

Bypassing Solid-State Intermediates by Solvent Engineering the Crystallization Pathway in Hybrid Organic-Inorganic Perovskites

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Supporting Information

ABSTRACT: Hybrid organic-inorganic perovskites (HOIPs), such as CH₃NH₃PbI₃ (MAPbI₃), are attractive for inexpensive, high-performance solar cells. Controlling HOIP thin-film quality and morphology, which is essential to achieve consistent solar-cell efficiencies, requires a fundamental understanding of the link between solution chemistry and crystallization pathways. To elucidate the effect of solvent choice and solution speciation on the crystallization pathway, we combined computational modeling of molecular-level solvent-solute interactions in HOIP growth solutions with



experimental monitoring of film phase evolution. Using density functional theory calculations and a Bayesian optimizationbased approach (PAL), we exhaustively searched the HOIP/solvent combinatorial space to obtain a ranked list of increasing HOIP/solvent intermolecular binding energy. Then, using in situ X-ray diffraction, we tested solvents of varying coordinating abilities with MAPbI₃ to correlate the PAL-generated ranking with the crystallization pathway. Weakly coordinating solvents (e.g., N-methyl-2-pyrrolidone) formed the perovskite via a two-step crystallization pathway, where a crystalline intermediate formed and was subsequently transformed to perovskite with heating, whereas strongly coordinating solvents (e.g., tetrahydrothiophene 1-oxide) formed the perovskite directly from solution. We propose that the solution coordination chemistry determines the crystallization pathway. Our integrated experimental-computational approach could be applied to study the interplay between solution chemistry and crystallization pathways for other solution-grown materials.

INTRODUCTION

Hybrid organic-inorganic perovskites (HOIPs), with the general formula $APbX_3$, where A = methylammonium, formamidinium, cesium and $X = Cl^{-}$, Br^{-} , I^{-} , are an exciting class of photovoltaic materials.¹⁻⁴ Beyond their impressive power conversion efficiencies of over 22%,⁵ HOIPs are solution-processable, lending themselves to a more readily scalable and lower-cost approach for solar cell manufacturing in comparison to established technologies. As with more traditional solar cell materials, HOIP device performance is correlated with film quality and morphology, which, in turn, are directly determined by the crystal growth conditions, including variables such as solvent, lead salt, and anneal temperatures and times. $^{6-12}$ However, the crystal growth mechanisms governing the solution-to-solid conversion for HOIPs, and the effects of the solvent on such mechanisms, are not yet fully understood. Here, we combine computational and experimental approaches to elucidate the role of solution speciation (i.e., the formation of Pb²⁺/solvent vs iodoplumbate

complexes) in directing the crystallization pathway in HOIP thin-film growth.

Recently, for solution-grown materials, ranging from proteins to zeolites to small molecules to ionic materials, "nonclassical" kinetic pathways to crystallization have been identified. These mechanisms can involve "on-pathway" roles for ionic clusters, amorphous particles, and poorly crystalline nanoparticles.^{13–15} When clusters or nanoparticles are involved in the crystallization process, solid-state intermediates often form and subsequently transform into the final, crystalline structure, in accordance with Ostwald's empirical "rule of stages". In many of these examples, the composition, morphology, and structure of the ultimate product as well as the properties of the resulting crystalline materials are, in part, dependent upon the crystallization pathway via which they

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grew.¹⁶ Numerous studies have noted that HOIP thin-film growth often proceeds via a two-step crystallization pathway, involving the formation of a solid-state intermediate, which forms during spin coating and transforms to the perovskite with heating.^{10,17–22} In the literature, multiple possible structures for the solid-state intermediate have been proposed,^{21,23,24} and it is clear that there are multiple different intermediates that form depending on the specific growth conditions used. In an attempt to control the transformation of these solid-state intermediates to the desired perovskite phase, multiple solvent engineering approaches have been introduced, including the addition of antisolvents to strip away tightly coordinated solvent molecules from the intermediate.²⁵ In this work, we ask the question "can the two-step crystallization pathway be avoided by an initial choice of solvent?".

