Increased resistance to photooxidation in Dion-Jacobson lead halide perovskites – implication for perovskite device stability

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SUMMARY: 2D metal halide perovskites have enabled significant stability improvements in perovskite devices, particularly in resistance to moisture. However, some 2D perovskites are even more susceptible to photooxidation compared to 3D perovskites. This is particularly true for more commonly investigated Ruddlesden-Popper (RP) perovskites that exhibit increased susceptibility to photoinduced degradation compared to Dion-Jacobson (DJ) perovskites. Comparisons between different RP and DJ perovskites reveal that this phenomenon cannot be explained by commonly proposed differences in superoxide ion generation, interlayer distance and lattice structural rigidity differences. Instead, the resistance to photooxidation of DJ perovskites can be attributed to decreased likelihood of double deprotonation events (compared to single deprotonation events in RP perovskites) required for the loss of organic cations and the perovskite decomposition. Consequently, DJ perovskites are less susceptible to oxidative degradation (both photo- and electrochemically induced), which leads to improved operational stability of solar cells based on these materials.

Keywords: lead halide perovskite photostability, 2D perovskite, Ruddlesden-Popper perovskites, Dion-Jacobson perovskites, perovskite solar cell stability

INTRODUCTION

2D metal halide perovskites, in the form of 2D/3D or quasi-2D active layers, have been proposed to replace more commonly used 3D metal halide perovskites in photovoltaic and (opto)electronic devices with improved stability.[1-3] 3D perovskites with the formula ABX_3, where A is Cs^+ or a small organic cation (methylammonium (MA) or formamidinium (FA)), B is divalent metal (most commonly Pb^{2+}), and X is halide anion, are known to be unstable upon exposure to ambient (oxygen, moisture), heat, and illumination.[2] While 2D perovskites, containing bulky spacer cations separating layers of corner-sharing $[BX_6]^{4-}$ octahedra, typically exhibit improved stability compared to 3D perovskites, further improvements in stability and understanding of their degradation mechanisms are still required.[1,2]

The stability improvements in solar cells (SCs) and light-emitting diodes (LEDs) with 2D perovskites are commonly attributed to increased hydrophobicity and reduced ion migration.[1-3] While stability of 3D perovskites, including photooxidation, has been extensively studied,[4-12] investigations of the stability of 2D perovskites,[13-21] particularly under illumination and/or presence of oxygen,[13-15,20] are scarce. In 3D perovskites, it has been established that perovskite degradation involves hole trapping or accumulation.[22-25] Excess holes oxidize iodide, which starts the chain of electrochemical reactions (iodide oxidation, organic cation deprotonation) which ultimately lead to perovskite degradation (**Note S1**). Hole accumulation is also responsible for accelerated performance degradation under open-circuit conditions[4] (**Note S2**), as well as halide segregation in mixed perovskite materials,[22-28] driven by photo- and/or electrochemically-induced holes.[22,23] The electrochemical redox reactions are exacerbated by exposure to oxygen, since oxygen acts as an electron scavenger which causes the excess of photogenerated holes in the perovskite, which are the primary source of degradation.[22] The degradation is further accelerated by exposure to both oxygen and moisture.[29-32]

While 2D materials offer improved resistance to moisture, they can still be sensitive to photooxidation and/or degrade under illumination.[13,15,16,20] In some cases, 2D materials, such as 2D PEA_2PbI_4 (PEA denotes phenethyl ammonium), 2D BA_2PbI_4 (BA denotes butyl ammonium) and quasi-2D $BA_2MA_{n-1}Pb_nI_{3n+1}$ (n=2,3), are less stable compared to the corresponding 3D perovskite[4,16,20] and the degradation can be observed for oxygen levels as low as 100 ppm.[20] Due to the observed instability of 2D materials under illumination, their suitability for stability enhancements has been questioned recently.[24] It is therefore important to understand photo- and electrochemical behavior of these materials, as they remain commonly proposed strategies to mitigate ion migration and reduce perovskite degradation.[1-3,22]

