STABILITY OF PEROVSKITE SOLAR CELLS

STABILITY OF PEROVSKITE SOLAR CELLS VIA CATION REPLACEMENT AND INTERFACIAL MODIFICATION

BY

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Abstract

Organic-inorganic hybrid perovskite solar cells (PSC) have been widely considered as a promising candidate for the next generation of photovoltaics (PV). The power conversion efficiency of a single junction PSC has achieved a maximum of 25.5% within only one decade, rivaling traditional PV technologies. While PSCs inspired a new era for photovoltaic development, they exhibited severe instability problems, thereby impeding their commercialization. Thus, the main projects in this thesis are to improve stability of PSCs.

To enhance the intrinsic stability of PSC, a hydrophobic five-membered ring cation is introduced to replace the unstable protype methyl-ammonium (MA) cation. In Chapter 2, the crystal structure of the new perovskite material, (C₄H₈NH₂)PbI₃ (PyPbI₃) is determined and illustrated by single crystal X-ray diffraction. UV absorption spectra, steady state photoluminescence and XRD results show it is a promising alternative to hybrid organic–inorganic perovskites due to its good water resistance and suitable bandgap.

The MA-based perovskites are unstable at high temperature or under moisture attack. To overcome this barrier, both thermal stability and water resistance of PyPbI₃ are investigated in Chapter 3. It presents not only prolonged moisture resistance up to 4 months in ambient conditions and a favorable bandgap of 1.80 eV, as determined by P- XRD and UV absorption, but also excellent thermal stability, as verified via the in situ thermal XRD technique.

The phase stability of PyPbI₃ is investigated in Chapter 4. The hybrid perovskite was synthesized successfully via a simple drop casting method. It presents not only excellent phase stability, but also low trap-state density, as confirmed via XRD and space-charge-limited currents measurements. The results indicate that Py-based perovskite is environmentally stable.

The commonly employed formamidinium (FA)-containing PSCs exhibit a severe phase instability problem. Here in Chapter 5, both phase stability and energy efficiency of FA-based PSCs are improved by treating the perovskite surface with pyrrolidinium hydroiodide (PyI) salts, resulting in a 1D perovskite structure (PyPbI₃), stacked on the original 3D perovskite. By employing in situ XRD measurements, we revealed that the temperature-dependent phase transition activation barrier was enhanced after forming the 1D/3D structure, resulting in a prolonged transition time by 30–40-fold. From the first-principle calculations, we found the thermodynamic energy difference between two phases reduced from -0.16 to -0.04 eV after the stacking of 1D PyPbI₃, offering additional lifetime improvement. Moreover, the champion 1D/3D bilayer PSC exhibits a boosted power conversion efficiency of 19.62%, versus 18.21% of the control. Such 1D/3D bilayer structure may be employed in PSCs to enhance their phase stability and photovoltaic performance.

Declaration of Academic Achievements

The major research results during my Ph.D. study (from September 2018 to November 2020) have been published or submitted to peer reviewed journals. The publications are listed as below:

As first/co-first author:

1. Alex Fan Xu, Na Liu, Fanlong Xie, Tinglu Song, Yue Ma, Pengxiang Zhang, Yang Bai, Yujing Li, Qi Chen, and Gu Xu. "Promoting Thermodynamic and Kinetic Stabilities of FA-based Perovskite by an in Situ Bilayer Structure." Reproduced with permission from *Nano Letters*, 2020, 20, 5, 3864–3871. Copyright © 2020 American Chemical Society

2. Alex Fan Xu, Ryan TaoranWang, Lory Wenjuan Yang, Elton Enchong Liu and Gu Xu. "An Environmentally Stable Organic–Inorganic Hybrid Perovskite Containing Py Cation with Low Trap-State Density." Reproduced from *Crystals*, 2020, 10, 272. Copyright of this paper from *Crystals* is retained by authors.

3. Alex Fan Xu, Ryan Taoran Wang, Lory Wenjuan Yang, Na Liu, Qi Chen, Ray LaPierre, Nebile Isik Goktas, and Gu Xu. "Pyrrolidinium containing perovskites with thermal stability and water resistance for photovoltaics." Reproduced with permission from *Journal of Materials Chemistry C*, 2019, 7, 11104-11108. Published as the front cover. Copyright © 2019 The Royal Society of Chemistry.

