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Multiple Stabilization Effects of Benzylhydrazine on Scalable Perovskite Precursor Inks for Improved Perovskite Solar Cell Production

Sean B. Reinecke, Vishal Yeddu, Dongyang Zhang, Chris Barr, Jeremy E. Wulff, Sergey V. Dayneko, Mohammad Reza Kokaba, and Makhsud I. Saidaminov*

Abstract: Perovskite precursor inks suffer various forms of degradation, such as iodide anion oxidation and organic cation breakdown, hindering reliable perovskite solar cell manufacturing. Here we report that benzylhydrazine hydrochloride (BHC) not only retards the buildup of iodine as previously reported but also prevents the breakdown of organic cations. Through investigating BHC and iodine chemical reactions, we elucidate protonation and dehydration mechanisms, converting BHC to harmless volatile compounds, thus preserving perovskite film crystallization and solar cell performance. This inhibition effect lasts nearly a month with minimal BHC, contrasting control inks without BHC where organic cations fully react in less than a week. This enhanced understanding, from additive stabilization to end products, promises improved perovskite solar cell production reliability.

Introduction

The principal advantages of perovskite solar cells (PSCs) are the accessibility of their constituent materials and the ease of depositing the perovskite layer using wet chemistry techniques.^[1–7] The perovskite precursor solution or ink, made by dissolving precursor salts in solvents, is deposited

by a variety of readily available methods and annealed to form a perovskite thin film. However, recent studies showed that the perovskite ink undergoes multiple degradation pathways, as depicted in Scheme 1, presenting a significant challenge for PSCs to become a competitive commercial option.^[8]

A perovskite ink that is suitable for scalable coating of films contains additional components that further exacerbate the instability of the ink. For instance, N-methyl-2-pyrrolidone (NMP) is typically used as a cosolvent alongside 2-methoxy-ethanol (2ME) in scalable perovskite inks to widen the processing window, and to slow down crystallization, thus resulting in a denser, smoother film with larger grains and more efficient PSCs.^[13–16] The NMP operates as a Lewis base to form adducts and complexes with perovskite precursors enabling homogeneous nucleation and inducing the formation of optically active perovskite phase of formamidinium lead iodide (α -FAPbI₃)^[17–19] However, NMP dramatically accelerates the reactions between the organic cations (reactions in Scheme 1C,D).^[20] This co-solvent, despite its issues, is needed for scalable coating of perovskite films. Methylammonium chloride (MACl) is another additive widely used in perovskite inks to lower the energy barrier for the transition to α -FAPbI₃ and improve crystal density.^[21–23] However, the MA⁺ cation deprotonates to MA which then reacts with the FA⁺ in the solution to form methyl formamidinium (MFA⁺)^[24] (Scheme 1A,C), which not only removes FA from the solution but also competitively forms optically inactive MFAPbI₃.^[20,25]

