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The role of solvents in the formation of methylammonium lead triiodide perovskite

Junke Jiang a,b, José Manuel Vicent-Luna a,b, Shuxia Tao a,b,⇑

aMaterials Science and Modelling, Department of Applied Physics, Eindhoven University of Technology, Eindhoven 5600MB, the Netherlands
bCenter for Computational Energy Research, Department of Applied Physics, Eindhoven University of Technology, Eindhoven 5600MB, the Netherlands

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Metal halide perovskites (MHPs) are gaining increasing attention as low-cost, high-performance semiconductors for optoelectronics. In particular, their solution processing is compatible with the large-scale manufacturing of thin-film devices, including solar cells and light-emitting diodes. Understanding the coordination chemistry in precursor-solvent solution and atomistic mechanisms of film formation is of great importance for optimizing the optoelectronic properties of the final films.

Using the methylammonium lead triiodide (MAPbI3) as an example, we study the complex evolution of the molecular species from the solution to the initial stage of the crystallization by using a combination of density functional theory (DFT) calculations and ab-initio molecular dynamics (AIMD) simulations. We focus on the widely employed solvents DMSO and DMF, analyze the structures and energies of the iodoplumbate complexes in the form of simple complex of [PbInLx]m−n and polymeric iodoplumbates of ([PbInLx]m−n)n. Based on the calculated formation enthalpies, we propose reaction schemes of MAPbI3 formation in DMSO, DMF and DMF-DMSO binary solvent and explain the advantages of the binary solvent.

We highlight the important role of NH-O hydrogen bonds in the formation of iodoplumbates monomers. Our calculations indicate unbalanced reaction energies at several elementary reaction steps in either DMF (formation of [PbInLn]2 being highly favourable) or DMSO (formation of [PbInLm]3 being retarded).

Mixing a small amount of DMSO in DMF gives rise to a better balance in the energies and, therefore, potentially better equilibria in the overall crystallization process and better quality of the final perovskite films.

1. Introduction

Metal halide perovskites (MHPs) are among the most studied semiconducting materials in the last decade due to their promising optoelectronic properties, making highly efficient solar cells and light-emitting diodes at low-cost. The impressive progress in achieved power conversion efficiency (PCE) has consolidated their popularity among photovoltaic materials [5–8]. The MHPs are made by simple solution-processed deposition techniques by mixing a metal-halide precursor with a halide salt in a solution. For instance, methylammonium iodide (MAI) is added to a lead halide (PbI2) solution in coordinating solvents, such as dimethylformamide (DMF) [9,10], dimethyl sulfoxide (DMSO) [9,11], and N-methyl-2-pyrrolidone (NMP) [12,13]. From the mixture, colloidal particles first form and then produce a MHPs film by solvent evaporation. However, in contrast to the simplicity of the synthesis, the physicochemical processes during the synthesis are very complex. The synthesis involves the solvation/de-solvation and complexation equilibria of all participating species at solvents-precursors, nucleation, and it evolves various intermediate phases in the two-step method [11,14,15], and/or iodoplumbate complexes in the one-step method [10,16,17].

Using MAPbI3 as an example, various complexes could be formed in a solution, depending on the type and the concentration of ions (MA+ cations and I− anions) or solvents (L) near the Pb metal ions. When I− anions together with MA+ cations are added to the lead iodide (PbI2) solution, competition in binding occurs between I− and solvent molecules to the Pb2+ cation. The I− anion and solvent molecules coordinate around the central Pb2+ cation, forming iodoplumbate complexes, i.e., [PbI2L1], [PbI2L1]−, [PbI2L2]2−, [PbI4L3]3−, and [PbI6L4]4− [14,18–22]. During the iodoplumbates formation, a small amount of I− is adequate to replace the solvent molecules, thus induce the formation of iodoplumbate spe-
cies [18,20]. Indeed, iodoplumbate complexes, such as [PbI$_4$L$_n$]$^-$ and [PbI$_4$L$_n$]$^{2-}$ can be stabilized in the presence of large excess iodide ions [18,19]. The high iodide coordinated iodoplumbate, such as [PbI$_5$L]$^-$ and [PbI$_5$L]$^{2-}$ is less often directly observed in experiments. However, their presence cannot be excluded, and it is speculated to play an important role in the final steps of the formation of MHPs [14,20–22].

