Figure 3c,d, shows the anticipated large single grain structures and also a subtle enlargement of grain size as observed from the surface. The corresponding *J*–*V* characteristics of NMA-MAPbI₃ devices prepared using TA and SA are presented in Figure 3e,f (measured device parameters given in Table S2, Supporting Information). Those prepared using TA had measured PCEs of 14.3% and 13% in reverse and forward scans with significant hysteresis observed. By contrast, the PCEs of SA cells were 20.1% and

19.6% in reverse and forward scans and showed reduced hysteresis. The PCE of NMA free MAPbI₃ also increased with the SA method (17.3% to 18.5% in reverse scan and 17.0% to 18.3% in forward scan), Table S2 of the Supporting Information. Thus it is clear that the SA treatment enhances efficiency and reduces hysteresis compared with the TA treatment and is an essential step to producing more efficient devices that can be further enhanced by the incorporation of NMA.

These results are consistent with those of Tsai et al., who reported that high-quality perovskite films with large grains out-of-plane, i.e., perpendicular to the substrate, are necessary to facilitate charge transport in 2D/3D PSCs; otherwise the bulky cation may function as charge transfer barrier inhibiting charge mobility.^[20] However, Wang et al. and Wolff et al. have confirmed that tunneling may occur through ultrathin polymer dielectrics located at the perovskite electron transport layer (ETL) interface, without sacrificing device performance.^[42,43] Our results demonstrate the general importance of morphological control in PSCs and whilst NMA may be beneficial to device performance, the importance of morphological control cannot be overlooked, here we identify a synergy between the bulky additive and the processing methodology.

2.4. Photoluminescence Studies of Charge Trapping and Transfer Dynamics

We now consider photoluminescence (PL) studies to investigate the impact of the NMA on charge trapping and transfer dynamics, and thus on device performance. As illustrated in **Figure 4a**, PL studies can probe charge trapping in deep, non-radiative trap states, as well as charge transfer to and surface recombination at the device HTL and ETL layers—all of which can result in quenching of PL intensity.^[44–46] The steady state PL of MAPbI₃ films prepared with different concentrations of NMA is shown in **Figure 4b**. It is apparent that the PL intensity increases as more NMA is added during processing—indicating NMA can suppress nonradiative recombination, consistent with NMA passivating trap states at grain surface, as discussed further below. The same trend is also observed in films sandwiched between charge transport layers, **Figure 4c**, where again an increase in the quantity of NMA added results in an enhancement of PL. By comparing the data in **Figure 4b,c**, PL quenching efficiency (PLQE) resulting from the charge transport layers (CTLs) was determined, **Figure 4d**. The PLQE was calculated from $PLQE \approx (I_0 - I)/I_0$, where I_0 is the peak intensity of PL intensity of the perovskite film alone, and I is the peak intensity of PL emission of perovskite with transport layers.^[44] It is apparent that here PLQE is invariant (within error) for NMA concentrations up to 0.25%, but reduces for higher concentrations, despite the inhibition of charge trapping. This loss of PLQE at high NMA concentrations is indicative of impeded charge transfer to the CTLs, consistent with the loss of J_{sc} observed in device J/V data.^[44,47,48]

The observed trends of steady state PL intensity with NMA concentration and charge transport layer addition were further investigated using time-correlated single photon counting (TCSPC), **Figure 4e,f** on bare films and also films interfaced with CTLs (see **Figure S5** of the Supporting Information for

comparisons on longer timescales). The data for bare films (**Figure 4e**) were fitted to biexponential decays (see Table S3 of the Supporting Information for fit parameters), where first fast decay phase is assigned to trapping into nonradiative deep traps, while the second decay phase is assigned to the bimolecular recombination of long-lived free charges.^[49] Increasing NMA concentration resulted in a significant reduction of the fast decay phase with τ_1 , the first decay phase lifetime, increasing from 1 to 13 ns and the relative amplitude of the slower decay phase increasing—indicative of slower and less charge trapping, respectively, which is consistent with NMA passivating nonradiative trap states.