4. Alex Fan Xu, Ryan Taoran Wang, Lory Wenjuan Yang, Victoria Jarvis, James F. Britten, and Gu Xu. "Pyrrolidinium lead iodide from crystallography: a new perovskite with low bandgap and good water resistance." Reproduced with permission from *Chemical Communications*, 2019, 55, 3251-3253. Copyright © 2019 The Royal Society of Chemistry.

As co-author:

5. Ryan Taoran Wang, Alex Fan Xu, Jason Yuanzhe Chen, Lory Wenjuan Yang, Gu Xu, Victoria Jarvis, and James F. Britten. "Reversing Organic-inorganic Hybrid Perovskite Degradation in Water via pH and Hydrogen Bonds." *The journal of physical chemistry letters*, 2019, 10, 22, 7245–7250. (My contribution was to provide experimental assistance and scientific problem discussion)

6. Ryan Taoran Wang, **Alex Fan Xu**, Lory Wenjuan Yang, Jason Yuanzhe Chen, Adrian Kitai and Gu Xu. "Magnetic-field-induced energy bandgap reduction of perovskite KMnF3." *Journal of Materials Chemistry C*, 2020, 8, 4164-4168. (My contribution was to provide scientific problem discussion)

7. Kelvin J. Xu, Ryan T. Wang, **Alex Fan Xu**, Jason Y. Chen, and Gu Xu. "Hysteresis and instability predicted in moisture degradation of perovskite solar cells." *ACS Applied Materials & Interfaces*, 2020, 12, 43, 48882–48889. (My contribution was to provide scientific problem discussion)

8. Ryan Taoran Wang, Lory Wenjuan Yang, Alex Fan Xu, Elton Enchong Liu, and Gu

Xu. "Achieving Nonenzymatic Blood Glucose Sensing by Uprooting Saturation." *Analytical Chemistry*, 2020, 92, 15, 10777–10782. (My contribution was to provide scientific problem discussion and help editing the manuscript)

9. LoryWenjuan Yang, Elton Enchong Liu, **Alex Fan Xu**, Jason Yuanzhe Chen, Ryan TaoranWang and Gu Xu. "Improving Linear Range Limitation of Non-Enzymatic Glucose Sensor by OH– Concentration." *Crystals*, 2020, 10, 186. (My contribution was to provide scientific problem discussion)

10. Ryan TaoranWang, Elton Enchong Liu, **Alex Fan Xu**, Lory Wenjuan Yang, Jason Yuanzhe Chen and Gu Xu. "Ethylammonium Lead Iodide Formation in MAPbI3 Precursor Solutions by DMF Decomposition and Organic Cation Exchange Reaction." *Crystals*, 2020, 10, 162. (My contribution was to provide experimental assistance)

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Chapter 1

Introduction

1.1. Solar energy background

The world's total energy consumption has been driven up significantly by the rapid growth of population in recent years^{1,2}, which inevitably increased the carbon emission, resulting in serious environmental and economic issues, such as global warming³. To alleviate the climate crisis and fulfill the increasing energy demands, it is thus imperative to develop renewable low-carbon energy resources^{4,5}, among which the solar energy attracted much attention in recent years⁶⁻¹⁰. It has been reported that the annual solar energy potential far exceeds the world's total energy consumption¹¹. Therefore, it would be of great significance to utilize the abundant solar power by photovoltaic (PV) cells to convert solar energy into electricity. In reality, however, only ~2% of the electricity is produced by PV², leaving a large space to further develop new PV materials of high efficiency and low $cost^{12,13}$. Among the emerging PV techniques, including quantum dot solar cell¹⁴, organic solar cell¹⁵, dye-sensitized solar cell¹⁶ etc., perovskite solar cell (PSC) shows the greatest potential, due not only to the comparative efficiency to the commercial silicon solar cells, but also the low manufacturing $cost^{17}$.