RESULTS AND DISCUSSION

Photochemical stability of 2D perovskites

There are two distinct classes of 2D/quasi-2D perovskite materials: Ruddlesden-Popper (RP) with formula $C_2A_{n-1}B_nX_{3n+1}$ and Dion-Jacobson (DJ) with formula $CA_{n-1}B_nX_{3n+1}$, where C is the bulky spacer cation, and n is the number of octahedral layers. As the offset between adjacent octahedral layers in RP and DJ halide perovskites can deviate from an ideal one observed in analogous 2D oxide perovskites, we classify different 2D perovskite materials as RP perovskites when $[BX_6]^{4-}$ octahedra are separated by a bilayer of monovalent organic cations bound with weak van der Waals forces, and as DJ perovskites when $[BX_6]^{4-}$ octahedra are separated by a single

layer of divalent organic cations which form hydrogen bonds with adjacent octahedral layers.[19,21] While it was claimed that quasi-2D RP and DJ perovskites have comparable stability under illumination,[19] DJ perovskites consistently result in more stable SCs, LEDs, and photodetectors (**Note S3**). Thus, we investigated the susceptibility of these materials to photooxidation to elucidate mechanisms of degradation and reasons for stability differences.

We observe dramatic differences in the photostability of six DJ vs. six RP 2D perovskites illuminated for 3 h (**Figures S1-S4**). DJ perovskites exhibit good photostability for both bromides and iodides. All RP iodide perovskites exhibit significant degradation, while RP bromide perovskites exhibit different trends depending on the spacer cation. In those RP bromide perovskites which degrade, the loss of spacer cation is observed (**Figure S5**). While all alkyl chain RP spacers exhibited poor stability, the presence of an aromatic ring does not guarantee stability (**Figure S6**). As iodide perovskites are more relevant for SCs and exhibit clear difference between RP (poor stability) and DJ (good stability) materials, we will focus on iodide perovskites.

There are two possible uses of RP or DJ perovskites in solar cells, as 3D/2D (3D perovskite capped with a 2D film) or quasi-2D (commonly n=3-5) absorber films. Here we will focus on stability of 2D films for applications in devices with 3D/2D absorber layers, since quasi-2D films typically contain multiple n phases and exhibit complex behavior under illumination (**Figure S7 & S8**),[18,33-35] as both degradation and phase transformation/disproportionation can occur since both small cations and bulky spacers are mobile in RP perovskites.[34,35] The process is further complicated by moisture exposure which facilitates phase transformations.[36] The presence of moisture can further complicate the stability comparisons between RP and DJ perovskites, since quasi-2D DJ perovskites have lower moisture resistance[37] and can exhibit formation of new phases in ambient air (**Figure S9**). Thus, to isolate the factors responsible for stability differences between DJ and RP perovskites, we focus on 2D materials (n=1) since they cannot exhibit disproportionation, and perform experiments in different atmospheres to distinguish effect of oxygen and moisture, as shown in **Figure 1**. Quasi-2D perovskites exhibit similar trends on atmosphere composition (**Figure S10**), and thus degradation mechanisms elucidated for 2D materials should be generally applicable.

For detailed investigations of stability differences, we selected four commonly studied 2D perovskite materials,[1] including two RP (BA-based and PEA-based) and two DJ (BDA-based and 4AMP-based) perovskites, where BDA denotes butane-1,4-diammonium and 4AMP denotes 4-(amino methyl) piperidinium). BA and BDA were chosen due to their similar structure, while PEA and 4AMP were chosen as commonly used spacers with more complex structure to examine generality of observed differences. Unlike DJ perovskites, both RP perovskites exhibit prominent decrease in the absorption in ambient and dry air, with the worst stability observed in ambient air due to accelerated degradation in the presence of both oxygen and water.[29-32] The degradation of RP perovskites clearly involves the loss of organic cations, as evidenced by the reduction of FTIR bands related to N-H stretching vibrations (region ~3100-3400 cm^{-1}),[5] CH_3 vibrations (~2800-3000 cm^{-1}),[36] N-H bending vibrations (~1650 cm^{-1}),[8] and C-H scissoring (~1470 cm^{-1}),[8] similar to photooxidative degradation of $MAPbI_3$ due to deprotonation of MA.[8] Degradation under illumination is also observed in a RP perovskite single crystal (**Figure S11**), starting from the edges consistent with previous reports.[13,33]