Transient PL data in the presence of CTLs are shown in **Figure 4f**. It is apparent that the addition of the CTLs results in a strong quenching of long-lived emission for NMA concentrations up to 0.25% (relative to data without CTLs, **Figure 4e**; **Figure S4**, Supporting Information), but that this quenching is less pronounced for higher NMA concentrations (0.5 and 1 vol%). This is indicative of high NMA concentrations impeding efficient transfer of free carriers to the CTLs, consistent with our discussion of the steady state PL data above. To quantify this effect, these data with CTLs were fit to triple exponential decays (see Table S4 of the Supporting Information for fit parameters, two exponential analyses gave poor fits), with the first and second decay phases assigned primarily to trap filling, and charge transfer, respectively, and the third decay phase to long-lived carriers unable to transfer to the CTLs. To quantify these long-lived carriers, the third decay life time (τ_3) was fixed as 300 ns, with its amplitude (A_3) representing the proportion of noncollected charges. This amplitude is plotted in **Figure 4g** versus NMA concentration, overlaid with the corresponding J_{sc} values. It is apparent this amplitude increases for NMA concentrations >0.25%, correlated with a loss of J_{sc} , consistent with this loss of J_{sc} for high NMA concentrations resulting from impeded charge transfer to the CTLs. This explains why bulky organic cation additives enhance PSC performance only at low additive concentrations, as observed here and elsewhere.^[6,26–29] Higher concentrations of bulky organic spacer cations impedes charge transfer to the CTL layers and thus confines charge in the active layer, lowering J_{sc} . We note this confinement may be beneficial for light-emitting diode (LED) applications, explaining why enhanced LED performance is observed at higher bulky cation concentrations, correlated with the formation of quasi 2D RP material morphologies.^[32,50,51]

Passivation of nonradiative trap states by NMA, as indicated by both the steady state and transient PL data, is also supported by ambient pressure photoemission spectroscopy data. Photoemission signal observed below the extrapolated VBE can be attributed to sub-bandgap electronic trap states.^[52] Integrating the photoemission signal for energies below the VBE (shaded areas in **Figure 2f**) indicate that this trap state density is some 70% larger for MAPbI₃ compared to NMA-MAPbI₃ (0.25% NMA), providing further evidence that NMA is efficient at trap state passivation. Increased trap state densities have been correlated with lower device V_{oc} , as trapped charge functions as recombination centers reducing quasi-Fermi level splitting in the perovskite layer.^[53] Supporting this correlation, **Figure 4h** plots τ_1 (assigned primarily to charge trapping) determined