1.2. Perovskite photovoltaics

1.2.1. The history and evolvement of perovskite PV

In 2009, Tsutomu Miyasaka et al.¹⁸ reported perovskite-sensitized solar cell by MAPbI₃ nanocrystals of 3.81% power conversion efficiency (PCE), which is the first research article about perovskite solar cell. However, little attention was attracted due to the poor stability of the devices. The second paper regarding perovskite solar cell was published at 2011, during which Nam-Gyu Park et al.¹⁹ fabricated perovskite quantum dot solar cell of an efficiency of 6.5%, making it the highest efficiency among all reported inorganic quantum dot sensitizers at that time. In 2012, a great breakthrough²⁰ was achieved by all-solid-state mesoscopic perovskite solar cells^{21,22}, which demonstrated significant improvement in both efficiency and stability of PSCs compared to their prototype in 2009. Such breakthrough encouraged the perovskite solar cell community to explore further about the details, making PSC one of the most popular topics²³, as suggested by the relationship between number of articles related to perovskite solar cell and publication year in Fig. 1.1. All data were obtained from the database of Web of Science. The number of the published papers increased from 1 in 2009 to more than 4000 in 2019. And the total number reaches to more than 18000 within a decade.



Figure 1.1 The relationship between number of articles and publication year. The data is obtained from the database of Web of Science. The topic is defined as 'perovskite solar cell'.



Figure 1.2 Best research cell efficiencies chart. Reproduced from NREL website²⁴: <u>https://www.nrel.gov/pv/cell-efficiency.html</u>; accessed on November, 2020.

As demonstrated in **Fig. 1.2**, the best perovskite cell exhibited an efficiency of 25.5%, which is the highest value among all single junction-based emerging PV technologies. Remarkably, the efficiency of the best PSC is even higher than the most employed

multicrystalline Si cell^{25,26} (~23.3%), second only to that of the single crystal Si cell (~26.1%). Due to the excellent properties of perovskite materials²⁷, such as long diffusion length²⁸, high absorption coefficient^{29,30}, suitable bandgap³¹, high defect tolerance³², etc., the efficiency of such devices raised from 3.8% to more than 25% within just a decade, as opposed to the 30 years of their Si counterparts, making perovskite a promising candidate for next generation of PV techniques.

1.2.2. Hybrid perovskite structure

The general formula of metal halide perovskite is expressed as ABX₃, where A, B and X stand for monovalent cation, metal cation and halide ion (X= I, Br, Cl), respectively. The crystal structure of ABX₃-type perovskite is shown in **Fig. 1.3**a. The corner-sharing BX₆ octahedra will form an extended three-dimensional (3D) network, where A cations embedded in the void spaces within the B–X framework. The formation of the 3D perovskite can be manipulated by Goldschmidt tolerance factor (TF) ^{33,34}, which is determined by the atomic type and radii of A, B, and X ions.



Figure 1.3 a) Crystal structure of ABX₃-type metal halide perovskites. b) TF of APbI₃ perovskites. The inset images depict the cation structures. Reproduced with permission from *Solar RRL*³⁵ and *Science*³⁶.

In general, perovskite material of a TF value between 0.8 and 1.0 is expected to form a cubic structure³³. As a result, only a few A-site cations such as methyl-ammonium¹⁸ (MA), formamidinium^{31,37} (FA) and cesium³⁸ (Cs), could be inserted to form a stable 3D perovskite structure, as summarized in **Fig. 1.3**b. Other cations are either too small or too large to fit in the void space³⁶. For B sites, most PSCs adopted lead (Pb) as the metal atom. Recently, Sn-based PSC was introduced to eliminate the toxicity of Pb³⁹, yet it suffered from low energy efficiency and poor chemical stability⁴⁰, which needs further investigation.

1.2.3. Device architecture

The structure of PSC consists of several layers: a transparent conductive oxide (TCO) that is coated on glass substrate, an electron transport layer (ETL), a perovskite absorber

layer, a hole transport layer (HTL), and a back contact (metal, carbon, etc.). Depending on the layer deposition sequence, PSCs could be divided into 'normal' and 'inverted' types⁴¹, as illustrated in **Fig. 1.4**. The structure of the inverted PSCs is not just a reversal from the normal devices, it also requires the alternation of the charge carrier transport layer and electrodes of appropriate properties^{42,43}, and alignment of the energy level^{44,45}. In this thesis, we mainly focused on the fabrication of normal PSC devices.



