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Understanding the Degradation of Methylenediammonium and Its Role in Phase-Stabilizing Formamidinium Lead Triiodide

Elisabeth A. Duijnste[#], Benjamin M. Gallant[#], Philippe Holzhey[#], Dominik J. Kubicki, Silvia Collavini, Bernd K. Sturza, Harry C. Sansom, Joel Smith, Matthias J. Gutmann, Santanu Saha, Murali Gedda, Mohamad I. Nugraha, Manuel Kober-Czerny, Chelsea Xia, Adam D. Wright, Yen-Hung Lin, Alexandra J. Ramadan, Andrew Matzen, Esther Y.-H. Hung, Seongrok Seo, Suer Zhou, Jongchul Lim, Thomas D. Anthopoulos, Marina R. Filip, Michael B. Johnston, Robin J. Nicholas, Juan Luis Delgado,^{*} and Henry J. Snaith^{*}



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ABSTRACT: Formamidinium lead triiodide (FAPbI₃) is the leading candidate for single-junction metal–halide perovskite photovoltaics, despite the metastability of this phase. To enhance its ambient-phase stability and produce world-record photovoltaic efficiencies, methylenediammonium dichloride (MDACl₂) has been used as an additive in FAPbI₃. MDA²⁺ has been reported as incorporated into the perovskite lattice alongside Cl[−]. However, the precise function and role of MDA²⁺ remain uncertain. Here, we grow FAPbI₃ single crystals from a solution containing MDACl₂ (FAPbI₃-M). We demonstrate that FAPbI₃-M crystals are stable against transformation to the photoinactive δ -phase for more than one year under ambient conditions. Critically, we reveal that MDA²⁺ is not the direct cause of the enhanced material stability.

Instead, MDA²⁺ degrades rapidly to produce ammonium and hexamethylenetetramine (HMTA). FAPbI₃ crystals grown from a solution containing HMTA (FAPbI₃-H) replicate the enhanced α -phase stability of FAPbI₃-M. However, we further determine that HMTA is unstable in the perovskite precursor solution, where reaction with FA⁺ is possible, leading instead to the formation of tetrahydrotriazinium (THTZ-H⁺). By a combination of liquid- and solid-state NMR techniques, we show that THTZ-H⁺ is selectively incorporated into the bulk of both FAPbI₃-M and FAPbI₃-H at ~0.5 mol % and infer that this addition is responsible for the improved α -phase stability.

MDA²⁺ degrades to HMTA-H⁺ + NH₄⁺. If FA⁺ is present, THTZ-H⁺ forms.



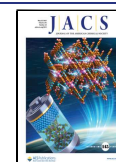
INTRODUCTION

Hybrid organic–inorganic metal–halide perovskites are recognized as one of the most promising emerging semiconducting materials for optoelectronic applications due to their excellent properties, including tunable band gaps,¹ high absorption coefficients,² and long charge-carrier diffusion lengths.³ Among the ABX₃ lead–halide perovskites reported to date, FAPbI₃ (FA⁺ is formamidinium, HC(NH₂)₂⁺)⁴ has the narrowest achievable band gap, allowing for the highest theoretical photovoltaic power conversion efficiency (PCE) in a single-junction architecture.⁵ For this reason, the majority of recent world-record PCE perovskite photovoltaics have employed FAPbI₃-based materials as their photoabsorbing layer.^{6–9} However, under ambient conditions, the cubic α -phase of FAPbI₃ is thermodynamically unstable with respect to transformation to a photoinactive hexagonal δ -phase polytype. Despite this, the phase transition is kinetically inhibited under ambient conditions permitting metastable α -FAPbI₃ to persist

for hours, days, and even months, depending strongly on processing conditions and the atmospheric conditions in which the processed material is stored.^{10,11} The phase stability of FAPbI₃ thin films and single crystals is necessary for their practical use. Significant efforts are directed at finding approaches to suppress the α -to- δ phase transition. In particular, smaller A-site cations have been used to stabilize the perovskite lattice by alloying with FA⁺. Most frequently used are MA⁺ (but which has been shown to introduce an unfavorable thermal instability^{12,13}) and the alkali-metal Cs⁺,^{14,15} often in conjunction with I[−], Br[−], and Cl[−] X-site

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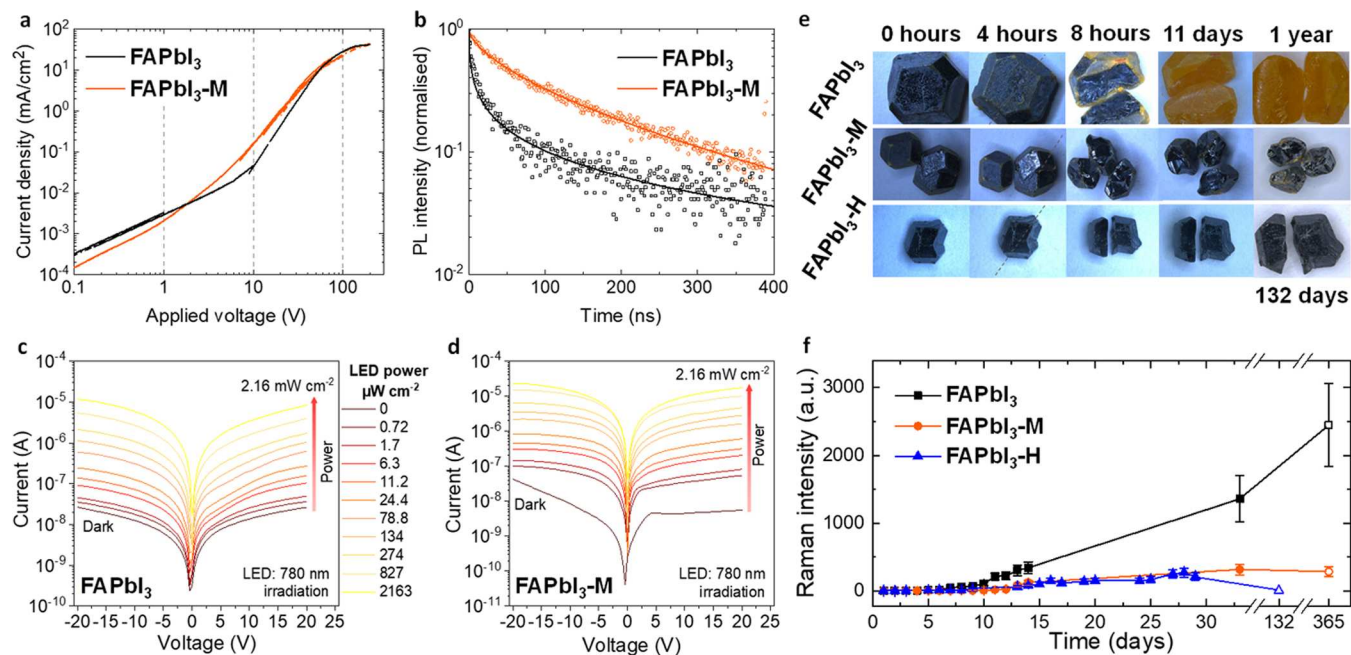