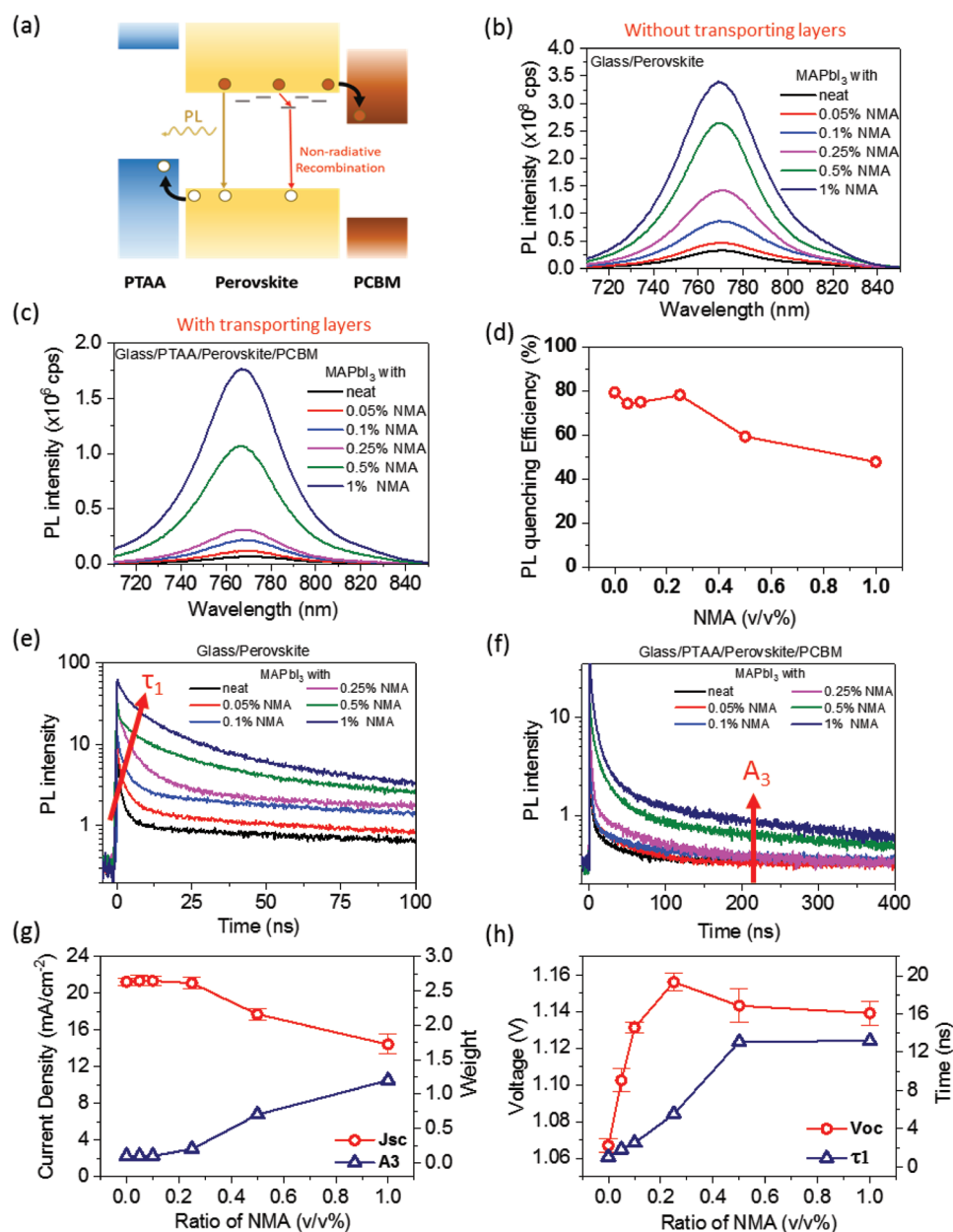


Figure 4. a) Schematic diagram of recombination and charge transfer pathways in PTAA/perovskite/PCBM films. b) Steady-state photoluminescence (PL) spectra of the MAPbI₃ with NMA from 0.05 to 1 vol% and c) the corresponding PL spectra of films sandwiched by PTAA and PCBM transport layers. d) The corresponding photoluminescence quenching efficiencies (PLQE) determined from the data in (b) and (c). e) Time-correlated single photon counting (TCSPC) decays of MAPbI₃ films with NMA from 0.05 to 1 vol% without transport layers and f) the corresponding TCSPC data for films sandwiched by the transport layers. g) Plots versus NMA % of device J_{sc} (red) and the amplitude of the slowest decay phase (A_3 , blue) obtained from fits to the TCSPC data in (f) for PTAA/perovskite/PCBM films. h) Plots versus NMA % of device V_{oc} (red) and τ_1 (blue) determined from fits of the TCSPC decays in (e) for perovskite films.

from the perovskite film TCSPC data (Figure 4e) and device V_{oc} versus NMA concentration. It is apparent that suppressed charge trapping (observed as a longer τ_1) correlates with a higher device V_{oc} (the small loss of V_{oc} at high NMA concentrations most probably is associated with a loss of charge transfer efficiency). As we discuss above, NMA is primarily located at grain surface. There is extensive evidence for trap location at grain surface in MAPbI₃.^[54] We thus conclude that NMA is able

to passivate grain surface trap states, resulting in the observed increase in device voltage with NMA concentration.