Besides the simple iodoplumbates discussed above, polymeric iodoplumbates were proposed to be formed, using the simple complexes, such as [PbI$_4$L$_n$], [PbI$_4$L$_n$]$^-$, or [PbI$_4$L$_n$]$^{2-}$ monomers as building blocks [18,23]. The atomistic structure, electronic, and optical properties of the polymeric species during the MHPs formation have been extensively investigated [17,18,23]. Oleksandra and co-workers [18,23] proposed the formation of polynuclear, i.e., formation of [([PbI$_{m}$L$_{n}$]$^{2-m}$)$_{m}$] from [PbI$_2$L$_n$], is essential in the formation of MHPs. It has been also proposed that the polymeric iodoplumbates in the form of [([PbI$_{m}$L$_{n}$]$^{2-m}$)$_{m}$] most likely occur when using a high concentration of lead-iodide in the precursor solutions [18,23]. However, an atomistic scale evolution of these molecular complexes remains unclear, and the crystallization pathways at various synthesizing conditions remain highly debated.

Another important factor that impacts the coordination chemistry of MHPs is the solvents [24,25]. The most commonly used solvents are DMF [9,10] and DMSO [5,11]. The usage of binary solvent, one as the basic solvent and another as co-solvent, i.e., coordinative additives, is also widely used in the synthesis of MHPs [13,14,26–28]. Among various co-solvents, DMSO is the most used one in combination with DMF [14,27,28]. It has been proposed from experiments that the use of DMF-DMSO binary solvent could retard the crystallization by forming MAI-PbI$_2$-DMSO complexes, and thus slowing down the nucleation rate of MHPs and therefore leads to higher quality films [29–31]. However, the atomistic origin of such effects and evolution of the relevant complexes involved in the crystallization is challenging to obtain in experiments due to the limitations in the spatio temporal resolutions.

The atomistic simulation is a powerful tool to investigate the fundamental aspects of chemical processes during crystallization at an atomic scale. However, due to the complexity of the species involved, theoretical studies are only emerging. Clancy et al. [32] investigated the relative stability of precursors in solution, and showed that the Mayer bond order could predict the solubility of the lead halide precursors in the solvent. Rothlisberger et al. [33] used metadynamics to investigate the nucleation of MHPs, mimicking a one-step synthesis route. Recently, Angelis et al. [19,21] have studied the formation of high-I-coordinated iodoplumbates. They concluded that a large amount of MAI is needed for the formation of iodine-rich iodoplumbates [19]. This implies the difficulty in the formation of [PbI$_{4}$L$_{n}$]$^{2-}$ and [PbI$_{4}$L$_{n}$]$^{4-}$, which are considered necessary for the formation of high-quality perovskite films [9,22,24–38]. To our knowledge, the conversion from the low-I-coordinated iodoplumbates (i.e., PbI$_2$) to high-I-coordinated iodoplumbates and their conversion to polymeric iodoplumbates is not systematically studied yet. Also, the highly dynamic formation process of the iodoplumbate complexes can be significantly affected by the A-cations as well as the type of solvents. The interplay of this process has not been deeply investigated and remains unclear.

In this work, using MAPbI$_3$ and two commonly employed solvents (DMF and DMSO), we investigate the evolution of the iodoplumbates in solutions using a combination of DFT and AIMD simulations. We obtain information on structures and reaction energies of elemental reaction steps from low to high-I-coordinated complexes and investigate how solvents impact the overall reaction pathways. We start with the commonly used solvents, DMF and DMSO study the impact of the co-solvent DMSO in DMF, by constructing a binary DMF-DMSO model. By analyzing the changes in the structures and energetics of elementary steps, we discuss the advantages of the binary solvent. Our work provides an atomistic understanding of the first steps of the crystallization of MHPs and forms a basis for further investigation of more complex perovskite systems or longer time scale simulations to model complete crystallization processes.