Figure 1. Single-crystal optoelectronics and stability. (a) PV-SCLC measurements for FAPbI₃ and FAPbI₃-M single crystals; (b) time-resolved photoluminescence measurements of FAPbI₃ and FAPbI₃-M. Current density–voltage curves in a N₂ environment of (c) FAPbI₃ and (d) FAPbI₃-M single-crystal photodetectors with Ag electrodes. (e) Optical microscope images of grown FAPbI₃, FAPbI₃-M, FAPbI₃-H crystals. The crystals are cleaved after 4 h. The crystals were kept in glass vials under ambient conditions (dark, relative humidity ~30 to 80%) throughout the measurement period. (f) Temporal evolution of δ -phase Raman peak intensity for FAPbI₃, FAPbI₃-M, FAPbI₃-H single crystals. The single crystals were kept in the air for the first 33 days. The long-term data at 132 and 365 days (no fill) correspond to vial-stored crystals.

alloying. Although promising, such approaches can introduce undesirable properties. Band gap increases induced by structural changes due to the inclusion of smaller cations¹⁶ are undesirable for single-junction photovoltaics. Furthermore, compositional inhomogeneities in the mixed-ion perovskites introduced during growth can render materials susceptible to ion segregation^{17,18} and non-radiative recombination losses¹⁹ under operation. It is therefore highly valuable to develop strategies to improve the stability of FAPbI₃ without diminishing its valuable properties.

In 2019, Min et al.²⁰ reported highly efficient α -FAPbI₃ solar cells based on polycrystalline thin films by incorporating a small amount of methylenediammonium dichloride (MDACl₂, 3.8 mol %) into the precursor solution while maintaining the inherent band gap of FAPbI₃. The authors attribute the high-certified PCE of 23.7% to the addition of MDACl₂ and report that MDA²⁺ leads to structural stabilization of α -FAPbI₃ via partial replacement of FA⁺ with MDA²⁺ alongside Cl⁻ incorporation at interstitial sites. Subsequently, Kim et al.²¹ propose that concurrent substitution of 3 mol % of Cs⁺ and MDA²⁺ on FA⁺ sites lowers the lattice strain and trap density in perovskite solar cells. In more recent works—again from Seok and co-workers—MDA²⁺ was twice used alongside FAPbI₃ to achieve the highest yet-reported certified efficiency for perovskite solar cells, 25.5%⁹ and subsequently 25.7%.^{8,22}

In order to isolate the role of MDACl₂, we here study the effect of its addition to the precursor solution during the growth of FAPbI₃ single crystals (denoted FAPbI₃-M). We find that the highly acidic MDA²⁺ cation is unstable in solution, degrading rapidly into ammonium and hexamethylenetetramine (HMTA). However, this degradation is further complicated by the presence of FA⁺ in the precursor solution, a reaction which can interrupt the degradation pathway and

instead lead to the formation of tetrahydro-1,3,5-triazinium (THTZ-H⁺). We find that of all the degradation products formed, it is THTZ-H⁺ that is present in FAPbI₃-M crystals. We show that FAPbI₃-M crystals grown possess vastly improved α -phase stability (>1 year in the air) and significantly reduced defect density.

RESULTS AND DISCUSSION

Single-Crystal Growth and Optoelectronic Performance. We grow the single crystals via the inverse temperature crystallization method.^{23,24} The control FAPbI₃ single crystals are prepared by dissolving equimolar FAI and PbI₂ in γ -butyrolactone (GBL). Crystal growth is directed by the addition of an appropriate seed crystal to this precursor solution. Heating to 95 °C leads to growth of the seed into an α -FAPbI₃ single crystal between 2 and 4 mm in length. For the FAPbI₃-M single crystals, we add 3.8 mol % (with respect to the Pb content) of MDACl₂ to the FAPbI₃ perovskite precursor solution. We note that in contrast to Min et al.,²⁰ we do not add MAcl to any of our precursor solutions, as we aim to isolate and investigate the effect of MDACl₂ on FAPbI₃-phase stability. Further details on crystal growth are discussed in [Supporting Note 1](#). We heat the single crystals in a vacuum oven at 180 °C for 30 min to remove residual solvent on the crystal surface. Single-crystal X-ray diffraction (SCXRD) confirms the three-dimensional (3D) perovskite phase in each case, with crystal structures solved in the *Pm3m* cubic space group, as previously reported.²⁵ Crystal data and structure refinement statistics are shown in [Table S1](#). We discuss our SCXRD measurements in detail in [Supporting Note 2](#), including our observation of a pronounced difference in the degree of twinning detected in FAPbI₃ crystals grown in the presence of different additives.

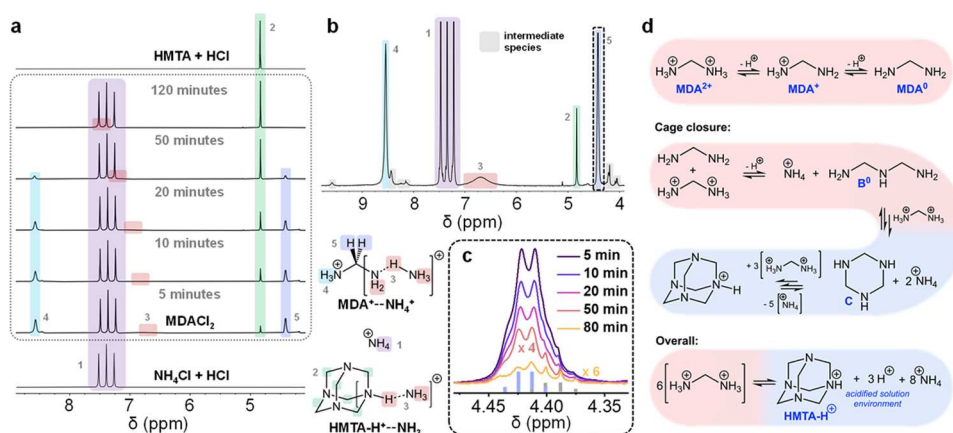


Figure 2. Degradation of MDA^{2+} . (a) ^1H solution nuclear magnetic resonance (NMR) spectra tracking the evolution of MDACl_2 upon dissolution in $\text{DMSO-}d_6$. Bottom: spectra acquired from acidified solution of ammonium chloride. Top: spectra acquired from acidified solution of (HMTA). Color scheme correlates detected signals with ^1H chemical environments in detected species. (b) Expanded ^1H NMR spectrum of 5 min after the initial dissolution of MDACl_2 in $\text{DMSO-}d_6$. (c) Evolution of ^1H NMR quartet signal corresponding to methylene environment in dominant degradation intermediate. (d) Degradation pathway of MDA^{2+} upon dissolution in a polar solvent. Hexamethylenetetramine (HMTA) and ammonia are represented in their protonated forms in line with our observations and on account of the acidic environment generated in solution as a result of the degradation.