Since superoxide ion (O_2^-) was proposed to participate in photooxidation reaction of 3D perovskites[4-11,29] and quasi-2D perovskites,[15,29] we performed electron paramagnetic resonance (EPR) spectroscopy measurements (**Figure 2A** and **Figure S12**) for both types of perovskites illuminated under different environments. Results show that there is no clear relationship between O_2^- generation and perovskite degradation as significant O_2^- is still generated in DJ perovskites (4AMPPbI$_4$ and BDAPbI$_4$) with negligible degradation, in agreement with O_2^- production in MAPbBr$_3$ which is not susceptible to photooxidation.[10,11]

Since O_2^- production simply indicates transfer of photogenerated electrons to oxygen molecules, which causes excess holes in the perovskite,[22] we hypothesize that DJ perovskites are more tolerant than RP perovskites to hole accumulation and investigate their electrochemical stability. Since iodide oxidation by excess holes under illumination leads to expulsion of iodide into the solution in 3D perovskites (**Note S1**), UV-VIS absorptions of RP and DJ perovskites in toluene solution were measured (**Figure 2B**). I_2 (at ~520 nm[20]) and I_3^- species (at ~290 nm and ~360 nm[22,28]) were observed in RP perovskites in the presence of oxygen signifying iodide expulsion from RP perovskites,[22] in agreement with film photostability trends and similar to previous report for $BA_2MA_{n-1}Pb_nI_{3n+1}$ (n = 1, 2, 3).[20] Negligible expulsion was observed in RP perovskites in argon or DJ perovskites in any environment. The photooxidative release of halides occurs due to the weakening of the Pb-X bond upon optical excitation.[27] Resulting iodine oxidation products include HI, I^* radicals, I_2, triiodide (I_3^-), and interstitial iodine defects (I_i^n, where n=-1, 0, +1).[27] The degradation process likely involves deprotonation of organic cation, since significant suppression of iodine expulsion is observed in films with high Cs content.[28] Similar to 3D organic precursor MAI,[8] both RP and DJ precursors (BAI, PEAI, BDAI, and 4AMPI) release iodide species into the solution (**Figure S13**) indicating that stability difference is related to the incorporation of spacer cation in the perovskite structure.

Electrochemical stability of 2D perovskites

The involvement of excess holes is investigated on BA_2PbI_4 films (as they are susceptible to photooxidation) and confirmed by decreased release of iodide species for films on hole transport layer (HTL) (**Figure 2C**), due to efficient hole extraction from perovskite (evidenced by reduced PL emission, **Figure S14 & S15**). In contrast, films on electron transport layer (ETL) degrade faster (**Figure S14**). Illumination of BA_2PbI_4 films on different substrates also results in differences in outgassing products (**Figure S16)**, namely butylamine, NH_3, iodobutane, and CH_3I gases. HI could not be observed due to the reaction between HI and column stationary phase.[38] The lowest outgassing was observed for films on indium tin oxide (ITO), which can extract both electrons and holes. For the samples on ETL (excess holes), we observe more outgassing of oxidation product CH_3I, while on self-assembled monolayer (excess electrons) we observe more outgassing of reduction product butylamine. These results strongly suggest that the degradation process is photoelectrochemical, similar to $MAPbI_3$ (**Note S1**). The electrochemical nature of the process is also confirmed by iodide expulsion into solution under bias[22-24] (**Figure 2D**), where significant expulsion occurs for RP but not for DJ perovskites. Consistent with this, devices with 2D RP perovskites after bias exhibit obvious corrosion of the electrode (absent for DJ perovskites, **Figure S17**) and lower I/Pb ratio in the perovskite film after bias (**Table S2**). Linear sweep voltammetry (LSV) measurements were used to investigate the deprotonation reaction in 2D perovskites with different spacers by biasing the perovskite with a reduction potential in the electrochemical cell (**Figure S18**), and the onset of rise in cathodic current for monoammonium