2. Methods

2.1. Density functional theory calculations

All DFT calculations were performed in the Kohn-Sham framework, using the Amsterdam Density Functional package (version ADF 2019.302) [39,40]. Geometry optimizations were done using the Perdew-Burke-Ernzerhof (PBE) functional [41]. A combination of Herman-Skillman numerical atomic orbitals (NAOs) with Slater type Triple-zeta (TZP) basis sets was used for heavy atoms (Pb and I), whereas for C, N, H, O, and S atoms, Double-zeta (DZP) basis sets were used. The cores 1s – 4d, 1s – 4p, and 1s – 2s were kept frozen, respectively, for Pb, I, and S, to speed up the calculations. Vibrational frequencies were obtained with the optimized configurations through numerical differentiation of the analytical gradient. The harmonic level approximation was applied to ensure that the optimized structures are located at global or local minima on the potential energy surface [42–44]. Fig. S1 shows a representative example of the distance dependence on the interaction energies between MAPbI$_3$ complexes and DMF solvents. The enthalpies were calculated at 298.15 K and 1 atm from the bond energies and vibrational frequencies by using a standard thermochemistry relation as described by Bickelhaupt et al. [45,46]. The solvents were simulated with both implicit solvation models (the COSMO dielectric continuum solvation scheme) [47] and explicit solvent molecules. The hybrid implicit-explicit models were chosen as it was proven to be useful for better describing the precursor chemistry of halide perovskites in previous publications [19,21,32,48].

2.2. Ab initio molecular dynamics simulation

AIMD simulations were also performed to study the dynamics of precursor-solvent interactions by using the CP2K code [49,50]. The QUICKSTEP, the electronic structure part of CP2K, uses the combined Gaussian and plane-wave (GPW) method to calculate forces and energies. The GPW method is based on the Kohn-Sham formulation of DFT and employs a hybrid scheme combining Gaussian and plane wave functions. The Born-Oppenheimer molecular dynamics (BOMD) simulations were executed by using a canonical ensemble (NVT) with a Nose-Hoover thermostat [51] at temperature 353 K (typical temperature for the crystallization process in experiments) [13,28,52–54]. All simulations made use of DFT at the PBE level with double-zeta basis sets (DZVP-MOLOPT for Pb, I, S, O, C, N, H) [55] and Goedecker-Teter-Hutter (GTH) pseudopotentials [56] with a 500 Ry density cut-off. A single k-point sampled at the Γ point was used to speed up the computation. The total simulation time of each calculation is 30 ps with a time step of 1 fs.

2.3. Structural models

To calculate the formation enthalpy of the iodoplumbates with increased iodide coordination, models [PbI$_{4}$L$_{n}$]$^{2-m}$ (m = 2, 3, 4, 5, 6; n = 6) for simple complex and [([PbI$_{m}$L$_{n}$]$^{2-m}$)$_{m}$] (m = 2, 3, 4; n = 6 – m) for polymeric iodoplumbates were used: m is the number of coordinated I$^{-}$, L is the solvent molecules, and n is the number of solvents. The scheme of the formation of both simple and polymeric iodoplumbates is shown in Fig. 1. In order to ensure charge neu-
3. Results and discussion

3.1. Formation enthalpies of iodoplumbates

The formation of iodoplumbate complexes is an important step for the MHPs crystallization. To gain insights into the formation of these iodoplumbates, we considered from low to high I-coordination, i.e., from [PbI2L4] to [PbI6L6] in this study. As illustrated in Fig. 1 (top), the conversion from low I-coordinated iodoplumbate (i.e., [PbI2L4]2- to high I-coordinated iodoplumbate ([PbI2L4]2-, [PbI3L3]1- and [PbI3L3]2-) involves reactions that require or release energy. It should be noted that the negative charge on the coordination sphere due to the access I- is compensated by positively charged MA+ ions in our simulations. The formation enthalpy of each step is calculated using Equations (1)–(4) as follows:

\[ [\text{PbI}_2\text{L}_4]^- + \text{MA}^+ \rightarrow [\text{PbI}_1\text{L}_4]^- + 2\text{MA}^+ \]  

\[ [\text{PbI}_2\text{L}_4]^- + 2\text{MA}^+ \rightarrow [\text{PbI}_3\text{L}_3]^- + 3\text{MA}^+ \]  

\[ [\text{PbI}_2\text{L}_4]^- + 3\text{MA}^+ \rightarrow [\text{PbI}_3\text{L}_3]^- + 4\text{MA}^+ \]  