Previous experimental and theoretical work suggests that the formation of solution complexes could play an important role in determining the crystallization pathway of HOIPs. UV-vis absorption spectroscopy studies of MAI/PbI₂ solutions indicate the formation of iodoplumbate complexes (PbI_n^{2-n}) in solution.^{12,26–28} Moreover, a comparison of the absorption spectra of as-deposited MAPbI₃ films to those of the solutions from which the films were deposited suggests that the observed solid-state intermediate consists of a mixture of iodoplumbate complexes of varying degrees of coordination.²⁷ In other work, we have shown that density functional theory (DFT) calculations are capable of representing experimental trends in $\Delta H_{\rm solv}$ as the solvent is varied. We have also described the benefit of a cost-effective ersatz of ΔH_{solv} in the guise of the unsaturated Mayer bond order (UMBO) regarding the solvation of Pb²⁺ ions.²⁹ Notably, both the enthalpy of solvation and the UMBO vary significantly as a function of the solvent, suggesting that the type and distribution of solution complexes will vary with solvent choice.

In a small number of studies, one-step crystallization of the perovskite has been reported. Specifically, methylammonium formate,³⁰ an ionic liquid, and a strongly coordinating solvent, tetrahydrothiophene 1-oxide (THTO),³¹ lead to the direct crystallization of MAPbI₃ films. These reports hint that solvent choice is critical for determining the crystallization pathway; however, the link between the solution chemistry and the first crystalline phase to appear during HOIP film growth has yet to be clearly established.

EXPERIMENTAL DESIGN

Our goal is to rank perovskite compositions and solvents, using computational approaches, to predict the experimentally observed crystallization pathway (i.e., one-step, with direct crystallization, or two-step, via a solid-state intermediate) as a function of solvent. We hypothesize that in strongly coordinating solvents, in which iodoplumbate complexes are disrupted, we will experimentally observe one-step crystallization: i.e., direct formation of the desired perovskite phase, bypassing the formation of any solid-state intermediates. To test this hypothesis, we implemented a 2-fold strategy: first, to use machine learning to computationally rank HOIP APbX₃ compositions with a given solvent in terms of the intermolecular binding energy between an APbX₃ monomer unit (which we shall call, from now on, a "HOIP monomer"), and second, to use that ranking to select solvents, which we then test experimentally to track the crystallization pathway of the HOIP films using in situ X-ray diffraction. It is essential in these experiments to only vary the solvent, while keeping everything else (e.g., starting materials, anneal temperatures and times, and final perovskite) constant. In this way, we can isolate the role solvent plays in defining the initial solution speciation and the subsequent crystallization pathway. For this reason, for all experiments, we have looked exclusively at MAPbI₃. We note, however, that this approach can be extended to look more broadly at a whole range of HOIP compositions once the initial concept is demonstrated.

MATERIALS AND METHODS

Computational Methods. As previously reported,³² our Bayesian optimization-based physical analytics pipeline (PAL) automatically calculates intermolecular binding energies for HOIP monomer/ solvent combinations. These calculations were performed for ABX₃ compositions in which $A \in \{MA^+, FA^+, Cs^+\}$, B = Pb, and $X \in A$ {Cl⁻,Br⁻,I⁻}. These variables give a total of nine possible HOIP combinations. N solvent molecules were used to calculate intermolecular binding energies. The eight different solvents used for these calculations were: tetrahydrothiophene 1-oxide (THTO), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), methacrolein (MCR), acetone (ACE), γbutyrolactone (GBL), and nitromethane (NM). Only "pure" solvents were taken into account (that is, no solvent blends were assessed). As the number of solvent molecules (N) increases, the intermolecular binding energy converges to the enthalpy of solvation; entropic effects are not considered (as DFT is effectively performed at 0 K). The enthalpy of solvation would be the ideal metric to use for our purposes here. It is, however, generally intractable to calculate, due to the large number of solvents required for convergence (e.g., on the order of 25 in the case of CsPbCl₃ in GBL). Thus, a combination of three explicit solvent molecules was used with an additional implicit solvation model (using the COSMO package) to take into account general electronic polarization of the solute.

The intermolecular binding energy was calculated by first determining the ground-state, geometry-optimized energies of three systems:

- *E*_{S₃-ABX₃} the total system of three solvent molecules (and the implicit model) with an ABX₃ salt
- E_{ABX_3} a subsystem consisting of an ABX₃ salt
- E_{S_3} a subsystem of three solvent molecules (and an implicit model)

The final value for a given system was then calculated as $\Delta \tilde{H}_{solv} = E_{S_1 - ABX_3} - E_{S_3} - E_{ABX_4}$.