spacers (BA and PEA) is found to be less negative than the onset for diammonium spacers (BDA and 4AMP). More importantly, RP perovskites degraded completely after scan, different from DJ perovskites (**Figure S19**). These results indicate the possibility that a difference in the reduction reaction (deprotonation of organic cation), rather than oxidation reaction (oxidation of iodide and formation of interstitial iodine defects, I_2, and/or I_3^-) could suppress the degradation pathway in DJ perovskites.

Mechanism of degradation under illumination and/or bias

Possible mechanisms for observed increased resistance of DJ perovskites to photooxidation are listed in **Figure 3A.** Extensive calculations were performed to examine different possibilities, as described **Notes S4-S6**, and depicted in **Figures S20-S27.** We found that increased photostability of DJ perovskites cannot be correlated to their structural rigidity (**Figure S21, Note S5**). In addition, hole-doping does not result in significant changes in radial distribution functions (**Figures S22** & **S23**) or phonon mode softening (**Figure S24** & **S25**) in both RP and DJ perovskites. Furthermore, the increased photostability of DJ perovskites cannot be generally correlated to shorter interlayer distance,[37] since DDDAPbI$_4$ with interlayer spacing of 16.02 Å is more stable than BA_2PbI_4 with interlayer spacing of 13.75 Å (**Figure 4**). RP and DJ perovskites also exhibit similar tendencies to localize excess holes on iodine (**Figures S26 &S27**, **Note S6**), as expected since valence band is mostly made of iodine 5p orbitals.

We then examined the energetics of organic spacer vacancy formation in neutral and positively charged systems (see **Note S4** for details). Since forming a charged spacer vacancy would be extremely energetically unfavourable, we investigate the existence of a singly (RP) or doubly (DJ) deprotonated state to neutralize the spacer (**Fig. S27-29, Tables S3&S4)**. By performing geometry relaxations starting from various geometries including a deprotonated spacer (**Tables S2 & S3, Figures S28 &S29** and Supplemental Data for computational methods), we find that introducing either a hole or an interstitial halide defect into a neutral pristine system modifies the potential energy surface to create a locally bound interhalide-proton protonated state, where the alkylammonium group is deprotonated (**Fig. S27)**. The interstitial iodine defects are found to lower the barrier for deprotonation and spacer vacancy formation. In addition, deprotonated state is unstable for I_i^- defects for DJ perovskite, while in RP perovskites these defects result in negative spacer vacancy formation energy (**Figure S29**), indicating that I_i^- defects can easily destabilize RP perovskite. Thus, we can conclude that differences in the likelihood of spacer vacancy formation, which requires single deprotonation on any RP spacer cation and double deprotonation on both sides of the same DJ spacer cation (less likely than two single deprotonation events at one side of any two different cations), are responsible for photostability differences between DJ and RP perovskites, as illustrated in **Figure 3b**.