To summarize this collection of observations, we conclude that at low concentrations NMA primarily passivates trap states at grain surface, resulting in higher device V_{oc} and PCE. However, higher NMA concentrations results in increasing inhibition of charge transfer to the transport layers, causing a loss of J_{sc} due to increased bimolecular recombination losses.

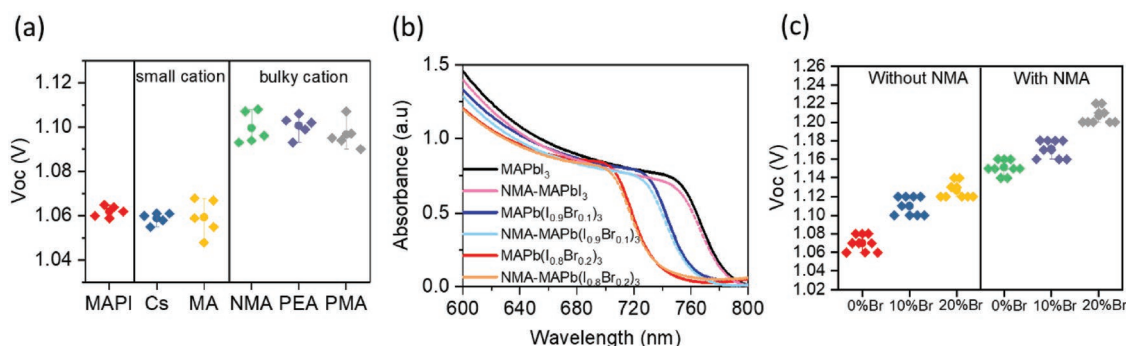


Figure 5. a) Measured V_{oc} of devices fabricated from MAPbI_3 and cation-doped MAPbI_3 . b) UV-vis spectra of films and c) the V_{oc} of devices fabricated from $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ ($x = 0, 0.1, 0.2$) with/without 0.25 vol% NMA.

2.5. Extension to Alternative Bulky Cation Additives and to Mixed Halide Perovskites

To validate our hypothesis and demonstrate the wider applicability of our results we turn to study to alternative bulky cation additives and to mixed halide perovskites, focusing on V_{oc} enhancement by additive addition. Figure 5a shows the V_{oc} values obtained following the addition of 0.05 vol% each of NMA, phenylethylammonium (PEA), and phenylmethylammonium (PMA), as well as the small cations Cs and MA (details in the Supporting Information). The corresponding $J-V$ data are shown in Figure S6 and Table S5 of the Supporting Information. It is apparent that adding the bulky cations, PEA and PMA, results in ≈ 40 mV enhancement of V_{oc} , similar to that observed for 0.05 vol% NMA, and similar increases in PCE. By contrast, addition of either Cs and MA (i.e., MA over stoichiometry) did not result in significant V_{oc} enhancement. It is evident that the trap state passivation resulting in enhanced performance is strongly dependent on cation size, most likely associated with the confinement of large cations at grain surface and boundaries, passivating trap states at these surface/boundaries.^[50]

We note that the effect of excess MAI on device performance was found to be dependent on HTL employed. Using PEDOT:PSS as HTL, excess MAI results in enhanced device V_{oc} , as we have previously reported,^[53] whilst with PTAA/PFN excess MAI did not enhance V_{oc} . The origin of this dependence is unclear but may be associated with the differing impact of the HTL on the perovskite film morphology and crystallinity.

Mixed iodide/bromide perovskites are attracting extensive interest for tandem solar cells, due to their wider bandgap relative to iodide-based perovskites. However, these wider bandgap perovskite devices typically suffer from increased V_{oc} losses, often attributed to increased nonradiative recombination losses.^[28,55–57] We therefore investigated whether NMA addition could also suppress nonradiative recombination losses, and thus increase V_{oc} , in mixed halide perovskite devices. Films and devices were fabricated with $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ absorber layers with and without 0.25 vol% NMA, at $x = 0, 0.1$, and 0.2 . The absorption spectra of the resultant films are shown in Figure 5b. The absorption onset of these films blue shifts with increasing Br content, from 1.59 to 1.63 and 1.68 eV for $x = 0, 0.1$, and 0.2 , respectively, independent of NMA addition. It is apparent from Figure 5c that NMA addition increases device