Experimental Methods. *Materials.* All materials were used as received. γ -butyrolactone (GBL, \geq 99%), *N*-methyl-2-pyrrolidone (NMP, anhydrous, 99.5%), tetrahydrothiophene 1-oxide (THTO, 96%), *N*,*N*-dimethylformamide (DMF, anhydrous, 99.8%), *N*,*N*'-dimethylpropylene urea (DMPU, 98%), and hexamethylphosphoramide (HMPA, 99%) were obtained from Sigma-Aldrich. Methylammonium iodide (MAI) was obtained from greatcellsolar (formerly Dyesol; Australia). Lead(II) iodide (PbI₂, 99.999%, trace metal basis) was obtained from TCI America.

Solution Preparation. Solutions of MAI and PbI_2 in a 3/1 MAI/ PbI₂ molar ratio were prepared by weighing the salts in air and adding the appropriate volume of solvent either from a Sure-Seal solvent bottle (solvent stored under nitrogen) or in a glovebox. 40 wt % solutions were prepared for all solvents except HMPA, for which 30 wt % solutions were prepared. The salts were dissolved by stirring at room temperature or at temperatures up to 70 °C, as needed. These solutions are undersaturated with respect to MAPbI₃, and no visible crystal formation occurs within the solutions prior to spin coating.

Substrate Preparation. Perovskite films were deposited onto indium tin oxide (ITO; 15 Ω /sq, 25 mm × 25 mm × 0.4 mm)-coated or fluorine-doped tin oxide (FTO; 7–8 Ω /sq, 10 mm × 10 mm × 2.2 mm)-coated glass substrates that had been cleaned by sequential sonication in acetone and then in isopropyl alcohol for 15 min and dried under a nitrogen flow. Subsequently, the substrates were



Figure 1. Hierarchical binning of the intermolecular binding energy determined by PAL, corresponding to different HOIP/solvent combinations. Column (a) shows binding energy results for the 72 pure halide systems as a function of solvent. Columns (b–d) show binding energy results for the 240 mixed-halide systems as a function of (b) solvent, (c) cation, and (d) halide composition. The prevalence of a given color shows its tendency to bind strongly (more negative) or weakly (less negative). Data have been rounded to the nearest 5 kcal/mol to account for sampling uncertainties. The width of each bar is proportional to the number of samples that exist within a given energy bin, indicating, for example, that the majority of the candidate binding energies lie within an energy of -15 kcal/mol. All results show the intermolecular binding energy of three solvent molecules with a given HOIP monomer. For a complete list of data used to create this figure, refer to Table S1.

plasma-cleaned in air for 5 min. If cleaned substrates were stored for future use (i.e., not used for film deposition immediately after sonication and plasma cleaning), they were plasma-cleaned a second time, just prior to spin coating, for 2-3 min.

Film Preparation. Perovskite films were prepared in a glovebox, using a built-in spin coater, by depositing ~100 μ L of the 40 wt % 3/1 MAI/PbI₂ solution on a clean substrate and spinning at 2500 rpm for 30 s. Upon removal from the spin coater, the films were placed in a sealed chamber under a glovebox atmosphere (i.e., nitrogen) to protect them from moisture in the air during transportation to the XRD instrument. The time between transferring the films from the spin coater to the XRD instrument and collecting the first room-temperature XRD pattern was typically 5 min.

In Situ XRD Characterization. Films were spin-coated and immediately transferred to the XRD instrument (Bruker D8 Discover General Area Detector Diffraction System (GADDS) with a Vantec 2D detector using Cu K α radiation and a 1 mm collimator), where they were loaded onto a custom-built temperature-controlled heating stage, which was maintained at room temperature at the time of loading. Films were kept inside the sealed chamber under a nitrogen flow during the entirety of the in situ XRD characterization. Immediately after loading the films, we collected a scan at room temperature. Once this room-temperature pattern had been collected, a heating program, consisting of a 1 °C/min ramp to 110 °C followed by a 60 min hold at 110 °C, was initiated. Scans were continuously collected during the entirety of the heating ramp. Each scan was either 1 or 4 min long. 2D pattern integration and background subtraction were performed using Bruker's DIFFRAC.SUITE EVA software. For each solvent, this set of XRD measurements was performed on at least two different samples.