Thus, from the obtained experimental data and theoretical calculations, as well as the literature reports on photo/electrochemical stability of 3D perovskites (**Notes S1, S7 & S8**), we propose that photooxidation of 2D perovskites involves the oxidation of iodide which results in the generation of mobile iodine species, and the reduction/deprotonation of organic cation, resulting in organic spacer vacancy formation and release of volatile degradation products. The first step in photooxidation process involves the localization of hole on I^-, weakening of Pb-I bond and the oxidation of I^- by the hole into oxidized iodine species (interstitial iodine defect, I_2, and/or

I_3^-).[39] Next, the deprotonation of spacer cation follows which becomes favorable in the presence of excess holes or interstitial iodide defects (**Note S4**), in particularly I_i^-, consistent with the report that I_3^- causes deprotonation of organic cation by forming strong hydrogen bonds with organic ammonium cations.[39] The significant role of iodide is also confirmed by rapid degradation of BA_2PbI_4 under illumination in the presence of excess iodine (**Figure S30**), similar to 3D perovskite degradation in presence of iodine.[6] As iodide oxidation occurs in all perovskites, to explain the differences in the degradation of RP and DJ perovskites, we need to consider the likelihood of the formation of cation vacancies after deprotonation, as illustrated in **Figure 3B.** Reduced cation vacancy formation in DJ perovskites results in suppressed ion diffusion since the ion diffusion in 2D perovskites proceeds layer-by-layer and the organic spacer cations in 2D perovskites serve ion-blocking function.[40] In agreement with this expectation, significantly lower activation energy for halide migration was reported for BA-based perovskite compared to BDA-based perovskite.[41]

Consistent with proposed mechanism, we observe significant degradation after bias in ambient near positive electrode in lateral geometry devices for RP perovskites (**Figure 5A-D**). Encapsulated BA_2PbI_4 exhibits the same degradation pattern (**Figure S31 A-C**), but it degrades slower than the sample without encapsulation. RP perovskites also exhibit more significant outgassing under illumination **(Figure 5E&F, Note S9**). From the GC-MS measurements **(Figure 5E&F, Note S9**), we can observe that iodide oxidation (resulting in I-containing degradation products such as CH_3I) is more prominent in RP perovskites, but it occurs both in RP and DJ perovskites in agreement with theoretical calculations. The outgassing of CH_3I could also potentially be morphology dependent, as films with larger grains and consequently fewer grain boundaries would degrade more slowly, as observed from the morphology comparison of $BDAPbI_4$ and $4AMPPbI_4$ (**Figure S32 A&B**). On the other hand, we observe NH_3 outgassing (which is a decomposition product originating from spacer cations) only in RP perovskites consistent with reduced likelihood of spacer vacancy formation in DJ perovskites. The proposed degradation mechanism is also consistent with the observed changes in *in situ* Raman measurements (**Figures S33-S35**), which show distinctly different patterns for RP and DJ perovskites. For both perovskites, no significant changes are observed in low wavenumber region corresponding to the inorganic part of perovskite lattice,[42-44] while for RP perovskites we observe more significant changes in the regions corresponding to different vibrations of organic cation.[45-49] In the case of BA_2PbI_4, which has the worst stability, we also observe that new peaks (at ~402 cm^{-1}, 518 cm^{-1} and 643 cm^{-1}), attributed to deformations of butylamine[45-47] and HI_2^-,[48] disappear after the second scan of the same area (**Figure S35**), consistent with the presence of loosely bound surface species. The outgassing of spacer cation decomposition products under illumination can also be directly observed using a colorimetric sensor for organic amines and/or gaseous ammonia bromocresol green (BG), as shown in **Figure S36**. Clear color change of BG is observed for BA_2PbI_4, but not for BDA_2PbI_4, in agreement with GC-MS results.

Therefore, we can conclude that the degradation under illumination in 2D perovskites, similar to their 3D counterparts, is mainly driven by electrochemical redox reactions. Excess photogenerated holes, which result either from imbalances in charge extraction or from the presence of oxygen which serves as electron scavenger, result in oxidation of iodide and generation of oxidized iodine species (interstitial iodine defect, I_2, and/or I_3^-).[39] These oxidized iodine species participate in further redox reactions, including deprotonation of organic cation,