We first investigate the impact of MDACl_2 on the electronic properties of the FAPbI_3 single crystals. To investigate the charge transport through the single crystals, we deposit gold electrodes on the crystals and perform pulsed-voltage space-charge-limited-current (PV-SCLC) measurements in which the dark current–voltage (J – V) characteristics are measured under vacuum, shown in Figure 1a.²⁶ The pulsed J – V traces of both samples show an Ohmic region at low voltages, where the slope, m ($m = \frac{d(\log(J))}{d(\log(V))}$), equals 1. From this region, we estimate a dark DC conductivity of 8.5×10^{-6} and 5.3×10^{-6} S m^{-1} for FAPbI_3 and $\text{FAPbI}_3\text{-M}$ crystals, respectively. We have previously shown that if the density of traps is larger than the density of static ionic space charge, the J – V curve deviates from being linear into a regime where m is larger than 2.^{26–28} From the voltage point at which this occurs, (V_{ons}), we can calculate a lower bound trap density (n_t) via: $n_t = \frac{2V_{\text{ons}}\epsilon_0\epsilon_r}{eL^2}$, where ϵ_0 is the vacuum permittivity, L the crystal thickness, e the electron charge, and ϵ_r is the low-frequency dielectric constant of the material, reported as 49.4 for FAPbI_3 .²⁹ We assume the same value for ϵ_r for $\text{FAPbI}_3\text{-M}$. We find that adding MDACl_2 to the precursor solution significantly reduces the trap density from a lower bound of 1.1×10^{12} cm^{-3} for FAPbI_3 to 4.3×10^{10} cm^{-3} for $\text{FAPbI}_3\text{-M}$.

The improvement in optoelectronic quality of these $\text{FAPbI}_3\text{-M}$ single crystals is supported by time-resolved photoluminescence (TRPL) measurements (depicted in Figure 1b). Fitting the TRPL decay traces reveals a significant increase in a lifetime from 47 ns for the FAPbI_3 single crystal to 121 ns for the $\text{FAPbI}_3\text{-M}$ single crystal at a fluence of 18 nJ cm^{-2} . More details on this measurement and the fitting are given in the Supporting Note 3. To assess if $\text{FAPbI}_3\text{-M}$ crystals also improve optoelectronic devices, we fabricate photodetectors from the single crystals. Figure 1c,d shows the current density curve of FAPbI_3 and $\text{FAPbI}_3\text{-M}$ single-crystal detectors. We observe a higher photoconductivity for $\text{FAPbI}_3\text{-M}$ photodetectors and an improved ON/OFF ratio (Supporting Figure S7).

Significantly, we also find that $\text{FAPbI}_3\text{-M}$ crystals possess substantially greater α -phase (black) stability in ambient air than neat FAPbI_3 . By visible light microscopy, we observe the growth of trace regions of a δ -phase (yellow) on the crystal surface of both materials after only a few hours of storage in the air (Figure 1e). For $\text{FAPbI}_3\text{-M}$, the degradation does not propagate significantly on the surface or into the bulk, as seen when we cleave the crystals after several hours. Notably, $\text{FAPbI}_3\text{-M}$ crystals remain predominantly in their α -phase after one year of storage in ambient air. By contrast, FAPbI_3 crystals display complete phase transformation to the photoinactive δ -phase within a few days (Figure 1e and Supporting Figure S8).

To quantitatively track the phase stability of the crystals, we monitor the absolute Raman intensity of the best resolved δ -phase peak (at a Raman shift of 108 cm^{-1}) under ambient conditions. As Figure 1f shows (complete Raman spectra shown in Figure S9), neat FAPbI_3 undergoes detectable δ -phase formation after 7 days. This onset occurs at 11 days for $\text{FAPbI}_3\text{-M}$. In Raman spectra of the same crystals after 1 year of storage in air-filled vials, we detect $(2.5 \pm 0.5) \times 10^3$ and $(0.25 \pm 0.06) \times 10^3$ δ -phase peak counts for FAPbI_3 and $\text{FAPbI}_3\text{-M}$, respectively. Peak intensity is proportional to the fraction of the probed surface layer in the δ -phase. Notably, the thickness of the probed layer for α -phase FAPbI_3 is estimated to be ~ 100 nm via the absorption coefficient (ca. 10^5 cm^{-1} at the Raman laser wavelength of 532 nm).³⁰ Thus, the onset of the δ -phase peak in Figure 1f corresponds to the degradation of only the top surface of the crystals. We obtain complementary degradation data of the bulk crystal by carrying out the same Raman measurement on the exposed interior of freshly cleaved crystals, different from those presented in Figure 1f. Cleaving a $\text{FAPbI}_3\text{-M}$ crystal after 285 days of aging gives a peak intensity ratio of $I_{\text{bulk}}/I_{\text{surface}} = 0.10 \pm 0.03$ for the δ -phase peak. This confirms that the observed δ -phase formation occurs predominantly in a thin surface layer of $\text{FAPbI}_3\text{-M}$ crystals, while the bulk remains largely unaffected. By contrast, the neat FAPbI_3 crystal is entirely converted to the δ -phase.

MDA²⁺ Solution Instability. Having established the substantial advantages of MDACl_2 addition for FAPbI_3