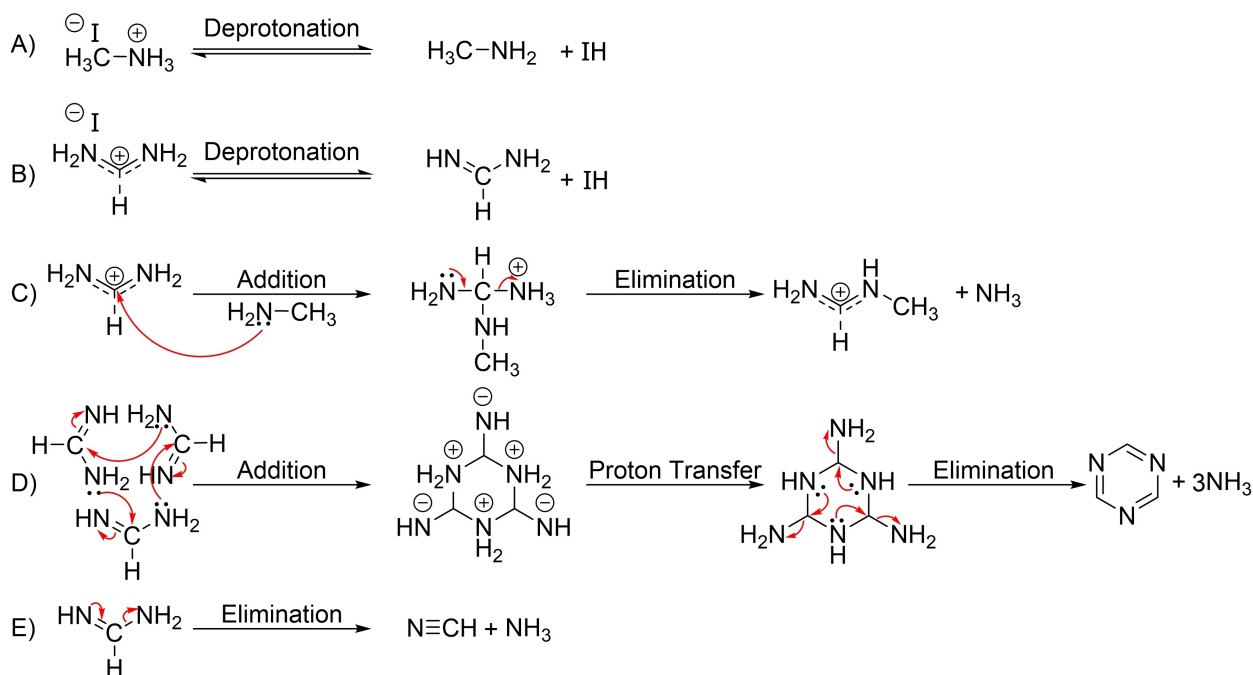
Multiple stabilizers have been reported to prevent some degradation pathways in perovskite inks. Sulfur, for instance, was found to prevent the deprotonation that initiates the FA⁺ and MA⁺ to MFA⁺ reaction, as well as the FA⁺ self-reaction to form sym-triazine and cyanide (Scheme 1A–E).^[20,26,27] Unfortunately, sulfur is not a suitable stabilizer for the perovskite ink optimized for scalable fabrication of films due to its insolubility in the primary solvent, 2ME. This solvent cannot be swapped out as it can form a uniform and conformal precursor film due to its rapid evaporation.^[28,29] Reactions in Scheme 1C–E require the deprotonated form of either MA⁺ (MA) or FA⁺ (FA) to proceed.^[12,30–32] thus, protonation of the solution is another viable strategy to stop all three forms of FA loss.^[33,34] The addition of organic acids has been found to be a viable method of minimizing this^[33,35,36] as has the addition of easily deprotonated alkanes.^[37] Hydroiodic acid is another stabilizer studied

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Scheme 1. Degradation pathways in perovskite inks: A) Deprotonation of MA^+ ;^[9] B) Deprotonation of FA^+ ; C) Addition of MA to FA^+ to form MFA^+ ;^[10] D) FA condensation reaction to sym-triazine;^[11,12] E) FA elimination reaction to form hydrocyanic acid.^[12]

before to protonate the ink, but it is not suitable due to it being a strong acid and its water content.^[11]

An ideal stabilizer of perovskite ink should prevent not some, but all known degradation pathways shown in Scheme 1. In other words, an ideal stabilizer should be (1) a weak Brønsted-Lowry acid to protonate the solution without solvent reactions,^[38] eventually preventing loss of organic cations; (2) a mild reducing agent to prevent loss of iodide; (3) readily soluble in polar solvents; (4) a solid, ideally, to not alter the perovskite ink solvent matrix. These same criteria are often used in biochemistry research, which is typically done in polar solvents, to simulate *in vivo* conditions. Benzylhydrazine, for instance, is often used in biochemistry to reduce enzymes in an acidic medium;^[39] benzylhydrazine hydrochloride (BHC) was indeed recently reported to be a promising perovskite precursor stabilizer to act as a sacrificial reductant in solution and in films to prevent I_2 buildup.^[36,40] Another reason that benzylhydrazine is used in biochemistry is to prevent oxidative deamination; a process that bears certain similarities to the mechanism of FA breakdown shown in Scheme 1.^[39] However, whether BHC can prevent FA breakdown pathways in perovskite inks is yet to be studied; what also remains to be known is what BHC converts to in perovskite inks, and how these products would affect the quality of perovskite films and the performance of ultimate solar cells.

Here we uncover multiple additional stabilization effects of BHC in perovskite inks. We show that it protonates the solution as a weak organic acid; it also reacts with the trace water in the solvent to reduce water-assisted deprotonation. And when it fully reacts, BHC's ultimate form is chemically

benign and does not worsen perovskite crystallization or its device performance.