triggering the chain reaction of degradation.[39] These reactions become irreversible due to loss of volatile reaction products, such as desorption of organic amine after organic ammonium cation deprotonation. As this occurs more readily in RP perovskites (where single deprotonation event can result in spacer cation vacancy) than in DJ perovskites (where two deprotonation events on the same spacer cation are needed to produce neutral amine which can then desorb), DJ perovskites exhibit improved photo/electrochemical stability, as evidenced by their improved stability under illumination (**Figure 1, Figure 4, Figures S1-S10**), their lack of significant expulsion of iodide in solution under illumination and bias (**Figure 2B** & **2D**), the lack of visible changes in the electrodes after bias (**Figure S17**), and the lack of degradation under LSV measurement (**Figure S19**) and bias in lateral devices (**Figure 5C** & **5D**), as summarized in (**Note S11**). Critical role of holes in the degradation process due to electrochemical redox reactions in RP perovskites is demonstrated by differences in perovskite degradation and outgassing of reaction products for perovskite deposited on HTL (excess electrons) and ETL (excess holes) (**Figure 2C, Figures S14-16**) and the degradation near positive electrode in lateral bias devices (**Figure 5A** & **B)**, while the iodine-induced degradation (**Figure S30**) is consistent with the hypothesized role of oxidized iodine species in the degradation process, with clear loss of spacer cation observed in proximity of I_2 bead under illumination in inert environment. The loss of organic cations as a key step towards perovskite degradation is evident from FTIR measurements (**Figure 1B & F**, **Figure S5A, Figure S10B, Figure S30b**), GC-MS measurements (**Figure S16A & B**, **Figure 5E**), colorimetric detection of organic amines and/or gaseous ammonia (**Figure S36**), and changes in Pb:I ratio after bias or illumination stability test (**Table S2**, **Table S8**).

Device Stability

Three different 3D perovskite compositions, CsFAMA triple cation perovskite, low Br perovskite, and MA-free perovskite, are considered to investigate generality of the approach. Overall photostability of different 3D/2D film combinations (**Figures S37-S40**) depends on 3D perovskite used, and for each 3D perovskite stability trends (DJ>RP) are consistent with those of 2D films. The performance of corresponding SC devices is summarized in **Figure 6**, **Figure S41-S43** and **Table S5**. The stability tests were performed without encapsulation in dry air to accelerate degradation due to photo/electrochemical redox reactions (under this condition, there will be higher hole accumulation since O_2 acts as electron scavenger,[22] and there will be increased loss of volatile decomposition products compared to devices with blanket encapsulation[38]). Slower degradation can be clearly observed for devices with 2D DJ capping layer for all 3D perovskite compositions, although the stability trends between spacers in the same family (BA vs. PEA, BDA vs. 4AMP) vary for different 3D perovskite compositions and can differ from trends observed in individual films. This can be attributed to possible differences in interfacial defects and charge accumulation in devices, which would be different for different 3D perovskites.

To further investigate this, additional characterizations were performed for different 2D capping layers for commonly used CsFAMA triple cation perovskite, which exhibits stable performance under illumination when encapsulated.[50] The obtained atomic force microscopy (AFM), Kelvin probe force microscopy (KPFM), and TRPL results, as well as composition investigations after tests are shown in **Figures S44-S46** and **Table S6-S8**, and summarized in **Note S10**. We can observe that no consistent pattern between DJ and RP perovskites in charge extraction from TRPL decay times for 3D/2D perovskite between HTL and ETL (corresponding to full device structure without the electrode, **Figure S46B** and **Table S6**) or from the change in