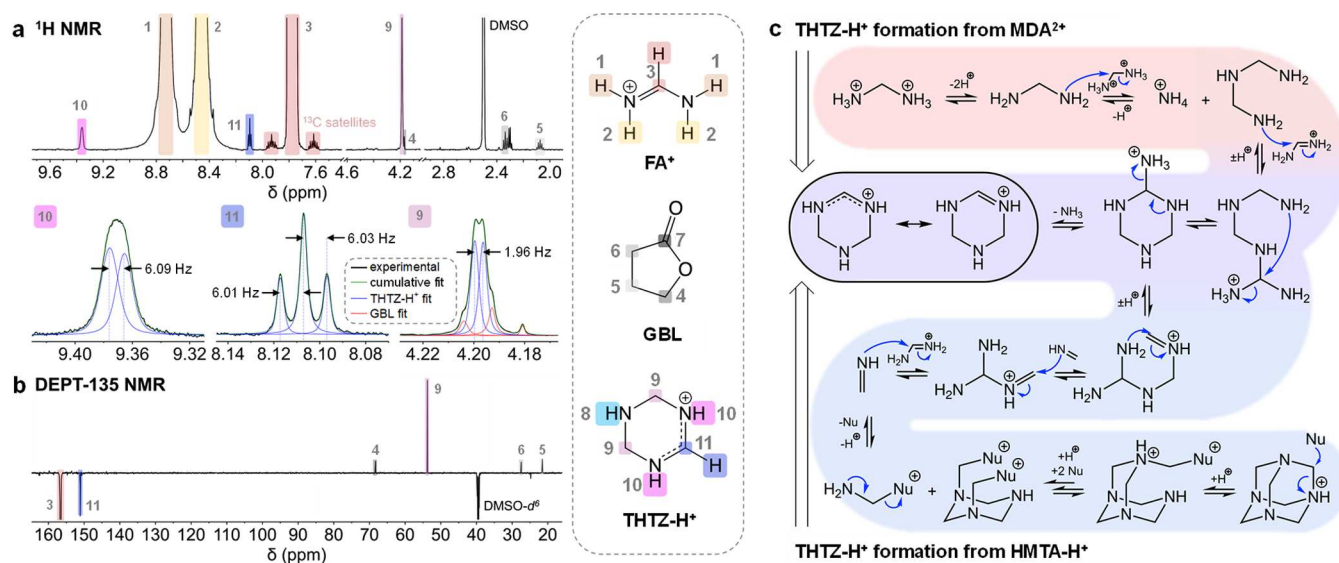


Figure 3. FAPbI₃-M single-crystal composition. ¹H solution (a) and directionless enhancement by polarization transfer (¹H–¹³C) (DEPT-135) (b) NMR spectra (600 MHz) of FAPbI₃-M single crystal dissolved in DMSO-*d*₆. Spectra are referenced to the DMSO signal. Insets below ¹H spectra show expansions of signals corresponding to THTZ-H⁺ with signal fitting and spin–spin coupling constants displayed in Hz. (c) Proposed mechanism for the formation of THTZ-H⁺ from MDA²⁺ (top left) or HMTA-H⁺ (bottom right) via generation of 2 equiv of methanimine and reaction with FA⁺. Nu corresponds to any available nucleophile in solution, most likely the HMTA additive. Further discussion is presented in Supporting Note 6.

single-crystal properties, we now investigate the activity of this additive in solution. It has been previously inferred that MDA²⁺ is incorporated within the cubic ABX₃ perovskite lattice on the A-site in solution-processed polycrystalline thin films based on FAPbI₃, and thus, A-site cation mixing is thought to be responsible for the enhanced α -phase stability.^{20,21} However, we find that MDA²⁺ degrades rapidly in precursor solutions. Figure 2a shows the ¹H solution NMR spectra acquired from a solution of MDACl₂ dissolved in DMSO-*d*₆ between 5 and 120 min after initial dissolution (expanded spectra shown in Supporting Figure S11). In Figure 2b, we show an expanded view of the earliest of these spectra, emphasizing the presence of a number of signals that appear to correspond to intermediate species that exist only transiently. At the shortest time after dissolution, the ¹H NMR spectrum already shows several unexpected species. We attribute the distinctive 1:1:1 triplet at 7.34 ppm to NH₄⁺, with the splitting due to spin–spin coupling of ¹H to the quadrupolar (*I* = 1) ¹⁴N nucleus (¹*J*_{N–¹H} = 50.8 Hz). The signal, initially at 7.34 ppm, rapidly shifts and stabilizes at 7.37 ppm, as is typical for ammonium species under varying pH conditions.³¹ This assignment is confirmed by comparison with the solution ¹H NMR spectra of NH₄Cl in DMSO-*d*₆ (Supporting Figure S12). ¹H–¹H correlation spectroscopy (COSY), depicted in Supporting Figure S13, reveals that the two other substantial signals initially present in the ¹H solution NMR of MDACl₂ solutions are spin–spin coupled and thus correspond to nuclei present in the same species. Figure 2c highlights the coupling of one of these signals (4.42 ppm), which we find is superposed on top of another low-intensity signal, both of which we interpret as quartets. Given C–C bond formation is unlikely under the conditions, the resolution of this spin-coupling along with the chemical shift suggests a CH_{*n*} environment adjacent to a ⁺NH₃ group. In Supporting Note 6, we present the findings from a series of further experiments investigating the evolution of intermediate degradation species

and discuss our interpretation. From all these data, we infer that the most likely assignment for the dominant intermediate observed is MDA⁺ in which the amine group is undergoing rapid chemical exchange with acidic NH₄⁺ in solution (Figure 2b). The accumulation of this species is mechanistically justified. When the charge-dense MDA²⁺ cation is dissolved in pH neutral, aprotic polar solvents such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and GBL, it is expected to act as a Brønsted acid, rapidly releasing H⁺ to become MDA⁺ and acidifying the solution environment, as shown in Figure 2d. Release of a second acidic H⁺ is possible, although less favorable in the acidified solution environment. However, this second deprotonation event yields neutral MDA⁰, a potent nucleophile. The presence of both MDA⁺ and MDA²⁺, a strong electrophile, renders both species unstable in solution with respect to the formation of NH₄⁺ and bis(aminomethyl)-ammonium (B⁺). Thus, under these conditions, MDA⁺ is the most stable form of this species. MDA⁺ can also act as an electrophile; however, its single charge renders it less reactive than MDA²⁺. It may also eliminate to produce NH₃ and methaniminium, CH₂=NH₂⁺. However, elimination reactions are typically slow, and the production of methaniminium—itsself a highly reactive electrophile—does not alter the course of the degradation. We propose a complete mechanistic description in Supporting Figure S15.

Transient deprotonation of B⁺ produces B⁰, another nucleophile, which reacts with further MDA²⁺ before rapidly cyclizing to form 1,3,5-triazinane (C). Repeated reaction of C with MDA²⁺ in conjunction with rapid cage-closure, driven entropically by the release of additional NH₄⁺, is expected to lead to the formation of HMTA-H⁺, as shown in Figure 2d. Experimentally, between 5 and 50 min after the initial dissolution of MDACl₂, a singlet signal of increasing intensity is observed in the ¹H solution NMR spectra at 4.83 ppm. By 120 min after initial dissolution, the spectrum consists only of this singlet, the 1:1:1 triplet corresponding to ammonium, and a broad singlet at 8.00 ppm. HMTA dissolved in DMSO-*d*₆ at

neutral pH shows a singlet at 4.56 ppm (Supporting Figure S16). However, incremental addition of hydrochloric acid to this solution produces a downfield shift of this singlet to 4.83 ppm in line with the reported monoprotic pK_{aH} value for HMTA (4.93),³² confirming the identity of the final product of MDA²⁺ degradation as HMTA-H⁺. Integration of the relevant ¹H NMR signals confirms the stoichiometric 8:1 ratio of NH₄⁺/HMTA-H⁺ expected by the proposed degradation route. As observed with MDA⁺, rapid chemical exchange between the acidic H⁺ of HMTA-H⁺ and ammonium leads to a broadened ¹H NMR signal at a chemical shift corresponding to the weighted average of the contributing chemical environments (7.45 ppm). We emphasize that despite the bias toward the formation of HMTA-H⁺ and NH₄⁺, as all reaction steps are mechanistically reversible, it should be expected that the system at dynamic equilibrium will include small quantities of all intermediates. Further, we note that our aim has not been to attempt to stabilize either MDA²⁺ or MDA⁺ in solution, which may be achievable, for example, by the addition of excess acid, but that this is certainly an avenue for further investigation.