To study the formation of polymeric iodoplumbates, we focus on the investigation of the formation of iodoplumbates dimers [PbI2L2]2-, ([PbI2L2]2-)3, and ([PbI2L2]2-2) from the simple iodoplumbates, [PbI3L3]1-, [PbI3L3]2-, and [PbI3L3]3-, respectively. These three iodoplumbates are commonly detected complexes in experiments [18,20,22,23]. The formation enthalpy of the polymeric iodoplumbates is evaluated by using Equations (5)–(7), as follows:

\[ [\text{PbI}_2\text{L}_4]^- + [\text{PbI}_2\text{L}_4]^- \rightarrow [\text{PbI}_2\text{L}_4]^- ]  

\[ [\text{PbI}_2\text{L}_4]^- + [\text{PbI}_2\text{L}_4]^- \rightarrow [\text{PbI}_3\text{L}_3]^- ]  

\[ [\text{PbI}_2\text{L}_4]^- + [\text{PbI}_2\text{L}_4]^- \rightarrow [\text{PbI}_2\text{L}_4]^- ]  

The formation enthalpies for all steps with respect to different solvents are summarized in Fig. 1. A negative formation enthalpy indicates that the corresponding iodoplumbates formation reaction is favourable. We first look at the step-by-step formation of iodoplumbate complexes from low to high I-coordination. For DMF, the reaction of all steps is favourable, evidenced by the negative formation enthalpies. In particular, the formation enthalpy from [PbI3L3]1- to [PbI3L3]2- is -0.72 eV, which is much more negative (about 0.5 eV) than other steps, indicating a rapid formation of [PbI3L3]2-. For DMSO, the formation enthalpies are all negative (in the range of about -0.4 to -0.5 eV), except for the step from [PbI3L3]2- to [PbI3L3]3-, which is close to 0 (-0.07 eV). This indicates that the formation of [PbI3L3]4- becomes unfavourable. When mixing a small amount of DMSO in DMF, i.e., using a DMF-DMSO binary solvent, we observe interesting changes in the reaction energetics compared to pure DMF or DMSO, respectively. While the formation enthalpy of all steps is negative, that from [PbI3L3]2- to [PbI3L3]3- becomes relatively small, being -0.19 eV.
compared to −0.72 and −0.48 eV for DMF and DMSO, respectively. This indicates the conversion from \([\text{PbI}_3\text{L}_6]^{1-}\) to \([\text{PbI}_4\text{L}_6]^{2-}\) becomes relatively difficult, i.e., relatively slower coordination reactions. It is worth noting that the conversion of \([\text{PbI}_4\text{L}_6]^{2-}\) to \([\text{PbI}_5\text{L}_6]^{3-}\) becomes more likely, evidenced by the much more negative reaction energy (−0.47 eV vs. −0.21/−0.07 eV) for DMF-DMSO binary compared to DMF or DMSO.

To gain insights into the underlying mechanisms of the significant changes in the reaction energies from \([\text{PbI}_3\text{L}_6]^{1-}\) to \([\text{PbI}_4\text{L}_6]^{2-}\) and from \([\text{PbI}_4\text{L}_6]^{2-}\) to \([\text{PbI}_5\text{L}_6]^{3-}\) by using DMF-DMSO binary solvent, we analyzed the atomistic structures of the relevant complexes. Neither significant changes nor general trends in the average Pb–I bond or Pb–O bond were found from \([\text{PbI}_2\text{L}_6]^{1-}\) up to \([\text{PbI}_6\text{L}_6]^{3-}\) (see Fig. S3). An interesting interaction pattern in hydrogen bonds, NH−O, between N–H bonds of MA+ cation and the O atom of the solvents, can be seen in Fig. 2. The number of NH−O hydrogen bonds in DMF or DMSO increases from \([\text{PbI}_2\text{L}_6]^{1-}\) to \([\text{PbI}_3\text{L}_6]^{1-}\) and to \([\text{PbI}_4\text{L}_6]^{2-}\) but decreases at \([\text{PbI}_5\text{L}_6]^{3-}\). The increase can be explained by the fact that more MA+ are added during the reaction from low to high l-coordinated complexes. Such increase is especially significant with a net increase of 2 NH−O hydrogen bonds from \([\text{PbI}_2\text{L}_6]^{1-}\) to \([\text{PbI}_3\text{L}_6]^{1-}\) and to \([\text{PbI}_4\text{L}_6]^{2-}\) but decreases at \([\text{PbI}_5\text{L}_6]^{3-}\). The consequence of this is the formation energy of \([\text{PbI}_3\text{L}_6]^{1-}\) becomes less negative (−0.19 eV vs. −0.72/−0.48 eV) and that of \([\text{PbI}_4\text{L}_6]^{2-}\) becomes more negative (−0.47 eV vs. −0.21/−0.07 eV). These findings show the importance of A-cation MA+ and the unique role of NH−O hydrogen bonds in the formation energies of iodoplumbates, a factor that has not been considered in previous studies to the best of our knowledge.