surface potential with illumination **Figure S45**. In the case of 4AMP, we observe positive change of surface potential and conventional hysteresis, while for BA, PEA, and BDA negative change of surface potential and reverse hysteresis are observed (hysteresis in all the devices is small, **Figure S41G**). For BA, we observe the lowest J_{sc} values and the longest TRPL decay times, consistent with less efficient charge extraction, and these devices also exhibit the shortest T_{80} lifetime under illumination (**Figure 7D**). For low Br 3D perovskite, we observe higher J_{sc} values for BA-based devices than for PEA, and longer T_{80} for BA than for PEA. The obtained results are consistent with dominant contribution of photo/electrochemical redox reactions to degradation under illumination, with 3D/2D interface in part affecting the degradation rate due to differences in interfacial defects and/or charge accumulation. Devices with RP and DJ capping layers show similar stability when stored in the dark in inert environment (**Figure S47**), also consistent with degradation under illumination dominated by photo/electrochemical redox reactions. This is further evidenced by the degradation patterns of encapsulated devices under forward bias with J_{sc}, under reverse bias and illumination (**Figure S48**) and OC stability testing (**Figure S49**), as well as observable electrode damage under OC testing **(Figure S49)**, where clear metal diffusion to the opposite electrode is observed, consistent with redox-reactions driven degradation leading to metal deposition on the opposite electrode due to migration of metal-iodide complexes followed by metal reduction.[51]

Conclusions

In this work, we demonstrate that DJ perovskites have increased resistance to photooxidation due to reduced formation of organic cation vacancies under illumination and/or bias, resulting in improved stability due to reversibility of photo/electrochemical reactions in the absence of loss of volatile reaction products, which makes them more suitable for applications in high stability devices. While the intrinsic stability difference related to reduced likelihood of formation of cation vacancies remains valid for all DJ materials, to maximize this advantage it is necessary to optimize device architecture to minimize detrimental hole accumulation during operation, as well as minimize the defects in the perovskite films.

EXPERIMENTAL PROCEDURES

Details of experimental procedures are provided in Supplemental Information.

SUPPLEMENTAL INFORMATION

Document S1. Notes S1-S11, Figures S1-S49, Tables S1-S8, Supplemental Experimental Procedures.

Data S1. Standardized data reporting for photovoltaic cells.

Data S2. Relaxed structures in exyz format.

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Aleksandra B. Djurišić (dalek@hku.hk).

Materials availability

This study did not generate new unique reagents.

Data and code availability

The data that support the plots within this paper and other findings of this study are available from the corresponding authors upon reasonable request. This paper does not report original code.

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AUTHOR CONTRIBUTIONS

A. B. D., J. P., and T. L. L. conceived the project, and A. B. D., J. P., A. M. C. N., A. H. B. and I. L. supervised the project. J.O. performed all computations with help and guidance from L.G. and I.L., Z. L. R. performed preparation and characterization of different perovskite thin films, with some of the samples prepared and/or characterized by T. L. L. and Z. Y. In addition, Z. L. R. and A. A. S. performed degradation experiments in solution under illumination and/or bias, Z. L. R. performed lateral bias experiments, T. L. L. performed cyclic voltammetry and KPFM measurements, J. B. performed GC-MS measurements, M. P. B. contributed to the GC-MS methodology and assisted with the measurements. and M. U. A. performed TRPL measurements. Y. L. H. performed EDX, EPR, *in situ* absorption and *in situ* XRD measurements, as well as Raman measurements together with G.Y. L. X. S. Q. prepared and characterized charge injection devices and samples for EDX. W. T. S. prepared BA_2PbI_4 single crystal, while J. Y. L., A.-K., and J. W. prepared NiO_x nanoparticles for solar cell fabrication. Y. L., Z. T. Y., D. Y. L., H. M., P. B. and T. Z. prepared and characterized solar cells under the guidance of G. L. and A. B. D.

DECLARATION OF INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

Supplemental information is available for this paper at https://xxxx.

Correspondence and requests for materials should be addressed to A.B.D., J. P. or I. L.

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FIGURE CAPTIONS

Figure 1. Absorption and FTIR spectra, respectively, of (A), (B) BA_2PbI_4 (C), (D) $BDAPbI_4$ (E), (F) PEA_2PbI_4 and (G), (H) $4AMPPbI_4$ exposed to simulated solar illumination (100 mW/cm^2) in different atmospheres. For ambient atmosphere, RH was 60%, for N_2+moisture RH was 40%.