FAPbI₃-MDACL₂ Precursor Solution Chemistry. Having identified that HMTA and NH₄Cl are the degradation products of MDACL₂ in the aprotic organic solvents, we now investigate if either degradation product plays an active role in improving FAPbI₃ crystal properties. We first perform the crystal growth as described above but with the separate addition of either HMTA or NH₄Cl. Each additive is added in the 8:1 stoichiometry expected when 3.8 mol % MDA²⁺ degrades entirely to NH₄⁺ (5.07 mol %) and HMTA-H⁺ (0.63 mol %). FAPbI₃ crystals grown with NH₄Cl additive alone undergo α -phase degradation at a rate comparable to FAPbI₃ single crystals grown without additives. Strikingly, however, FAPbI₃ crystals grown in the presence of HMTA (FAPbI₃-H) show neither surface degradation nor bulk degradation to the δ -phase (Figure 1e). We quantify the stability of FAPbI₃-H using Raman spectroscopy, as we report above for FAPbI₃ and FAPbI₃-M crystals, and find that, after 132 days of ambient air aging, FAPbI₃-H crystals show no evidence (0 counts, background subtracted) of δ -phase formation (Figure 1f).

Having established that replacing MDACL₂ addition with a corresponding quantity of HMTA mimics the α -phase stability enhancement of FAPbI₃-M, we conduct liquid-state ¹H and directionless enhancement by polarization transfer (DEPT-135, ¹H-¹³C) NMR spectroscopy (Figure 3a,b, respectively) on solutions of FAPbI₃-M crystals dissolved in DMSO-*d*₆. Unexpectedly, we do not detect the presence of HMTA-H⁺. Instead, in the ¹H spectrum, we observe signals at 9.36 (d, 6.09 Hz), 8.10 (t, 6.02 Hz), and 4.19 (d, 1.96 Hz) ppm in 2:1:4 stoichiometry. Analysis of the fine structure of each of these signals suggests spin-spin coupling between nuclei giving rise to the signals at 8.10 and 9.36 ppm, with a *J*-coupling constant consistent with vicinal ¹H-¹H coupling trans across a sp² system (³*J*_{H9-H10} ~ 6 Hz). To confirm this, we carry out ¹H-¹H COSY (Supporting Figure S17). These data confirm the ³*J*_{H9-H10} coupling, while an off-diagonal cross-peak between signals at 9.36 and 4.19 ppm suggests spin-spin coupling and thus atomic proximity between these chemical environments. The DEPT-135 ¹³C spectrum shows a CH/CH₃ signal (151.1 ppm) with a chemical shift comparable to the methine of FA⁺ (156.6 ppm) and a CH₂ signal at 53.8 ppm, indicating an electron-depleted sp³ environment. These data are consistent with the presence of tetrahydro-1,3,5-triazinium (THTZ-

H⁺).³³ Integration of ¹H methine signals in both species indicates that THTZ-H⁺ is present in solution at ~0.5 mol % with respect to FA⁺. From these findings, it is evident that the degradation of MDA²⁺ is further complicated by the presence of other organic cations in our precursor solutions, in this instance FA⁺.

Acquisition of ¹H NMR spectra over time upon the addition of 3.8 mol % MDACL₂ to a solution of FAI in DMSO-*d*₆ initially shows the formation of only HMTA-H⁺ and NH₄⁺ (Supporting Figure S18). However, upon aging, a third product gradually evolves, THTZ-H⁺. From this, we infer that, while HMTA-H⁺ and NH₄⁺ are the kinetic products of MDACL₂ degradation, in the presence of FA⁺, THTZ-H⁺ is a slower-forming but thermodynamically favored product. We account mechanistically for the formation of THTZ-H⁺ from MDA²⁺ in Figure 3c (highlighted red-purple). MDA⁰-initiated cage formation (Figure 2d) is interrupted by the addition of FA⁺. Cyclization with a single FA⁺ cation leads to THTZ-H⁺.

That all steps in the reactions of Figure 3c are either substitutions or eliminations and thus mechanistically reversible, which is critical to the activity of MDA²⁺ in FAPbI₃ crystal growth for two reasons. First, reversibility ensures that the whole reaction pathway is in dynamic equilibrium in solution. Thus, although HMTA-H⁺ formation occurs most rapidly, gradual evolution of a more favorable product by subsequent consumption of HMTA-H⁺ is possible, as emphasized in Figure 3c (highlighted blue-purple). This explains the gradual formation of THTZ-H⁺ in solution over time from a solution of MDACL₂ and FAI (Supporting Figure S18). Second, the selective removal of any species from such a dynamic system disturbs it from equilibrium, resulting in the production of more of the species removed, in line with Chatelier's principle.³⁴ Repeated incorporation of THTZ-H⁺ into the solid state of a growing single crystal depletes its concentration remaining in solution, resulting in the production of further THTZ-H⁺. By this mechanism, ultimately, all MDA²⁺ added can be converted to THTZ-H⁺ via HMTA-H⁺ and incorporated into a growing single crystal, despite THTZ-H⁺ only ever being present in solution at very low concentration. As with all mechanistic details presented in this work, however, we emphasize that this scheme should be interpreted as a mechanistic justification only. We have not conducted extensive mechanistic studies and have only identified a relatively small number of the species displayed in the mechanistic schemes. This represents a chemically feasible route between the species we have clearly identified.

Significantly, the analysis above depends on the formation of THTZ-H⁺ by decomposition of HMTA (via protonation by weakly acidic FA⁺), as proposed in Figure 3c (highlighted blue). Thus, one test of our proposed mechanism is to confirm this is indeed the case. To do so, we obtain ¹H NMR spectra when single crystals grown in the presence of HMTA (FAPbI₃-H) or NH₄Cl are dissolved in DMSO-*d*₆ (Supporting Figures S20 and S21). In line with the mechanism presented, we find that signals corresponding to THTZ-H⁺ are observed in the spectra of all crystals grown with either HMTA or MDACL₂ present in their precursor solution but not when NH₄Cl alone is added. The absence of any signals in these spectra corresponding to ammonium or HMTA confirms that these additives are not included in the materials. We have therefore correlated the enhanced α -phase stability of FAPbI₃-M and FAPbI₃-H crystals with the presence of THTZ-H⁺ in solutions of dissolved single crystals.