Figure 1.4 Normal and inverted structures of perovskite solar cells. Reproduced with permission from *ChemSusChem*⁴⁶.

The commonly adopted ETL materials for normal PSCs include SnO_2^{47} , TiO_2^{48} , $Al_2O_3^{49}$, etc. Organic molecules such as 2,2',7,7'-Tetrakis(N,N-di-p-methoxy-phenylamine)-9,9'-spirobiuorene (spiro-OMeTAD)²¹ and poly[bis(4-phenyl)-(2,4,6-trimethylphenyl)amine (PTAA)⁵⁰ have been widely employed as HTL materials in high efficiency devices. However, high costs and complicated synthetic routes^{51,52} of these materials remain an obstacle for large scale production, which need to be addressed in the future.

1.3. Problems to overcome

There are 3 factors that will influence the commercialization of PV techniques including cost, efficiency and lifetime, which are known as the golden triangle⁵³ (**Fig. 1.5**a). The comparison of perovskite and silicon solar cells based on the golden triangle were demonstrated in **Fig 1.5**b, which showed that the cost of PSC is much lower than that of the Si cell, while the champion efficiency of PSC is comparable to that of the Si cell, leaving only the challenge of the lifetime for the PSC device, which is much shorter than 25 years of commercialized Si cells^{41,53-55}.



Figure 1.5 The comparison of perovskite and silicon solar cells. a) Golden triangle of solar cells, cost, efficiency, and lifetime are considered. b) The comparison of perovskite and silicon solar cells based on golden triangle. Reproduced with permission from *Nature Communications*⁵³.

Although the operational stability of a solar cell device can be influenced by various

factors⁵⁶, such as the degradation of charge transport layers^{49,57,58} and electrodes^{59,60}, ion migration⁶¹, illumination condition⁶²⁻⁶⁴, etc., the stability of the absorbing layer plays the most vital role, as it can absorb photons and generate free charge carriers⁶⁵. In PSC, the perovskite absorbing layer was found to be unstable, which decomposes when being exposed to external stress⁴¹. For example, the MAPbI₃ perovskite decomposes in water⁶⁶ or at temperature above 85 $^{\circ}C^{67}$. This degradation was observed even in encapsulated PSC devices⁶⁸. On the other hand, although FAPbI₃ was believed to be more stable than MAPbI₃⁶⁹, and showed the enhanced thermal⁷⁰ and chemical stability⁶⁹, it suffered from undesirable phase instability problems. As depicted in Fig. 1.6b, the black phase of α -FAPbI₃, which is photoactive, will be spontaneously transferred into the yellow phase of δ -FAPbI₃, which is photo-inactive, thereby stopping their photovoltaic function and causing a short lifetime of the device. Similar phase transition was also observed in CsPbI₃ perovskite, where the cubic phase of CsPbI₃ will be transformed into yellow orthorhombic phase. Such undesirable α -to- δ phase transitions occurred at room temperature under ambient conditions, which impedes the practical applications of PSCs.



Figure 1.6 Crystalline structure and polymorphic phase transitions of (a) CsPbI₃ and (b) FAPbI₃ perovskites. Reproduced with permission from *ACS Energy Letters*⁷¹.

To resolve the PSC instability problems, various strategies have been developed. In this section, only a short review will be presented. More detailed discussion regarding perovskite stability enhancement works could be found from Chapter 2-5. As the perovskite has been reported as intrinsically thermodynamically unstable^{69,72,73}, which is not suitable for developing long term products, replacing the undesirable A cation by other alternatives seems to be a straightforward method⁷⁴⁻⁷⁶. Moreover, compositional

engineering has also been investigated to enhance the efficiency and stability of PSCs, where various cations and anions were combined to form a mixed perovskite structure^{77-⁸⁰, such as FA_{0.9}Cs_{0.1}Pb(I_{0.92}Br_{0.08})₃⁸¹. Interface engineering⁸² has been considered as another effective approach. An additional layer will be inserted between ETL and perovskite layer⁸³, or between perovskite and HTL layer⁸⁴⁻⁸⁶ (Interface 2 or 3 in **Fig. 1.4**), to stop the invasion of water molecules⁸⁴, as well as to passivate the perovskite surface⁸⁷, leading to an enhanced stability and efficiency of the devices.}