RESULTS AND DISCUSSION

Computational Ranking of HOIP Monomer Binding Energies. To explore the solvent coordination strength for several different solvents and a large number of HOIP compositions, we used our previously described Bayesian optimization-based PAL.³² The PAL codebase has two key components: a Gaussian process regression (GPR)-based Bayesian optimizer and an automated calculator of $\Delta \tilde{H}_{solv}$ for the HOIP monomer/solvent. The result is the discovery of HOIP/solvent pairs that maximize the intermolecular binding energy. This quantity is found via DFT for maximum accuracy and represents the strength of interaction between a candidate HOIP monomer and the solvent molecules, which are bound to it. In this work, we use PAL to exhaustively sample, and thus rank, HOIP monomer solubilities.

HOIPs exhibit an ABX₃ stoichiometry, in which A is a cation that can be organic, such as methylammonium (CH₃NH₃⁺; MA^+) or formamidinium (CH(NH₂)₂⁺; FA⁺), or inorganic, such as cesium (Cs^+) . B is a metal ion, in our case lead(II) ion (Pb²⁺), and X is a halide (I⁻, Br⁻, or Cl⁻). Using PAL, we automated the calculation of $\Delta \tilde{H}_{
m solv}$ (where $\Delta \tilde{H}$ indicates an approximate ΔH energy as an intermolecular binding energy) for 72 possible HOIP monomer/solvent combinations made from the prior mentioned cations, halides, and eight solvents: THTO, DMSO, DMF, NMP, MCR, ACE, GBL, and NM. Further, we extended this approach to the fully mixed halide systems, totaling 240 possible combinations. It should be noted that we chose to use a small number of explicit solvent molecules (N = 3) rather than representing a full solvation shell (approximately 25 solvent molecules) to keep the computational expense of DFT manageable. To ameliorate this approximation, we also employ an implicit solvent model (COSMO) to provide a mean dielectric medium.³³

After all 72 pure halide and 240 mixed-halide DFT calculations were complete, the results were pooled together in such a way as to illustrate trends (Figure 1 and Table S1).

The more negative the intermolecular binding energy, the more tightly bound the solvent molecule is to a HOIP salt. For instance, THTO (seen as red) is the most prevalent at the top of the solvent column (Figure 1b), showing itself to be a good solvent choice for multiple HOIP compositions, including MAPbI₃, MAPbI₂Br, and MAPbICl₂ (Table S1). In contrast, NM (magenta) occupies the bottom of the solvent column, showing its tendency to bind weakly to the HOIP monomers. Taken together, we observe that the strongest binding arises from a higher proportion of HOIPs solvated by THTO, preferentially containing MA⁺ and I⁻ over alternative choices of A-site cations and halides, respectively. We plot the results of pure halide systems as a function of solvent (Figure 1a) to illustrate the fact that general solvent trends do not rely on HOIP salt composition.

On the basis of Figure 1, we identified four solvents for experimental studies: THTO, DMF, NMP, and GBL. These solvents were chosen to span a large range of intermolecular binding energies covered in the ranked list. To ensure that our experiments were exclusively probing the role of solvent, we kept the MAPbI₃ HOIP composition constant and only varied the solvent (shown in Table 1). Of the four chosen solvents,

Table 1. DFT-Generated Intermolecular Binding Energies between MAPbI₃ and a Single Solvent Molecule

solvent	intermolecular binding energy (1 solvent, kcal/mol) a
THTO	-14.5
NMP	-13.2
DMF	-12.6
GBL	-9.9

^{*a*}An error of 1.2 kcal/mol was calculated as the standard deviation from sampling FAPbBrClI to THTO on the basis of 16 random starting configurations.

PAL-generated computations predict THTO to exhibit the strongest intermolecular binding energy with an $MAPbI_3$ monomer. NMP and DMF have intermediate binding energy values, and GBL has the lowest binding energy. This ranked list of candidates for experiments is used to test the hypothesis linking solvation strength to crystallization pathway.

Experimental in Situ XRD Monitoring of HOIP Thin-Film Phase Evolution. To establish a correlation between the PAL results and the crystallization pathway, we performed in situ XRD on MAPbI₃ films, grown from the four chosen solvents (Table 1), to follow the phase evolution of the films as a function of time and temperature.