Results and Discussion

To study the effect of BHC on perovskite ink degradation pathways, we prepared a 1 M perovskite precursor solution by dissolving 1 M FAI and 1 M PbI_2 in 2-methoxyethanol and N-methyl-2-pyrrolidone at a 19/1 volume ratio. MAI (0.3 M) was added to this solution to aid in crystallization^[25,41] along with $0.25 \mu\text{M}$ L- α -phosphatidylcholine to increase surface tension while blade coating. This solution is referred to as control ink. Such perovskite ink is widely used in upscaling PSCs.^[42] We then added 1.2 mM of BHC to the control ink to create the BHC ink. All precursor solutions were stored in glass vials with polytetrafluoroethylene-lined plastic caps within a laboratory fumehood and were only opened as necessary for analysis.

We used ^1H nuclear magnetic resonance (NMR) spectroscopy to track the degradation pathways of organic components of the ink. The precise tracking of FA breakdown is difficult due to it forming several products (Scheme 1C–E) and the overlap of their ^1H NMR peaks (Figure 1A): the peak corresponding to sym-triazine (Scheme 1D) occurs at 9.3 ppm which overlaps with the central amine proton of MFA (Scheme 1C), making it difficult to directly quantify them; the hydrocyanic acid (Scheme 1E) has a very low boiling point (25.6°C) and a high volatility meaning it is easily lost to vaporization. Regardless of the chemical pathway, for each mole of FA lost one mole of ammonia is produced: we hence instead

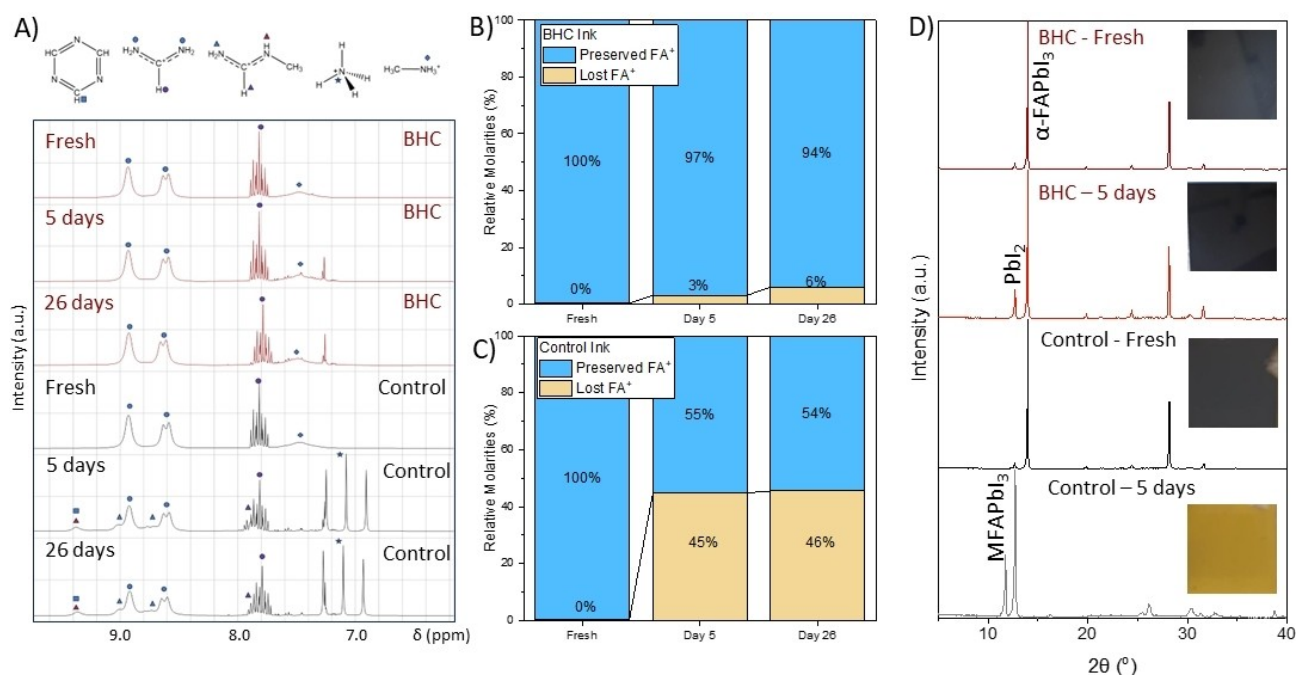


Figure 1. Characterization of perovskite ink with and without BHC: A) ^1H NMR spectra of perovskite solutions over time along with peak assignments for FA^+ and its degradation products. Red-colored spectra represent BHC-doped ink, and the black-colored spectra represent the control ink. B–C) Integration values of ^1H NMR peaks originating from FA^+ in control and BHC-inks. D) XRD profiles of films made with fresh ink and 5-day-old ink. Insets are the images of corresponding films. Note the overlap of the fresh and day 5 ink XRD results for the BHC-doped ink.