In this thesis, we focus on improving the intrinsic stability of perovskite. To achieve that, a hydrophobic five-membered ring molecule (pyrrolidine, Py) was employed to replace the protype MA cations, as the strong hydrophobic nature of pyrrolidine rings may repel the invasion of water molecules, thereby enhancing the moisture resistance of perovskite. Moreover, unlike the hydrophobic aziridine or azetidine molecules, which suffer severe ring strain, pyrrolidine is less strained and more stable. We therefore introduced pyrrolidine salts into the PbI₂ lattice and named this new perovskite as PyPbI₃. It exhibits not only excellent water resistance, but also suitable optical properties. The results are presented and discussed in Chapter 2. Moreover, the thermal (Chapter 3) and phase stability (Chapter 4) of PyPbI₃ has also been investigated, which indicated that PyPbI₃ is an environmentally stable material that may be applicable into PV.

Next, the PyPbI₃ was adopted as an interfacial modification layer to improve the phase stability of FA-based PSCs, which is presented in Chapter 5. The champion

1D/3D bilayer PSC exhibits a boosted power conversion efficiency of 19.62%, as well as much longer lifetime than the controlled sample. Additionally, the effects of 1D PyPbI₃ on the phase transition behavior of FA-based perovskite were also investigated by kinetic and thermodynamic analysis. Our results revealed an increased phase transition activation barrier, as well as a reduced thermodynamic driving force in the 1D/3D structures, which enhanced perovskite phase stability dramatically.

A summary regarding all these works, as well as the outlooks for perovskite PV research directions are discussed in Chapter 6.

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Chapter 2

Pyrrolidinium lead iodide from crystallography: a new perovskite with low bandgap and good water resistance

Author contributions: Me and Dr. Gu Xu conceived the idea. I synthesized the material. Dr. James F. Britten and Victoria Jarvis conducted the single crystal XRD measurements. Ryan T. Wang, Lory W. Yang and I measured the material properties. I wrote the manuscript and Dr. Gu Xu edited the manuscript. All authors have read and agreed to the published version of the manuscript. This chapter is published in *Chemical Communications*, 2019.

2.1. Introduction

The growing demands for clean energy have made photovoltaics a popular research area.^{1,2} Among the many types, perovskite solar cells (PSC) have attracted much attention due to their desirable properties, such as tunable bandgap, strong optical absorption, and long carrier diffusion lengths, making them a promising candidate for practical applications.^{2,3} First introduced in 2009,⁴ the typical PSC incorporates methylammonium (MA) into the general perovskite formula of ABX₃, with MA cation surrounded by octahedral units of lead halide (PbX₃, X = I or Br). Within a decade, the PSC has achieved a prominent energy efficiency of 23.3%,⁵ rivaling already commercialized silicon solar cells.

However, despite the favorable efficiency, these PSCs have stability problems, resulting a very short lifetime. The MAPbI₃ structure degrades within hours upon exposure to the moisture environment. This is attributed to the hygroscopic nature of methyl ammonium, which leads to the degradation of the perovskite.^{6,7}

In order to fight against the moisture instability, in addition to the usual strategies, such as encapsulation, and surface modification, which have been proven to be less effective⁸⁻¹¹, a more straightforward approach should be to replace the MA cations, the root cause of the problem. For example, formamidine (FA) was found to be the organic cation that forms a similar perovskite with PbX₃.^{12,13} But the FAPbI₃ perovskite solar cells only presented an energy efficiency of 4.3%, as demonstrated by Koh in 2014.¹²