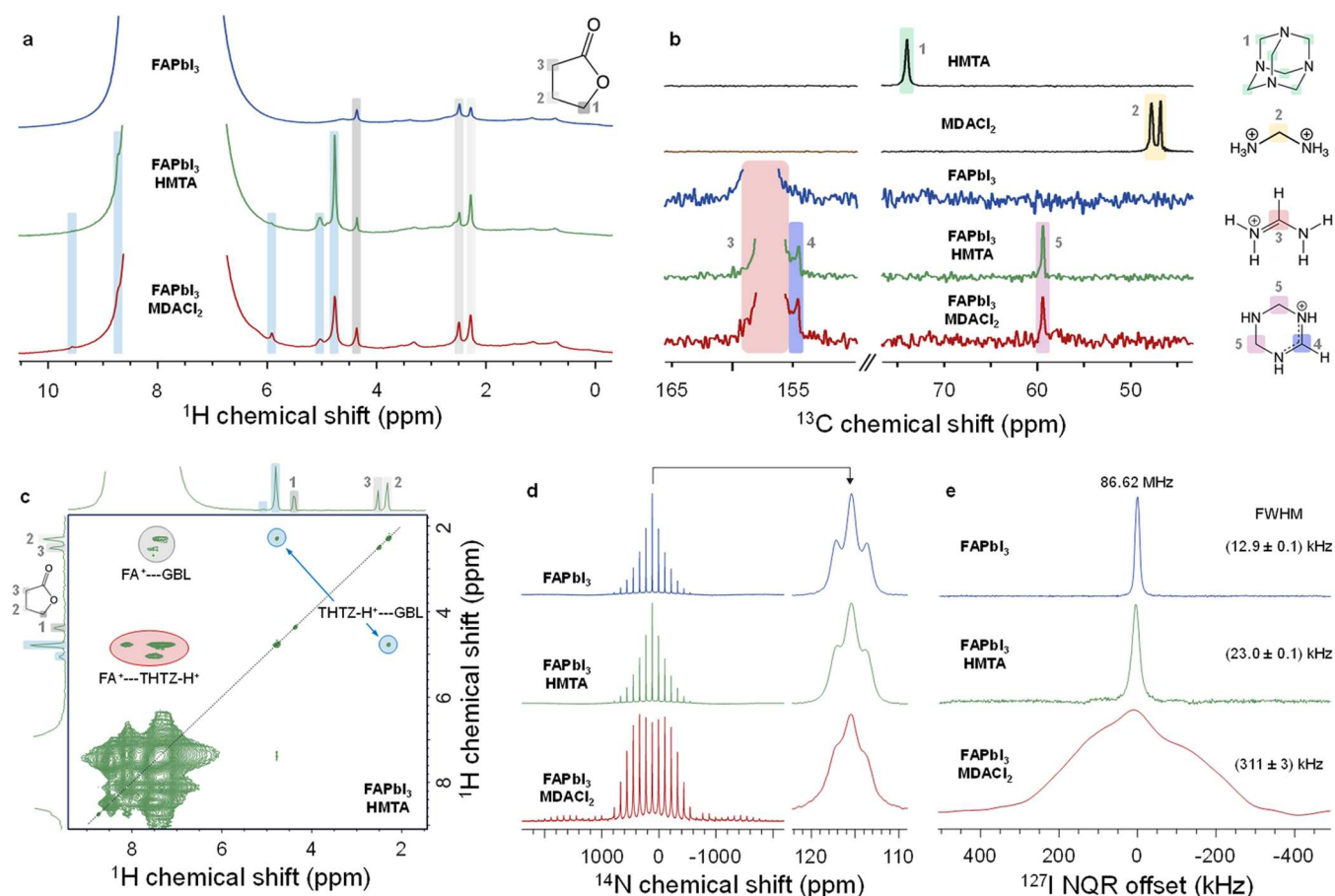


Figure 4. Solid-state characterization of the FAPbI₃ single crystal. (a) ¹H MAS (50 kHz) NMR spectra of neat FAPbI₃, FAPbI₃-H, and FAPbI₃-M crystals. Signals highlighted in blue cannot be unambiguously assigned. (b) ¹³C echo-detected (12 kHz MAS) NMR spectra comparing different FAPbI₃ crystals with additives employed in their growth. (c) ¹H-¹H (50 kHz MAS) spin-diffusion spectrum of FAPbI₃-H. (d) ¹⁴N (4 kHz MAS) NMR spectra of FAPbI₃, FAPbI₃-H, and FAPbI₃-M crystals (left). The central signal of the spectral envelope is shown in the inset to the right. (e) ¹²⁷I NQR spectra of FAPbI₃, FAPbI₃-H, and FAPbI₃-M crystals. The color schemes correlate detected signals with chemical environments of relevant nuclei in detected species.

Solid-State Compositional Analysis of FAPbI₃ Single Crystals.

When FAPbI₃-M or FAPbI₃-H single crystals are dissolved, a solution rich in FA⁺ and with only trace quantities of THTZ-H⁺ is produced. However, as we have shown, THTZ-H⁺ formation occurs spontaneously in solutions containing FA⁺ alongside MDA²⁺, HMTA, CH₂=NH₂⁺, or many intermediates in the decomposition of these. Therefore, the observation of THTZ-H⁺ in solutions of dissolved crystals does not confirm that this species is present in the crystals in the solid state. Kinetic entrapment of another intermediate species during crystal growth, e.g., CH₂=NH₂⁺, might be expected to produce the same solution once dissolved. Nor do our liquid-state experiments provide any evidence of how a new organic species might be incorporated into the perovskite material structurally. Moreover, density functional theory (DFT) calculations assign a steric radius of 2.65 Å for THTZ-H⁺ (details of our calculations are given in Supporting Note 7). This value is only slightly larger than those for dimethylammonium (DMA⁺, 2.43 Å), ethylammonium (EA⁺, 2.42 Å), and guanidinium (GUA⁺, 2.40 Å). These three cations have all been reported as forming metastable mixed-cation 3D perovskite phases with FA⁺.^{35–37} As discussed in Supporting Note 7, these data alone do not allow us to conclude whether THTZ-H⁺ incorporates the 3D APbI₃ perovskite A-site. Therefore, to better investigate the composition of the crystals,

we conduct a range of solid-state NMR (ssNMR) measurements.

In Figure 4a, we show ¹H magic angle spinning (MAS) NMR spectra of FAPbI₃, FAPbI₃-M, and FAPbI₃-H crystals. While the spectra are dominated by intense FA⁺ signals (6–9 ppm), several additional, well-resolved signals (highlighted in blue) are present in both FAPbI₃-M and FAPbI₃-H spectra that are not present in neat FAPbI₃ crystals. These signals correspond to ¹H environments in organic species other than FA⁺. Although it is not possible to assign these signals based on the ¹H spectra alone, we note their close correspondence to those observed in liquid ¹H NMR of the same crystals (Figure 3a). Further, we observe clear evidence of GBL in all three crystals, suggesting that small quantities of the processing solvent are entrapped within the crystals, despite prolonged vacuum drying (110 °C, overnight).^{11,38} By recording quantitative ¹H solid-state NMR spectra, and assuming the same number of hydrogen nuclei in FA⁺ and the additive, we estimate that the new species is present at ~0.5 mol % in both FAPbI₃-M and FAPbI₃-H crystals (see Supporting Figure S24 for the integrated regions).