From the energies shown in Fig. 1 (bottom), most polymeric complexes can be formed in DMF (evidenced by the negative formation enthalpies) with one exception: the formation energy of \([\text{PbI}_2\text{L}_3]^{1-}\) being almost zero, −0.03 eV. Another important trend is that the energies in DMSO are all more positive than those in DMF, in particular, the formation energy of \([\text{PbI}_3\text{L}_6]^{1-}\) is as high as 0.39 eV. The overall trend can be readily explained by the solvent coordination power of these two solvents with a general trend of DMSO > DMF [21,36,58–62]. Indeed, the atomicistic structure in Fig. S5 shows the two \([\text{PbI}_2\text{L}_3]^{1-}\) monomers cannot or only weakly interact with each other in DMSO because of the strong coordination/interaction of DMSO molecules with Pb2+, giving rise to the large positive reaction energy of 0.39 eV. A higher likelihood of forming polynuclear complexes can be expected for solvents with weaker coordination ability, such as DMF. This is because the solvent with weak coordination can be replaced more easily by the I− in the adjacent monomer (see Fig. S5). The DMF-DMSO binary solvent gives values between those of DMF and DMSO for \([\text{PbI}_4\text{L}_6]^{2-}\) and \([\text{PbI}_5\text{L}_6]^{3-}\), but brings down the value for \([\text{PbI}_3\text{L}_3]^{1-}\) to below zero (−0.10 eV).

From the reactions of the simple and polymeric iodoplumbates, a combined reaction scheme can be constructed in Fig. 1 and the effect of the solvents can be analyzed. For DMF, the step-by-step reaction from low to high-l-iodoplumbate is all favourable, especially the formation from \([\text{PbI}_2\text{L}_3]^{1-}\) to \([\text{PbI}_3\text{L}_6]^{1-}\), indicating a rapid formation of \([\text{PbI}_4\text{L}_6]^{2-}\). Polymeric complexes such as \([\text{PbI}_2\text{L}_3]^{2-}\) and \([\text{PbI}_3\text{L}_3]^{2-}\) can be formed except for the \([\text{PbI}_3\text{L}_3]^{1-}\). The overall energy pathway indicates a rapid conversion from low to high-l-coordinated PbI._complex. For DMSO, all reaction energies at each step, including the formation of simple and polymeric complex, have become more positive compared to those in DMF. In particular, the step from \([\text{PbI}_4\text{L}_6]^{2-}\) to \([\text{PbI}_5\text{L}_6]^{3-}\) becomes much more difficult with a reaction energy of close to 0 (−0.07 eV). This indicates the formation of high-l-coordinated complex, such as \([\text{PbI}_5\text{L}_6]^{3-}\) is hindered. When mixing a small amount of DMSO in DMF, the reaction energies of all reaction steps fall nicely in a range of −0.50 to −0.10 eV, slowing down the fast conversion from \([\text{PbI}_6\text{L}_6]^{2-}\) to \([\text{PbI}_4\text{L}_6]^{2-}\) in DMF and speeding up the difficult conversion from \([\text{PbI}_4\text{L}_6]^{2-}\) to \([\text{PbI}_3\text{L}_3]^{2-}\) in DMSO. Such balanced energetics can potentially lead to better equilibria among all reaction steps and therefore better final perovskite films. Our analysis is in agreement with several experimental findings that point to the fact when mixing DMSO in DMF, the formation of MAI-PbI._DMSO complexes slows down the overall nucleation rate and therefore leads to higher quality final film [29,30].