First, we focus on the behavior of the THTO and NMP systems. The XRD results show that, when NMP is employed to prepare MAPbI₃ thin films, a liquid film forms upon spin coating (Figure 2a and Figure S1), as evidenced by visual inspection and the absence of an increase in background scattering with respect to the bare ITO-coated glass substrate. As soon as heating begins, at a rate of 1 °C/min, a crystalline intermediate forms, together with a comparatively small amount of perovskite. The intermediate diffraction peaks appear at locations close to those previously reported for the intermediate formed using the same (i.e., 3/1) MAI/PbX₂ stoichiometric ratio but different solvents.^{10,17,18} As the heating ramp progresses, the intermediate is completely transformed to the perovskite after 60 min at 110 °C. When THTO, the solvent with the highest binding energy (i.e., the most strongly coordinating solvent), is used, a liquid film forms upon spin coating, as evidenced by visual inspection and the absence of any increase in background scattering with respect to the bare ITO substrate, just as with NMP (Figure 2b and Figure S2). The film remains liquid until 65 °C, as indicated by the lack of any increase in background scattering during heating. At 65 °C, we observe the first evidence of formation of a crystalline phase. In contrast to NMP, no crystalline intermediate is



Figure 2. XRD patterns of perovskite thin films spin-coated using different solvents taken at key time points during heating (heating ramp of $1 \degree C$ /min from room temperature to 110 °C, followed by a 60 min hold at 110 °C) showing the overall structural evolution. Markers indicate characteristic peak locations for the intermediate (red #) and the perovskite (green +) and are used to track the transformations. Panel (a) for NMP shows the simultaneous formation of a crystalline intermediate and the perovskite from a liquid film when heating begins, followed by the intermediate fully transforming to the perovskite. Panel (b) for THTO shows direct formation of the perovskite from a liquid film. See Figures S1 and S2 for raw 2D XRD patterns from which the 1D patterns were generated.

detected and the first crystalline phase to appear is the perovskite.

DMF and GBL, the two other weakly coordinating solvents that we studied, presented behaviors similar to those observed with NMP. For both DMF and GBL, a crystalline intermediate forms immediately upon spin coating, with a complete (or almost complete) absence of the perovskite (Figure 3 and



Figure 3. XRD patterns of perovskite thin films spin-coated from two weakly coordinating solvents (DMF and GBL) taken before the start of, and after the completion of, the 1 °C/min heating ramp. These patterns are denoted as the initial and final traces, respectively. Initial XRD patterns were taken at room temperature immediately after spin coating. Final patterns were taken after holding the temperature for 1 h at 97 and 92 °C, for DMF and GBL, respectively. Markers indicate characteristic peak locations for the intermediate (red #) and the perovskite (green +) and are used to track the transformations. Both DMF (a) and GBL (b) show the immediate formation of a crystalline intermediate to the perovskite. See Figures S3 and S4 for raw 2D XRD patterns from which the 1D patterns were generated.

Figures S3 and S4). When the DMF and GBL films are heated to 97 and 92 °C, respectively, the crystalline intermediate transforms to the perovskite. The perovskite peak intensities for DMF and GBL are lower than those observed with NMP due to the use of slightly lower annealing temperatures, which are likely to yield films with poorer crystallinity. Even though both the DMF and GBL systems consistently form a solid-state intermediate, which subsequently transforms to the perovskite, the intermediate steps (i.e., the steps spanning the time from the formation of the intermediate to the end of the heating ramp) were less consistent and less well resolved than those observed for NMP.

To explore whether other strongly coordinating solvents could also suppress the formation of solid-state intermediates and confirm that THTO was not a unique case, we identified two additional solvents, N,N'-dimethylpropyleneurea (DMPU) and hexamethylphosphoramide (HMPA), which were not originally ranked among the PAL-generated list. Our calculation of the intermolecular binding energies of MAPbI₃/ DMPU and MAPbI₃/HMPA revealed that the binding energies of both of these systems were even higher in value than that for MAPbI₃/THTO (Figure 4a). From these computational results, we predict that both DMPU and HMPA would be strongly coordinating solvents. Comparing the in situ XRD plots for thin films formed from THTO (Figure 2b), DMPU, and HMPA (Figure 4b and Figures S5 and S6) demonstrates that, in all three cases, the perovskite peaks are the first peaks to appear, underscoring the similarities in crystallization pathway among these strongly coordinating solvents. We also observed several unidentified, variable peaks $(q = 13 \text{ and } 18.6 \text{ nm}^{-1})$ that we attribute to an impurity phase.