Although the efficiency could be improved by modifying the device fabrication technology, the FAPbI₃ perovskites are still unstable.¹²⁻¹⁷ Worse off, inorganic counterparts such as CsPbI₃, achieved even lower efficiency of 2.9% while retains instability.^{18,19} More recently, azetidine (Az) containing perovskite was finally discovered to exhibit excellent water resistance, due possibly to the hydrophobic nature of the higher basicity of azetidine. ^{15,20} Unfortunately, it presents a bandgap of 2.15 eV, plus a 2D/3D distorted structure, leading to an impractical energy efficiency of <1%.¹⁵

It is therefore the purpose of this study, to resolve the challenge of PSC stability by finding a better substitute for the MA cations, based on the postulation that, the 4-membered hetero-cycles suffer severe ring strain, thus limiting the azetidine dipole orientations, which leads to the blue-shift of the absorption spectrum, viz., a higher bandgap.²¹ As the first attempt, 5-membered hetero-cycles, such as pyrrolidine (Py, C₄H₈NH), was introduced into the perovskite to narrow the bandgap of AzPbI₃.

2.2. Results and discussion

2.2.1. Structure details of PyPbI₃

Single crystal XRD reveals that, a 3D hexagonal perovskite of PyPbI₃ was formed. With low ring strain, suitable tolerance factor of 1.026,²² and intrinsic hydrophobicity, it is found that the newly synthesized PyPbI₃ not only retains the same water resistance, but also exhibits a lower bandgap, formulating a possible answer to the long-standing challenge of PSCs.

The experimental details and single crystal data of PyPbI₃ were summarized in ESI

(see Appendix: Supporting Material, for Chapter 2).

To illustrate the formation of the PyPbI₃ perovskite, single crystal XRD result was displayed in **Fig. 2.1**. Comparing with the database, it is clear that a new perovskite of PyPbI₃ was synthesized successfully. ^{15,23}



Figure 2.1 Calculated XRD pattern of (C₄H₈NH₂)PbI₃ from single crystal data.

The structure refinement was initiated with the atomic coordinates reported by O. Weber etc. al.²⁴ The space group P6₃/mmc was initially assumed for the structure and was later confirmed by the structure refinement result, which can approximately be obtained by substituting imidazole with pyrrolidine, as shown in **Fig. 2.2** of a perspective view. The asymmetric units of the PyPbI₃ include one lead, one iodine, and one pyrrolidinium cation. As a result, the crystal structure is of the hexagonal

perovskite-type, but with the same ABX₃ as the others. Six organic pyrrolidine cations are arranged hexagonally around the octahedral chain and the compound crystallizes following hexagonal space group P6₃/mmc. The structure refinement shows that PyPbI₃ has lattice constants a, c of 9.3117(5) Å and 8.1080(4) Å, and a volume of 608.84(7) Å³, respectively.



Figure 2.2 Crystal structure of (C₄H₈NH₂)PbI₃; lead yellow, iodine purple, carbon black, nitrogen blue and hydrogen grey.



Figure 2.3 Crystal structure of (C₄H₈NH₂)PbI₃, viewed along c-axis.

The bond distance of Pb-I is 3.2501(6) Å, and the $\overline{3}m$ symmetry of Pb indicate that

the octahedron chains in our perovskite are more regular than in other perovskites, such as MgSiO₃, where the Si-O distance in the $[SiO_6]^-$ octahedron varies from 1.7827(7) to 1.8005(3) Å,²⁵ or hexagonal imidazolium lead iodide, where the bond length of Pb-I varies from 3.225(2) to 3.240(3) Å.²⁴

The Pb-I chains of the PyPbI₃ were found to be disordered, when viewed along the c-axis, as shown in **Fig. 2.3**, where the iodine ions are partially eclipsed instead of fully staggered. One possible cause is the large space between the long chains, due to the bonding length of Pb-I, resulting in two possible ways to extend the octahedral chains. Despite the inter-chain disordering, the intra-chain regularity is assumed to be well maintained.