focused on tracking ammonia which is equimolar to the lost FA^+ . The ammonia was protonated to ammonium via the addition of a small amount of hydroiodic acid (1 μL into 600 μL ink aliquots) which then appeared as a distinct 1:1:1 triplet at 7.08 ppm in the ^1H NMR spectra.^[43]

Figures 1B–C show relative molarities of remaining and lost FA^+ (equimolar to NH_4^+) in the inks with and without BHC after aging. Nearly half of FA^+ was lost in the control ink within 5 days of aging, while we observed only 3% FA^+ loss in the presence of BHC during that same time. NMR Figures also show that the loss of FA^+ slows massively once the MA^+ has been completely used up as the reaction of MA^0 with FA^+ to form MFA^+ (Scheme 1C) is the dominant FA^+ degradation pathway:^[20,24] therefore, the control ink has a much-retarded FA^+ loss rate following the complete loss of MA^+ after 5 days of aging.

We have also performed visual and structural inspection of the films prepared from fresh and aged inks. Both BHC doped and control inks, when fresh, turned black upon annealing (Figure 1D), indicating formation of the α -phase perovskite. This was further confirmed by the X-ray diffraction (XRD) results.

After five days of aging of inks, the BHC-doped ink formed a black film that was visually and structurally identical to the film made by fresh ink (Figure 1D). However, the film created by the 5-day aged control ink was yellow, which would normally indicate δ -phase perovskite (Figure 1D); additionally, there is a strong diffraction peak at $2\theta = 11.7^\circ$, very close to the expected δ -phase (2H) peak at 11.8° . But the yellow film failed to form a black α -phase

perovskite when heated to 150°C indicating that it is instead a non-perovskite phase formed from organic degradation products, principally MFA^+ (the δ -phase would convert to black α -phase at 150°C).^[20]

We then attempted to restore the aged control ink by adding the BHC: this changed the colour of the ink from orange back to yellow, indicating a reduction of the iodine species but this ink still failed to produce a black α -phase of perovskite film. Further BHC addition up to 0.1 M ($\sim 100\times$ more than in the BHC-doped ink) also failed to make the ink viable (Figure S1) and resulted in yellowish films. Thus, the failure of the ink cannot be attributed to the reversible iodide-to-iodine reaction as the addition of excess reductant could not restore the ink. We hence conclude that BHC has additional benefits to ink stability besides reducing iodine as we will reveal below.

Full Lifetime Analysis of Benzyhydrazine

To understand the full impact of BHC on the ink, a detailed NMR study (^1H , ^1H - ^{13}C Heteronuclear Single Quantum Coherence (HSQC), and ^1H - ^{13}C , and ^1H - ^{15}N Heteronuclear Multiple Bond Correlation (HMBC)) was performed on the reaction of BHC and iodine in isolation. The ^1H , ^1H - ^{13}C HSQC and ^1H - ^{15}N HMBC spectra were used to identify functional groups and bridging methylene carbon/hydrogen pairs. The ^1H - ^{13}C HMBC spectrum was used to verify that these structures were bonded to the phenyl ring.

A solution of BHC and a small excess of iodine was prepared in dimethyl sulfoxide- d_6 . This solution was left to react for 6 hours before the NMR studies. An additional ^1H NMR scan was performed at the end of the 16-hour-long sequence (Figure 2A).