We note that in contrast to the intermediate peaks, which disappear concomitantly with the appearance of the perovskite peaks, these impurity peaks occur at later times and changes in intensity are not correlated with the appearance of the perovskite peaks.

DISCUSSION

This study has demonstrated that machine learning-accelerated computational predictions of lead salt solubilization at the molecular scale can accurately predict macroscale perovskite thin-film crystallization pathways for a given HOIP/solvent combination. We exhaustively searched a HOIP/solvent combinatorial space to maximize a property of interest (the HOIP monomer/solvent intermolecular binding energy) and thereby obtain a ranked list of HOIP/solvent combinations with increasingly effective HOIP solubilization. To avoid complications from changing the final perovskite composition, the experiments focused solely on MAPbI₃ compositions, but we emphasize that PAL can handle any HOIP composition. The PAL results in Figure 1 show that, while the absolute values vary with composition, trends in binding strength as the solvent choice is varied remain consistent across composition space.

In situ XRD correlated the PAL-generated ranking with experimental observations of the crystallization pathway (i.e., the presence or absence of solid-state intermediate formation). We experimentally tested six different solvents with the MAPbI₃ perovskite and found that the three weakly coordinating solvents (NMP, DMF, and GBL) form the perovskite via a two-step crystallization pathway, where a crystalline intermediate forms and is subsequently transformed to the perovskite with heating. In contrast, the three strongly coordinating solvents (THTO, DMPU, and HMPA) we tested formed the perovskite directly from solution. These data confirmed our hypothesis that the crystallization pathway of HOIPs is directly related to the coordinating ability of the solvent and, thus, the solution speciation. Specifically, we propose that strongly bound iodoplumbate complexes form in weakly coordinating solvents, leading to the formation of solidstate intermediates, whereas in strongly coordinating solvents solvent molecules break up the iodoplumbate complexes and the perovskite can form directly via ion by ion growth (Figure 5). UV-vis absorption spectroscopy studies on MAI/PbI₂ solutions, in which equilibrium constants for the formation of PbI₄²⁻ from PbI₃⁻ were determined for various solvents, suggest that solvents with a higher Lewis basicity can inhibit the formation of iodoplumbate complexes by occupying a higher number of coordination sites in comparison to the iodide ions.¹² Other work supports that, on average, solution complexes formed in strongly coordinating solvents have a higher coordination number and a lower iodide ligand number in comparison to those formed in weakly coordinating solvents (Figure 5).³⁵ Furthermore, the presence of iodoplumbate complexes in solutions of weakly coordinating solvents promotes the formation of larger solution species (i.e., clusters). These clusters, in turn, lead to the formation of solid-state intermediates, as suggested by the observation of $[Pb_{18}I_{44}]^{8-}$ clusters in the solid-state intermediates that form in GBL solutions.²⁴

While the crystallization behaviors of the films formed from THTO, DMPU, and HMPA were very similar, there was greater variability among the DMF, NMP, and GBL films. We propose that the higher variability of the solid-state phase



Figure 4. (a) DFT calculations of intermolecular binding energies between MAPbI₃ and a solvent molecule of THTO/DMPU/HMPA. The energy-minimized structures are presented. In all three structures, the solvent molecule is shown at the bottom, coordinated to the brown Pb cation. The interatomic Pb–O distances for THTO, DMPU, and HMPA are 2.71, 2.70, and 2.66 Å, respectively. Color key: pink, iodine; brown, lead; dark blue, nitrogen; light blue, carbon; white, hydrogen; red, oxygen; yellow, sulfur. (b) XRD patterns of a perovskite thin film spin-coated from the DMPU and HMPA solutions at key time points during heating (heating ramp of 1 °C/min from room temperature to 110 °C followed by a 60 min hold at 110 °C) showing the overall structural evolution. The green + marker indicates the location of the characteristic peak for the perovskite and is used to track the transformation. As with the THTO solvent, the first crystalline phase to appear is the perovskite. See Figures S5 and S6 for raw 2D XRD patterns from which the 1D patterns were generated.