Figure 2. (A) EPR spectra of BA_2PbI_4 and $BDAPbI_4$ perovskite samples with 5-(Diethoxyphosphoryl)-5-methyl-1-pyrroline-N-oxide (DEPMPO) under illumination in dry air, N_2 and N_2+H_2O are also shown. EPR spectrum of DEPMPO with 5% w/w of H_2O_2 illuminated in ambient (multiplied by 0.02 for scale) is also shown for reference of DEPMPO probe peaks. (B) absorption spectra of toluene solutions after 1 h exposure of immersed perovskite films on glass substrates BA_2PbI_4, $4AMPPbI_4$, PEA_2PbI_4, $BDAPbI_4$ and $HDAPbI_4$ to simulated solar illumination (1 Sun) in ambient (HDA denotes hexane-1,6-diammonium). The absorption spectrum of toluene solution of perovskite film BA_2PbI_4 exposed to illumination in Ar atmosphere is also shown, and the inset shows schematic diagram of the measurement. (C) Absorption spectra of toluene solutions of immersed BA_2PbI_4 films on different substrates (ITO, NiO_x/ITO, 2PACz/NiO_x/ITO, where ITO denotes indium tin oxide and 2PACz denotes [2-(9H-carbazol-9-yl)ethyl]phosphonic acid)) after exposure to simulated solar illumination (1 Sun); peaks corresponding to iodine I_2 and triiodide I_3^- absorption are labelled. (D) Absorption spectra of DCM solution with 0.1M Bu_4NPF_6 after 20 s immersion of the 2D perovskite samples with bias of 1.2 V vs. Ag/AgCl. The absorption spectrum after 20 s immersion of BA_2PbI_4 without bias is also shown, consistent with previously established window of stability (<30 min)[24] in absence of bias or illumination. The insets in panels b), c) and d) show schematics diagrams of the measurements.

Figure 3. (A) Schematic illustration of the possible mechanisms contributing to increased photostability of DJ perovskites (B) Schematic illustration of the proposed process highlighting differences in the formation of cation vacancies in DJ and RP perovskites. In RP perovskites, organic amine is readily lost after deprotonation of the ammonium cation leading to the formation of cation vacancies. This results in the enhancement of ion migration, facilitating degradation of the perovskite layer. On the other hand, in the case of DJ perovskites a higher density of excess holes would be needed for simultaneous deprotonation of the cation on both sides to create cation vacancy, which makes this double deprotonation event less likely. As the electrochemical reactions are reversible in the absence of loss of volatile reaction products, singly deprotonated cations which remain bound can revert to protonated state. Consequently, no vacancies are formed thus the release of halides is suppressed, preventing the degradation of DJ materials.

Figure 4. Absorption spectra of (A) BA_2PbI_4 and (B) $DDDAPbI_4$ and XRD patterns of (C) BA_2PbI_4 and (D) $DDDAPbI_4$ after simulated solar illumination (100 mW/cm^2) in argon and dry air. Insets show the interlayer spacings.

Figure 5. Microscope images of (A) BA_2PbI_4, (B) $BDAPbI_4$, (C) PEA_2PbI_4, and (D) $4AMPPbI_4$ lateral geometry devices with ITO electrodes separated by 110 µm gap before (left) and after (right) bias of 10 µA current for 20 min without illumination in ambient (~60% RH). Scale bar is 20 µm. GC-MS signal corresponding to (E) ammonia and (F) CH_3I for fresh and aged samples of different 2D perovskites.

Figure 6. I-V curves (reverse scan, the best performance devices listed in **Table S5**) of solar cells with 3D/2D (BA, PEA, BDA, 4AMP) perovskite layer for different 3D perovskite compositions: (A) triple cation CsFAMA (B) Low Br and (C) MA-free; (D), (E), (F) Corresponding normalized PCE as a function

of time of illumination (1 Sun, 100 mW/cm^2) in dry air without encapsulation. Temperature during stability test was 30ºC.