The ($^1\text{H},^{13}\text{C}$) (10.1 δ , 193.4 δ) crosspeak shown in Figure 2B represents a typical aldehyde signature. From the increasing value of the ^1H signal peak at $\delta=10.1$ over 16 hours seen in Figure 2A, the aldehyde was identified as the final product. The presence of this aldehyde was confirmed by HSQC analysis of an authentic benzaldehyde standard (Figure S2A). This finding agrees with previous work in the biochemistry and organic chemistry fields that have shown that benzylic diazonium converts to benzyl alcohol and can then be oxidized to benzaldehyde under aqueous conditions.^[39,44–46]

The extremely downfield ^1H - ^{15}N HMBC crosspeak shown in Figure 2C was identified as corresponding to a diimide or azo compound. Four bridging Ph- CH_2 -X HSQC signals were identified between 4.5 and 5.5 ppm (Figure 2D). The relevant bridging groups were assigned as follows: (^1H : δ 4.48, ^{13}C : δ 63.4) benzyl alcohol; (^1H : δ 4.64, ^{13}C : 45.96) BHC; (^1H : δ 4.74, ^{13}C : 46.63) diazonium; (^1H : δ 5.43, ^{13}C : 57.42) a diimide. The benzyl diazonium was likely stabilized by the use of DMSO as a solvent, enabling its detection.^[46] The presence of alcohol was further confirmed by comparison with an authentic standard (Figure S2B). The above

assignments were made by comparing experimental and literature values. Based on these intermediates, and the final product, we propose reaction Scheme 2 to represent the full lifetime cycle of BHC in the presence of iodine.

The reaction scheme 2 reveals the source of the improved chemical stability of target perovskite ink, with each mole of BHC releasing seven moles of free protons and absorbing one mole of water. Protonation of the perovskite precursor solution can prevent Scheme 1A–B reactions, which in turn prevents Scheme 1C–E reactions. Additionally, small quantities of water, which typically exist in the original solvent mixture, are known to greatly accelerate the loss of organic cations by facilitating their deprotonation.^[20,34] The conversion of the diazonium ion to benzyl alcohol consumes water (Scheme 2B). This removal of water by BHC is further evidenced by the lack of a distinct 3.3 δ ^1H NMR peak (Figure S3) typical of the unavoidable water contamination of DMSO d_6 .^[47] This same reaction sequence also appears to apply to the free base of the BHC salt (Figure S4).

The Impact of BHC on the Performance of Perovskite Solar Cells

To verify that the increased ink stability was not at a cost of efficiency of ultimate devices, we fabricated perovskite solar cells in an indium tin oxide (ITO)/ SnO_2 /perovskite/spiro-

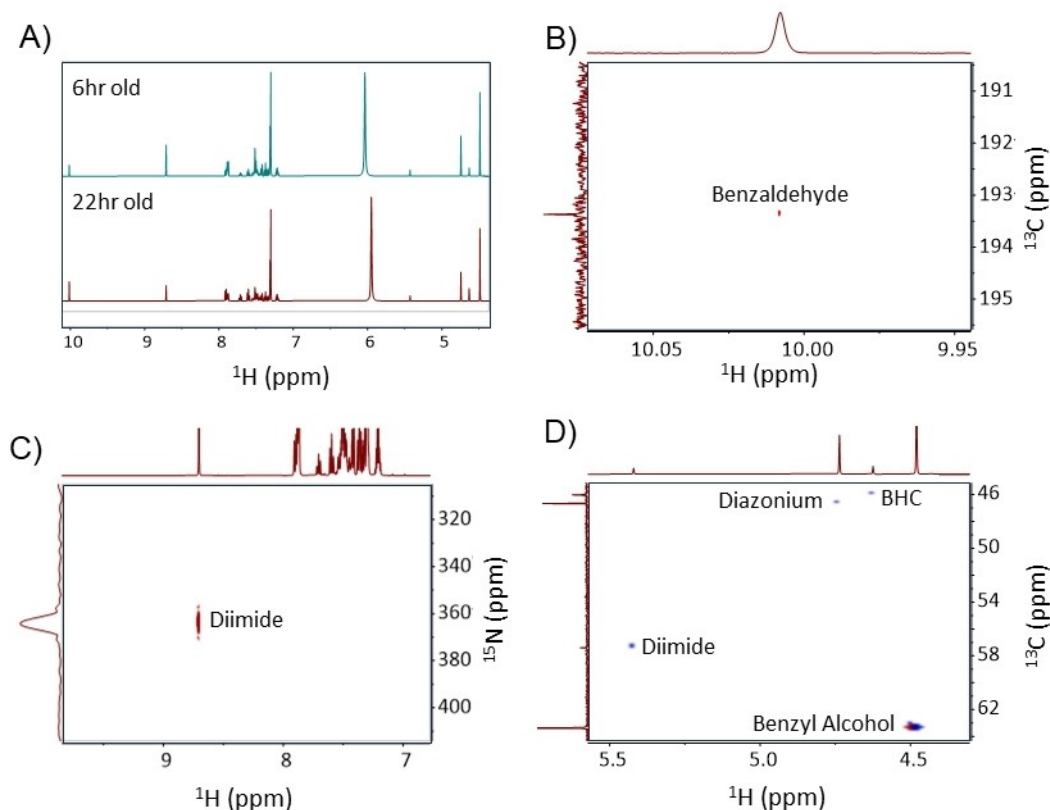
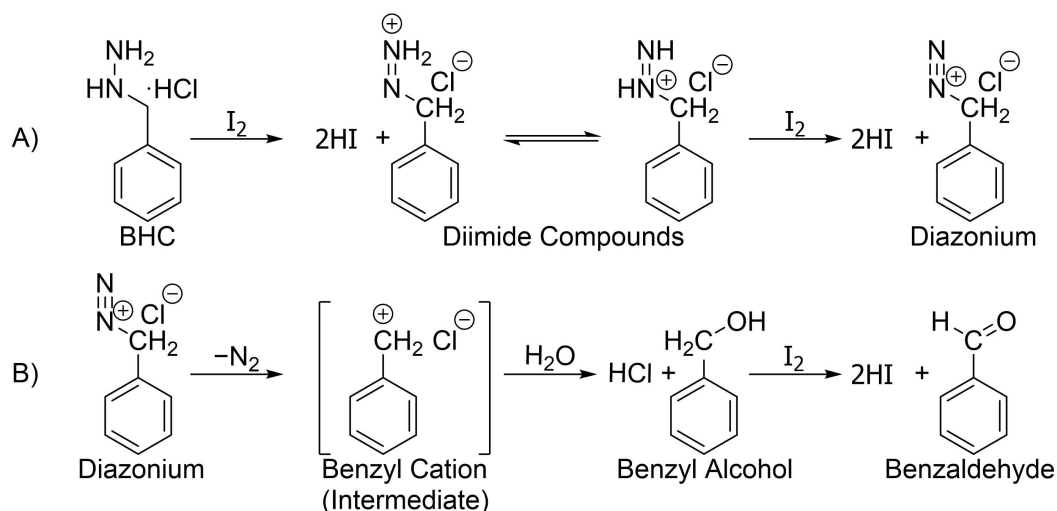