transformation dynamics for these solvents is due to the formation of multiple species in solution and the associated solution equilibria, which lead to more complicated crystallization pathways with the formation of multiple solid-state intermediates under similar conditions. While in this work we have not structurally characterized the crystalline intermediates, in other work, single-crystal XRD studies of isolated crystalline intermediates formed in a variety of solution compositions emphasize the importance of the complexation interactions between the lead(II) centers and ligands available in solution (i.e., solvent molecules and halide ions).^{10,18,21} By monitoring frequency shifts for the solvent's vibrational modes as a function of thin-film composition, Fourier transform infrared spectroscopy has shed light on Pb/solvent complexation interactions and solvent entrapment in as-deposited films, which contained solid-state precursors.²⁰ Additionally, in other work, Raman spectra of HOIP growth solutions and the resulting thin films have provided information on cluster formation and demonstrated solvent and cluster incorporation into the intermediate structures.²⁴ Other experimental studies indicate that solvent coordinating ability is not the sole factor to determine the crystallization pathway. For example, Li et al. found that the substrate's temperature upon film deposition also plays a role in directing the crystallization pathway (e.g.,

they detected the formation of a crystalline intermediate from DMPU solutions). 11

The proposed link between solution chemistry and crystallization pathways in HOIPs (Figure 5) can be used to analyze several literature studies of crystallization pathways for HOIPs. For example, recent in situ grazing-incidence wideangle X-ray scattering (GIWAXS) work has shown that $Cs_{0.17}FA_{0.83}Pb(I_{0.83}Br_{0.17})_3$ and $MA_{0.17}FA_{0.83}Pb(I_{0.83}Br_{0.17})_3$ form crystalline intermediates when they are grown using DMSO and a 4/1 DMF/DMSO blend.³⁶ This result is consistent with PAL predictions that, for similar compositions, there is weak solvation of the HOIP monomers. Another in situ GIWAXS study indicates that, when a 4/1 DMF/DMSO blend is employed, $Cs_xFA_yMA_{1-x-y}Pb(I_{2.55}Br_{0.45})_3$ forms a wet, disordered colloidal phase, which has been referred to as a sol-gel phase, but does not form a solid-state intermediate.²² This sol-gel state has been observed for a variety of mixed and nonmixed HOIP compositions.^{22,36} However, adding Rb⁺ to the mix to prepare a $Cs_xFA_yRb_zMA_{1-x-y-z}Pb(I_{1-z}Br_z)_3$ composition, while still using a 4/1 DMF/DMSO blend, favors the formation of a previously unobserved solid-state intermediate.²² A triple-cation mixed-halide perovskite, $Cs_xFA_yMA_{1-x-y}Pb(I_{1-z}Br_z)_3$, also forms $MA_2Pb_3I_2 \cdot 2DMSO$ as an intermediate when it is prepared with a 3/7 DMF/DMSO



Figure 5. Schematic representation of the proposed relationship between solvent coordination strength and crystallization pathways for HOIPs. For strongly coordinating solvents (top), we propose a one-step crystallization pathway (solution to perovskite). For weakly coordinating solvents (bottom), we propose a two-step crystallization pathway (solution to solid-state intermediate to perovskite). Color key for the spheres: blue represents solvent molecules, gray represents Pb^{2+} ions, green represents MA^+ ions, and orange represents I^- ions.

blend but instead forms the vellow δ (i.e., nonperovskite) phase when a 3/1 DMF/DMSO blend is used.³⁷ Taken together, these results emphasize that both solvent and HOIP composition play a role in determining the crystallization pathway and suggest that there are additional pathways for HOIP growth, beyond those shown in Figure 5. Interestingly, FAPbBr₃ synthesized with a 4/1 DMF/DMSO blend forms a sol-gel phase but no solid-state intermediate.²² According to our PAL predictions (Table S1), in the pure solvents, FAPbBr₃/DMSO (-25 kcal/mol) and FAPbBr₃/DMF (-15 kcal/mol) have binding energies similar to that of MAPbI₃/ DMF (-25 kcal/mol), a combination for which we did observe a solid-state intermediate. The experimental observation of only an amorphous sol-gel phase underscores that, as the perovskite composition changes, the range of binding energies for which no solid-state intermediates are observed will most likely change.