To confirm that the additive detected in the solid state is indeed THTZ-H⁺, we perform ¹³C MAS NMR (Figure 4b). As in the case of ¹H, we observe new signals (154.5, 59.4 ppm) in FAPbI₃-M and FAPbI₃-H, which are identical in both

materials, but are absent in reference FAPbI₃. This result corroborates that the same species is present in FAPbI₃-M and FAPbI₃-H despite their differing growth environments. The new signals do not correspond to MDACl₂ (46.8, 47.7 ppm), HMTA (74.0 ppm), or δ -FAPbI₃ (157.3 ppm, Supporting Figure S25). Instead, they closely match those expected for THTZ-H⁺ as observed via DEPT-135 in solution (151.1, 53.8 ppm) (Figure 3b).

Having detected the presence of THTZ-H⁺ in the single crystals, we next seek to elucidate its mode of incorporation within the perovskite material. This question is important since THTZ-H⁺ may be too large to replace FA⁺ on the A-site, and therefore, how it might interact with the ABX₃ material is unclear. We first perform a ¹H–¹H spin-diffusion (SD) experiment, which relies on the exchange of magnetization between dipolar-coupled protons, which necessarily are in atomic-level contact on the order of tens of Å.³⁹ SD therefore indicates whether the different local ¹H environments are present within the same phase, which is the prerequisite for their being dipolar coupled.³⁹ Figure 4c shows the ¹H–¹H SD spectrum of FAPbI₃-H. We observe intense cross-peaks between FA⁺ and THTZ-H⁺, as well as between GBL and both cations. Thus, we infer that a mixed phase containing THTZ-H⁺ and FA⁺ exists in FAPbI₃-H and FAPbI₃-M rather than an isolated THTZ-H⁺ secondary phase. Further discussion of the SD experiments regarding structural models of THTZ-H⁺ incorporation is given in Supporting Note 8.

We next use ¹⁴N MAS NMR to establish if the stabilization protocol leads to any detectable change to the local structure of the FA⁺ cations. It has previously been shown that ¹⁴N MAS NMR can be employed as a sensitive technique to probe perovskite lattice distortions from the perspective of A-site cation dynamics.^{37,40,41} ¹⁴N is a quadrupolar (*I* = 1) nucleus, and its NMR lineshape is determined by the symmetry of the local environment. In cubic α -FAPbI₃, FA⁺ rapidly reorients on a ps timescale, giving a near-isotropic electric field around the ¹⁴N nuclei. The interaction between the small residual electric field gradient (EFG) at the ¹⁴N nucleus and the electric quadrupole moment (*eQ*) of the ¹⁴N nuclear spin leads to a relatively narrow FA⁺ signal linewidth and a narrow envelope of spinning sidebands.⁴² Incorporation of additive ions in the ABX₃ lattice or distortions in the cuboctahedral haloplumbate structure de-symmetrize the A-site, leading to increased anisotropy in FA⁺ dynamics, an increased EFG at the FA⁺ ¹⁴N nuclei and a broadening of the spectral envelope.^{37,40,41} ¹⁴N MAS NMR reveals a pronounced broadening of the spectral envelope of FAPbI₃-M, which is not observed in the spectra of either FAPbI₃-H or neat FAPbI₃ (Figure 4d). This implies the incorporation of a new species into FAPbI₃-M crystals that is not present under the growth conditions of FAPbI₃-H or neat FAPbI₃. Considering the consistency between the ¹³C and ¹H ssNMR spectra and the comparable quantities of THTZ-H⁺ detected in FAPbI₃-M and FAPbI₃-H crystals, we attribute this broadening to the presence of chloride in FAPbI₃-M crystals. To confirm and quantify the presence of chloride, we perform electron probe microanalysis (EPMA) on FAPbI₃-M and FAPbI₃ crystals. These measurements show that chloride makes up ~0.8 atom % of total halide content inside the bulk of FAPbI₃-M (Supporting Note 9).

Incorporation of THTZ-H⁺ into the α -FAPbI₃ phase might be expected to also result in changes in ¹⁴N MAS NMR. However, we detect no significant difference between FAPbI₃-

H and reference FAPbI₃, where spectral broadening due to chloride incorporation is absent. The absence in the spectra of signals corresponding to ¹⁴N in incorporated THTZ-H⁺ suggests that these signals are substantially broadened with intensity spread across a large number of spinning sidebands resulting in their not being detectable. This result suggests that the EFGs at the ¹⁴N nuclei of THTZ-H⁺ are relatively large, most likely due to incorporated THTZ-H⁺ being static, consistent with its strong coordination to the ABX₃ structure.

To better isolate the independent effects of THTZ-H⁺ and chloride incorporation, we conduct ¹²⁷I nuclear quadrupole resonance (NQR) spectroscopy on the three materials (Figure 4e). NQR measurements are carried out without an external magnetic field and are a direct measure of the strength of the local EFG. Because the electric quadrupole moment of ¹²⁷I is remarkably large (–71 Q fm^{–2}, compared to the value for ¹⁴N: 2 Q fm^{–2}), small structural changes lead to large changes to the NQR frequency. Interrogation of the full-width half-maxima (FWHM) of the NQR transition at 86.62 MHz shows resolvable differences between all three FAPbI₃ materials. We attribute the doubling of the FWHM in FAPbI₃-H relative to FAPbI₃ to the incorporation of THTZ-H⁺ into the perovskite structure, which leads to the emergence of a distribution of ¹²⁷I local environments (static disorder) throughout the bulk. This would not be the case if THTZ-H⁺ were merely adsorbed on the surface of the crystal or kinetically trapped in a pocket of entrapped precursor solution during crystallization (as is the case during agglomeration and formation of crystal inclusions).⁴³ The formation of a solid solution, whereby THTZ-H⁺ is distributed homogeneously throughout the bulk, is therefore the only scenario that agrees with the experimental ¹H–¹H spin-diffusion and ¹²⁷I NQR data (discussed further in Supporting Note 8). As our steric radius calculations (Supporting Note 7) indicate a substantially larger radius for THTZ-H⁺ (2.65 Å) than even FA⁺ (2.24 Å), we preclude interstitial THTZ-H⁺ as the mode of incorporation, although neither our NMR nor NQR measurements are capable of confirming this explicitly. We therefore propose a substitutional solid solution whereby one or more ions in the α -FAPbI₃ structure are replaced by THTZ-H⁺, consistent with THTZ-H⁺ being static and strongly coordinated within the ABX₃ structure, as inferred from our ¹⁴N NMR. The same ¹²⁷I NQR transition (86.62 MHz) in FAPbI₃-M crystals is broadened by approximately an order of magnitude more than FAPbI₃-H, in line with additional disordering induced by the incorporation of chloride in addition to THTZ-H⁺. Previous work assessing the impact of bromide substitution in α -FAPbI₃ on ¹²⁷I NQR broadening suggests approximately a 1% halide substitution, consistent with our EPMA results.⁴⁴