Figure 2. Full lifetime analysis of benzyldiazine: A) ^1H NMR spectrum of BHC and its oxidation products after being allowed to react for 6 and 22 hrs at the beginning and end of the 16-hour NMR ageing experiment. B) ^1H - ^{13}C HSQC spectrum, focused on the aldehyde section. C) ^1H - ^{15}N HMBC spectrum, and D) ^1H - ^{13}C HSQC spectrum, focused on bridging $-\text{CH}_2-$ section.



Scheme 2. BHC conversion pathway in a solvent that resembles perovskite ink: A) Reaction of BHC and iodine to form a diazonium salt. B) Substitution of nitrogen leaving group with hydroxyl group and subsequent oxidation to aldehyde.

OMeTAD/gold (Au) structure following our earlier work.^[50] SnO₂, perovskite and spiro-OMeTAD were blade-coated in ambient air, while the gold electrode was prepared by thermal evaporation. The BHC devices performed better both on average and in terms of the champion device achieving an efficiency of 19.6% (Figure 3A). This device had a fill factor (FF) of 76.9%, a short-circuit current (J_{sc}) of

25.1 mA cm⁻² and an open-circuit voltage (V_{oc}) of 1.02 V (Figure 3B). The champion device from control ink had a PCE of 19.1%, a FF of 78.6%, a J_{sc} of 24.9 mA cm⁻² and a V_{oc} 0.98 V. Figure S5 provides further device statistics.

To evaluate the quality of perovskite films, we studied their morphology with a scanning electron microscope (SEM). Figures 3C and D show compact films without