This work highlights how the solution speciation can dictate the crystallization pathway of solution-grown materials. Importantly, our findings suggest that control over solution speciation can be gained by making small, albeit rational, changes to the growth solution composition, guided by computational studies. In the case of HOIPs, judiciously selecting a particular solvent can direct the crystallization pathway by altering the relative populations of free, wellsolvated ions, iodoplumbate complexes, and, possibly, larger clusters. Similar effects have been observed in zeolites. For example, using a specific additive can change the predominant growth species in silicalite-1 growth solutions from soluble silicate species to amorphous silica nanoparticles.³⁸ In turn, the solution speciation directs the crystallization pathway, where either monomer addition (a "classical" growth mode) or nanoparticle addition (a "nonclassical" pathway) can proceed. Furthermore, each crystallization pathway leads to distinct crystal sizes and morphologies. This correlation among solution speciation (controlled by the careful selection of solvent and/or additives, and including the formation of clusters), crystallization pathway (where solid-state intermediates can form), and crystal properties (e.g., size and morphology) has also been recently identified as important for metal organic frameworks³⁹ and other zeolites.^{40,41} Establishing relationships between solution chemistry and crystallization pathways has also been shown to be important for organic polymorphic compounds.⁴²⁻⁴⁴ Compounds such as p-aminobenzoic acid,⁴⁴ tetrolic acid,⁴² and glycine,⁴³ where H bonding can lead to the formation of dimers, serve as interesting examples of how molecular assembly in solution can influence which polymorph forms and the crystallization kinetics. These systems emphasize the need for in-depth studies on how molecular assembly in solution (including the formation of growth units and their attachment to the growing crystal) influences polymorphic selectivity. The current study is, therefore, also relevant to the design and synthesis of materials for other applications.

The ability to crystallize the perovskite directly from solution allows for longer annealing times, since crystallization is delayed.^{18,30,45} With longer annealing times, a larger fraction of the heating time is available for grain ripening, as opposed to the intermediate-to-perovskite phase transformation. HOIP films synthesized by retarding crystal growth using an ionic liquid (i.e., methylammonium formate) have been reported to exhibit larger and more highly oriented crystal grains in comparison to the films prepared using the two-step process (i.e., via a solid-state intermediate).^{30,45} Notably, increasing both the grain size and degree of orientation has been correlated to improved device performances.⁶ For example, using THTO to grow $(C_4H_9NH_3)_2C_5Pb_2I_7$ layered HOIP thin films improved crystallinity and film morphology, which resulted in improved charge transport.⁴⁶ Additionally, a blend of methylamine in ethanol with tetrahydrofuran can be employed as a strongly coordinating solvent to crystallize MAPbI₃ directly from solution, resulting in smooth and compact films, which in turn exhibit high photovoltaic performance.⁴⁷ Moreover, a one-step route to synthesize perovskite thin films may provide greater control over the final film quality, as the initial state of the system (a solution of wellsolvated ions) is known and should be consistent across experiments. In contrast, in the two-step pathway, the solidstate intermediate is more likely to vary in composition and structure, even if the same solvent is used.²⁴ Such variations in intermediate structure and composition can alter the crystallization kinetics and lead to variations in film quality and device performance.^{10,18} Direct formation of HOIPs from solution could provide greater control over thin-film synthesis by delaying crystallization and, thus, widening the processing window. Our XRD results show that, when THTO, DMPU, or HMPA and a 1 °C/min heating ramp are used, MAPbI₃ thin films remain liquid for over 30 min. These data indicate that the as-deposited films should be stable at room temperature for at least 30 min. This ample processing window time provides flexibility to optimize the spin-coating parameters and the time of antisolvent addition to yield improved morphologies and device performances.

CONCLUSIONS

This work has made progress toward understanding the interplay between the solution coordination chemistry and the crystallization pathway leading to perovskite formation. We combined DFT calculations within a Bayesian optimization codebase, PAL, which model molecular-level interactions between HOIP monomers and solvent molecules, with XRD, which can provide information about the long-range order (i.e., reveal the crystalline phase) within thin films during growth. In doing so, we have bridged the large gap in time and length scale between two different stages of crystallization: prenucleation, where DFT calculations leave off, and growth, where XRD takes over. This Bayesian-based computational approach is broadly extensible to larger combinatorial problems, as well as the optimization of virtually any chosen objective function for which a metric of success can be chosen. Our integrated experimental and computational approach could be applied to learn how to direct the crystallization pathway of other solution-grown materials by the careful selection of solvent and associated solution speciation.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.9b01461.

PAL-generated ranked list of 240 mixed-halide HOIP/ solvent combinations with intermolecular binding energies and 2D XRD patterns with the corresponding 1D integrations for all six solvent systems (PDF)

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Notes

The authors declare no competing financial interest.

[&]This research was performed while M.P. was affiliated with the University of Arizona in Tucson, AZ.

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