V_{oc} (and device PCE, Table S6, Supporting Information) for all three iodide/bromide ratios, indicative of passivation of trap states. The champion $J-V$ performance of $\text{MAPb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ and $\text{MAPb}(\text{I}_{0.8}\text{Br}_{0.2})_3$ devices with and without NMA are shown in Figure S7 and Table S6 of the Supporting Information. Average $J-V$ parameters of $\text{MAPb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ and $\text{MAPb}(\text{I}_{0.8}\text{Br}_{0.2})_3$ are listed in Table S7 of the Supporting Information, with the $\text{MAPb}(\text{I}_{0.8}\text{Br}_{0.2})_3$ device with NMA yielding devices with a V_{oc} of $1.21 (\pm 0.01)$ V. It is therefore apparent that the use of NMA to suppress nonradiative recombination losses and enhance V_{oc} is also applicable to mixed halide, wider bandgap perovskite devices.

Finally, we provide a brief comparison of our work to existing studies employing bulky cation additive-perovskite active layers. In the case of butylammonium (BA), phenylalkylamine (PEA), and choline salt enhancements in V_{oc} (50–100 mV) in MAPbI_3 or mixed cation/halide perovskites have been reported.^[6,7,26,28] Such enhancements have been observed in both n-i-p (conventional)^[28] and p-i-n (inverted) device architectures,^[6,7,26] consistent with these enhancements results from bulk grain surface/boundary trap passivation, independent of device architecture. Wang et al. demonstrated that BA can drive the formation of 2D/3D grain boundaries orientated parallel to the charge transport direction, which may be beneficial to charge transport.

We determine that at low concentrations, the bulky NMA cation is mostly primarily at grain surfaces and thus does not impede charge transport at an optimized NMA concentration (0.25 vol%). Our observation agrees with Zheng et al. and Wang et al., who deposited an additional bulky cation layer on perovskite films, i.e., localized at the surface, demonstrating no reduction in photocurrent but rather a V_{oc} enhancement.^[6,7] Here we have demonstrated that NMA, at an optimized concentration of 0.25 vol%, can be used to achieve one of the highest reported V_{oc} values without reducing light absorption, and at higher concentrations the additive functions as a charge transfer barrier, evidenced by the reduction in measured current density.

3. Conclusions

The use of bulky organic amine additives in the processing of organometal halide perovskites has been shown to be a promising method to enhance photovoltaic device performance. However, the origins of this performance enhancement, in

terms of charge carrier dynamics and morphological control are often still unclear. Here we have demonstrated how the bulky cation, NMA can successfully passivate the surface of MAPbI₃. Inverted p–i–n planar architecture devices using an NMA-MAPbI₃ absorber layer yield power conversion efficiency of up to 20.1%. We show that NMA is located on grain surfaces rather than mixed into the MAPbI₃ bulk phase, promoting, at low concentrations with solvent assisted thermal annealing, monolithic crystal growth perpendicular to the substrate, favorable for charge transport. Steady state and transient PL data, and photoemission spectra are all indicative of NMA passivating surface traps, resulting in a high open-circuit voltage (V_{oc}) of 1.16 V at an optimum processing concentration of NMA of 0.25 vol%. However, higher concentrations of NMA (≥ 0.5 vol%) resulted in inhibition of charge transfer to charge transporting layers, resulting in a reduced J_{sc} and PCE. Analogous V_{oc} enhancements are also observed by replacing NMA with other bulky cations, including as PEA or PMA, but are not observed for smaller cation replacement, showing cation size is crucial to increasing device V_{oc} . Finally, we also show that this concept may also be applied to wide bandgap MAPb(I_{1-x}Br_x)₃ perovskites, where V_{oc} is enhanced from 1.14 to 1.22 V, of particular interest for application in tandem perovskite solar cells.

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.

Keywords

bulky cation additive, crystal growth, grain structure, perovskite solar cells, surface analysis

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