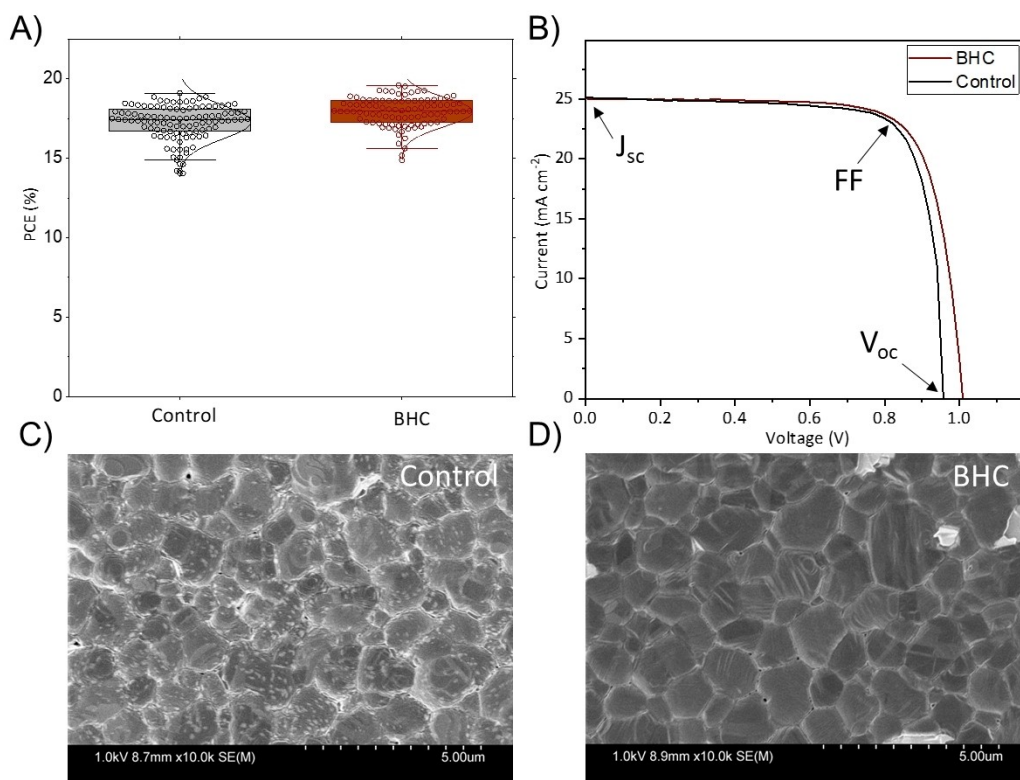


Figure 3. Characterization of films and devices. A) Efficiency of 104 control and 95 BHC-doped perovskite solar cells fabricated by blade-coating. The boxes indicate the 25th and 75th percentiles. The whiskers indicate the 5th and 95th percentiles. The mean is represented by the line dividing the boxes. B) $J-V$ curve of champion pixel from both devices. C–D) Surface SEM images of films made from fresh control and BHC-doped inks.

pinholes. Bright particulates seen in Figure 3C are due to lead iodide (as organic cations are lost in the control ink, stoichiometric precursor ratio is lost, and free lead iodide is found in the resultant film). The lack of stoichiometric ratio management in the control ink might explain the lower reproducibility of the resultant devices.^[48,49]

We also tested the stability of blade-coated perovskite films made from control and BHC inks under exposure to light and heat (Figure S6). Unencapsulated FA-based perovskites are known to undergo photo-thermal degradation under these conditions.^[12,40] Consistent with our findings above, we observed that BHC also slows FA loss in the films, likely because it acts as a sacrificial antioxidant.

Conclusions

The high instability of perovskite precursor inks has proven a significant roadblock to their commercial viability. Borrowing knowledge from the field of biochemistry in preventing amine degradation, we have shown that BHC has additional positive effects on the stability of perovskite ink besides reduction of iodine back to iodide. The cause of this is elucidated by detailed NMR investigation of the products and intermediates, and the reactions that occur to form these compounds. BHC protonates the precursor solution and thus shifts the equilibrium of the deprotonation reaction of the organic cations back towards the reactants. This deprotonation is the first stage of the various chemical degradation reactions in perovskite ink. BHC also aids stability by absorbing water, due to the electrophilic nature of the resulting diazonium cation. We reported nearly 20% efficiency for all-scalable n-i-p FAPbI₃ perovskite solar cells using this ink indicating no loss of performance in the presence of BHC.

Author contributions

S.R. performed and processed 1D NMR, and XRD. S.R. created reaction Schemes. D.Z. prepared devices, performed SEM and solar cell characterization. S.D., M.K., C.B. V.Y. participated in design of the study. C.B. performed 2D NMR which was processed and interpreted by S.R. D.Z. and J.W. helped with the review & editing of the manuscript. S.R. and M.I.S. wrote the manuscript. M.I.S. directed the whole project.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: reduction · semiconductors · azo compounds · perovskite solar cells · perovskite inks

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