3.2. Formation dynamics of MHPs with different solvents

We next investigate the dynamical evolution [64–68] of the relevant complexes starting from \([\text{PbI}_3\text{L}_3]^{1-}\) by using ab-initio molecular dynamics (AIMD) simulations. The reason for starting with \([\text{PbI}_3\text{L}_3]^{1-}\) is twofold: (i) for saving computational cost; (ii) the formation enthalpies starting from \([\text{PbI}_3\text{L}_3]^{1-}\) are with a significant difference, especially the value of DMSO is remarkably positive. All simulations were done for 30 ps at an experimental crystallization temperature 353 K [13,28,52–54]. The trajectory of the initial 5 ps in each simulation is discarded for the data analysis because of the relatively large temperature and energy oscillation (see Fig. S6).

Fig. 3 illustrates the snapshots of the beginning and the end of the frames in the AIMD simulations. For the DMF, we observe formation of high-l-coordinated iodoplumbate such as \([\text{PbI}_4\text{L}_6]^{2-}\) and \([\text{PbI}_5\text{L}_6]^{3-}\) readily within only 30 ps, and face sharing polymeric complexes, indicating a relatively fast nucleation rate. In contrast, in DMSO, we only observe a small amount of corner-sharing polymeric complexes, with the majority of the species preserving the feature of starting monomer \([\text{PbI}_3\text{L}_3]^{1-}\). Moving to the DMF-DMSO binary, we find a large block of PbI complex that is centered
by fully-coordinated iodoplumbates, which is surrounded by some corner-sharing \([\text{PbI}_3\text{L}_n]^{1-}\). We speculate such complex is a starting point for the formation of 3D perovskite structure (fully coordinated \(\text{PbI}_x\) complex that is cornered shared with each other). Indeed, Rothlisberger et al. \([33, 69]\) demonstrated a slow transition from edge-sharing octahedra to the corner-sharing octahedra after hundreds of nanoseconds using metadynamics. This explains the reason we do not observe a full transition to 3D perovskites in the time scale of our AIMD simulations. The quantitative trends are however well captured in our MD simulations which corroborates the findings from the thermodynamical analysis presented above.

To zoom in to the atomistic details of the simulations from Fig. 3, we plot in Fig. 4 the short-range radial distribution function \(g(r)\) and cumulative radial distribution functions \(\text{int}[g(r)]\) (coordination number) for Pb–I and Pb–O bonds in different solvents. The \(g(r)\) of Pb–I shows that the iodine mainly interacts with Pb at the typical Pb–I bond distance of slightly longer than 3.0 Å, which agrees with the results from Angelis et al. \([70]\) by using Car-Parrinello molecular dynamics (CPMD) simulations for the two-step formation of MAPbI\(_3\). The \(\text{int}[g(r)]\) of Pb–I shows that the average coordination number of iodine to the Pb is between 3 and 4 for DMSO and DMF, and larger than 4 for the DMF-DMSO binary solvent. This trend is supported by the trend seen in Pb–O bonds, where the number of the Pb–O coordination, being about 0.2, is the smallest in the binary solvent, with DMF being 1 and DMSO being 0.5, respectively. This is in concordance with the NH–O (hydrogen bonds between MA\(^+\) and solvents) shown in Fig. S7, where the solvents with the highest NH–O coordination lead to the lowest Pb–O coordination and viceversa. This suggests that the mutual interactions between DMF and DMSO and with the MA\(^+\) cations affect the formation and molecular structure of the PbI\(_x\) complexes.

The first peak of the Pb–I and Pb–O \(g(r)\) is displaced to slightly longer distances in the case of DMF-DMSO binary solvents (from 3.05 to 3.15 Å for Pb–I and from 2.65 to 2.75 Å for Pb–O bonds, respectively). This facilitates the PbI\(_x\) complexes clustering as well as the removal of the solvent in further steps of the crystallization process \([29, 30]\). These findings are in agreement with the formation enthalpies described in Fig. 1 and support the use of DMF-DMSO binary solvent for promoting the growth of high 1-coordinated iodoplumbates, i.e., the first step of the crystallization process.