CONCLUSIONS

Precisely determining the composition and structure of complex materials is often crucial, yet highly involved. Here, we have demonstrated that growth of α -FAPbI₃ single crystals in the presence of MDACl₂, a high-performance additive, leads to significantly reduced trap density and improved ambient α -phase stability. However, by systematically studying the solution growth conditions, we find that MDA²⁺ degrades rapidly in solution and thus cannot be incorporated into the α -FAPbI₃ material, in contrast to previous assumptions. Instead, we show that HMTA-H⁺ and NH₄⁺ are generated in solution as the majority degradation products. From this informed position, we propose and demonstrate an evolved form of this

highly phase-stable material, FAPbI₃-H. However, utilizing a multidisciplinary suite of characterization techniques, we find that neither FAPbI₃-M nor FAPbI₃-H crystals show evidence of incorporation of MDA²⁺, HMTA-H⁺, NH₄⁺, or any other intermediates in the degradation of MDA²⁺. Instead, THTZ-H⁺ is detected in these crystals. We also discover that chloride is present in FAPbI₃-M crystals. However, the comparable α -phase stability of our FAPbI₃-H material allows us to isolate that it is THTZ-H⁺, not chloride, that leads to the improved stability. We rationalize the formation of THTZ-H⁺ mechanistically and perform experiments confirming that this new cation is distributed homogeneously throughout the single crystals. Using a combination of ¹H-¹H spin-diffusion solid-state NMR and ¹²⁷I nuclear quadrupole resonance spectroscopy, we determine that the THTZ-H⁺ cations are incorporated into the perovskite structure in atomic-level contact with FA⁺ and leading to an appreciable distortion of the cuboctahedral symmetry. Our work will have direct consequences for the future development of high-efficiency and high-stability perovskite photovoltaic devices.

■ ASSOCIATED CONTENT

Data Availability Statement

All relevant data are provided in the figures, table, and Supplementary Information. The raw NMR, SCXRD, PV-SCLC, and Raman data as well as input files of the DFT calculations and optimized geometries are available on Oxford University Research Archive.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.3c01531>.

Experimental section: materials and synthesis, X-ray diffraction, electrical characterization, photodetectors, Raman spectroscopy, NMR spectroscopy, first principles calculations, electron probe microanalysis (PDF)

Accession Codes

CCDC 2243417–2243418 and 2243718 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

Henry J. Snaith – Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom; orcid.org/0000-0001-8511-790X;
Email: henry.snaith@physics.ox.ac.uk

Juan Luis Delgado – POLYMAT, University of the Basque Country UPV/EHU, 20018 Donostia–San Sebastián, Spain; Ikerbasque, Basque Foundation for Science, 48013 Bilbao, Spain; orcid.org/0000-0002-6948-8062;
Email: juanluis.delgado@polymat.eu

Authors

Elisabeth A. Duijnste – Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom; orcid.org/0000-0002-7002-1523

Benjamin M. Gallant – Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom; orcid.org/0000-0001-7413-291X

Philippe Holzhey – Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom; orcid.org/0000-0003-3688-1607

Dominik J. Kubicki – Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom; orcid.org/0000-0002-9231-6779

Silvia Collavini – POLYMAT, University of the Basque Country UPV/EHU, 20018 Donostia–San Sebastián, Spain; orcid.org/0000-0002-2455-1136

Bernd K. Sturda – Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom; orcid.org/0000-0001-6533-4958

Harry C. Sansom – Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom; orcid.org/0000-0003-0329-2822

Joel Smith – Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom; orcid.org/0000-0001-6889-4408

Matthias J. Gutmann – ISIS Facility, STFC Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Oxfordshire OX11 0QX, United Kingdom; orcid.org/0000-0001-7737-3364

Santanu Saha – Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom; orcid.org/0000-0001-7334-7214

Murali Gedda – King Abdullah University of Science and Technology (KAUST), KAUST Solar Center (KSC), Thuwal 23955-6900, Saudi Arabia; orcid.org/0000-0003-1247-6623

Mohamad I. Nugraha – King Abdullah University of Science and Technology (KAUST), KAUST Solar Center (KSC), Thuwal 23955-6900, Saudi Arabia; Research Center for Advanced Materials, National Research and Innovation Agency (BRIN), South Tangerang 15314 Banten, Indonesia; orcid.org/0000-0001-9352-1902

Manuel Kober-Czerny – Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom; orcid.org/0000-0002-7807-3133

Chelsea Xia – Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom; orcid.org/0000-0001-7920-6973

Adam D. Wright – Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom; orcid.org/0000-0003-0721-7854

Yen-Hung Lin – Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom; orcid.org/0000-0001-6819-1235

Alexandra J. Ramadan – Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom; Department of Physics and Astronomy, The University of Sheffield, Sheffield S3 7RH, United Kingdom; orcid.org/0000-0003-4572-3459

Andrew Matzen – Department of Earth Sciences, University of Oxford, Oxford OX1 3AN, United Kingdom; orcid.org/0009-0005-2422-2737

Esther Y.-H. Hung – Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom; orcid.org/0000-0002-1176-2700

Seongrok Seo – Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom; orcid.org/0009-0000-6032-2747

Suer Zhou – Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom; orcid.org/0000-0002-7507-9943

Jongchul Lim – Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom; Graduate School of Energy Science and Technology (GEST), Chungnam National University, Daejeon 34134, Korea; orcid.org/0000-0001-8609-8747

Thomas D. Anthopoulos – King Abdullah University of Science and Technology (KAUST), KAUST Solar Center (KSC), Thuwal 23955-6900, Saudi Arabia; orcid.org/0000-0002-0978-8813

Marina R. Filip – Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom; orcid.org/0000-0003-2925-172X

Michael B. Johnston – Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom; orcid.org/0000-0002-0301-8033

Robin J. Nicholas – Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom; orcid.org/0000-0001-9025-0465

Complete contact information is available at: <https://pubs.acs.org/10.1021/jacs.3c01531>

Author Contributions

*E.A.D., B.M.G., and P.H. contributed equally to this work.

Notes

The authors declare the following competing financial interest(s): H.J.S. is a co-founder and Chief Scientific Officer of Oxford PV Ltd., a company industrialising perovskite PV. A patent has been filed by Oxford University related to this work.

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