Fig. 3. Snapshots of the initial and final state of the precursor-solvent mixture during 30 ps AIMD simulation for (a) DMF, (b) DMSO, and (c) DMF-DMSO binary solvents, respectively. The homogeneous mixture of ions contains 6 [PbI\(_3\)]\(^-\), 6 MA\(^+\), and 18 solvents. The snapshots are shown with 2 × 2 supercells, with the unit cell highlighted by the simulation boxes.
4. Conclusions

In summary, to understand the coordination chemistry during the formation of MHPs, we study the interactions of perovskite precursors with solvents by combining DFT and AIMD calculations. We construct a reaction scheme for the crystallization of MAPbI₃ at the early stage by combining reactions that form simple and polymeric PbI₂ complexes and analyze the effect of the commonly used solvents, DMF, DMSO as well as DMF-DMSO binary solvents. For DMF and DMSO, the step-by-step reactions from low to high I⁻ iodoplumbate are all favourable, as well as for [PbI₂L₆]₂⁻ and ([PbI₄⁻L₃]²⁻)₂ polymeric complexes. While DMF favors the formation of low-coordination complexes from [PbI₃L₆]¹⁻ to [PbI₄L₆]²⁻, DMSO hinders reaction of high-coordinated complexes from [PbI₄L₆]²⁻ to [PbI₅L₆]³⁻. However, when using DMSO as an additive for DMF, the reaction energies are better balanced than for the pure solvents, i.e., the formation of low-coordinated complexes is slower compared to the fast conversion in DMF or DMSO, while the formation of high-coordinated complexes is promoted. Thus, the overall energy pathway is well balanced by mixing a small amount of DMSO in DMF, leading to a better equilibrium in all the reaction steps. This energetic balance in the reactions of iodoplumbates monomers can be explained because of the formation of NH—O hydrogen bonds between the MA cations and the solvents. For the pure DMF and DMSO solvents, the NH—O hydrogen bond number highly increases from [PbI₃L₆]¹⁻ to [PbI₄L₆]²⁻, explaining

Fig. 4. Short-range radial distribution function g(rij) (left) and cumulative radial distribution functions int[g(rij)] (right) of (a) Pb—I, and (b) Pb—O for DMF, DMSO, and DMF-DMSO binary solvents, respectively.
the largely negative reaction energies compared to the reactions before and after this step. However, the trend is interrupted at [Pbl₄L₆]⁻³ and the number of NH₄ decreases. Interestingly, for DMF-DMSO binary solvents, the number of NH₄+ hydrogen bonds slightly increases from [Pbl₄L₆]²⁻ to [Pbl₄L₆]⁻³, causing a more negative reaction energy associated to the formation of high-coordinated [Pbl₄L₆]⁻³ complexes.

The dynamical results from AIMD simulations confirmed our predictions of the thermodynamic properties obtained with the DFT calculations. In DMF, while high-l-coordinated Pbl₄ complexes quickly form, they exhibit face-sharing configuration. For DMSO, we found that the majority of the species remain unreacted. However, the mixture of DMF and DMSO in a binary solvent promotes not only high-l-coordinated iodoplumbates, but also Pbl₄ complexes with a corner-sharing feature, which can be used as nucleation centers to form 3D perovskites. The structural analysis of the Pbl-I and Pbl-O bonds is in concordance with the NH₄+ hydrogen bonds detailed above. The radial distribution functions and the coordination numbers reveal that the binary DMF-DMSO solvents promote higher Pbl-I coordination at the same time that hinder the interaction between the lead atoms and the solvents, which facilitates their removal in further steps of the crystallization process.

Our results provide insights into the role of precursors and solvents in the thermodynamics and kinetics of perovskite formation. The detailed atomistic analysis offers a unique and experimentally inaccessible insight regarding the early stages of the perovskite crystallization and provides an important basis for future work on more complex perovskite compositions and/or a complete crystalization process. Moreover, additives (e.g., Cl⁻ and F⁻) and anti-solvent (e.g., chlorobenzene) are proven to be also highly effective to improve the quality of perovskite films. We anticipate that the different additives will tailor the thermodynamics and kinetics of perovskite crystallization, meritting further experimental and theoretical investigations.

Declaration of Competing Interest

The authors declare that they have no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jechem.2021.12.030.

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