The organic pyrrolidine cations around the lead iodide chains neutralize the negative charges of the octahedra and separate the chains by hydrogen bonds. As shown by **Fig. 2.3**, the pyrrolidine cations are highly disordered due to their 12-fold dipole orientations, the same as MA cations in a cubic phase.²¹ The orientational disorder in the pyrrolidinium cations can be related to the rotational disorder of the PbI₃ chains along the chain axis. The large gap between the pyrrolidine and the octahedra chains allow for the organic cations to arrange in various ways, which bears close resemblance to that found in imidazolium lead iodide.²⁴ On the other hand, within pyrrolidinium magnesium bromide, PyMnBr₃, the pyrrolidine cations exhibit only 2 possible orientations,²⁶ which is due possibly to the smaller spacing between the chains.



Figure 2.4 Pyrrolidinium lead iodide (a) SEM image of PyPbI₃ thin film and (b) PL measurement.

2.2.2. Thin film properties of PyPbI₃

The SEM image of the PyPbI₃ (**Fig. 2.4**a, taken by JEOL JSM-7000F) shows that the film consists of many large grains, around 2-3 μ m in size, which are comparable to that of other perovskite films found in literature.^{12,13,27} Also, there is little grain boundary coverage in the area, presumably favorable to the solar cell performance.¹⁵

The bandgap of PyPbI₃ was assessed by DU-800 Spectrophotometer, using FTO glass as the substrate. Absorption spectra measured between 450 and 900 nm reveal a bandgap of the material at 1.80 eV as derived from the Tauc plot. An absorption coefficient of ~2.183×10⁴ cm⁻¹ was obtained at a wavelength of 690 nm with an average film thickness of 500 nm which is determined by profilometer. The photoluminescence result was also shown in **Fig. 2.4**b, which peaks around 680 nm (~1.82 eV), consistent with the absorption result (**Fig. 2.5**).



Figure 2.5 (a) Absorption spectra and (b) Tauc plot of PyPbI₃ (298K).



Figure 2.6 XRD patterns of PyPbI₃ before dripping water (red) and after dripping water (black).

To test the water stability of PyPbI₃ films, they were immersed in water for 1 hour (**Fig. S2.1**, ESI). Thin film XRD was measured before and after the immersion. The major peaks in the diffraction patterns matched well to each other, showing a much better water resistance than that of the MA,¹⁵ as demonstrated by **Fig. 2.6**.

2.3. Summary

To conclude, 5-membered hetero-cycles of pyrrolidine (C₄H₈NH), were introduced into the PbI₃ perovskite, in order to improve the water stability of the MA perovskite, and reduce the bandgap of the AzPbI₃. Single crystal XRD shows that a hexagonal perovskite of pyrrolidinium lead iodide was formed for the first time. PyPbI₃ has a bandgap of about 1.80 eV, well below that of AzPbI₃ (~2.15 eV), which is capable of attaining an optimal energy efficiency above 26% according to Shockley- Queisser's Limit. Therefore, the good moisture resistance further reveals PyPbI₃ a promising candidate for an optimal perovskite solar cell.

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Chapter 3

Pyrrolidinium containing perovskites with thermal stability and water resistance for photovoltaics

Author contributions: Dr. Gu Xu and I conceived the idea. Ryan T. Wang, Lory W. Yang and I conducted most of the experiments. Dr. Nebile Isik Goktasb and Dr. Ray LaPierre helped to measure the steady state photoluminescence spectra. Na Liu and Dr. Qi Chen measured the defect density of the material. I wrote the manuscript and Dr. Gu Xu edited the manuscript. Dr. Gu Xu designed the front cover image; me and Dr. Gu Xu together made the image. All authors have read and agreed to the published version of the manuscript. This chapter is published in *Journal of Materials Chemistry C* as the front cover (page 37), 2019.

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PAPER Gu Xu *et al.* Pyrrolidinium containing perovskites with thermal stability and water resistance for photovoltaics

3.1. Introduction

With the rapid improvement of the power conversion efficiency (PCE) from 3.8% to 24.2%¹ in less than one decade, perovskite solar cells (PSCs) have been widely considered as a promising candidate for next generation photovoltaic due to their suitable bandgap², excellent absorption property³ and simple solution-processed synthesis methods^{4.5}. However, despite their impressive performance, a major bottleneck of the commercialization remains. The PSCs are not only unstable in humid environment^{6.7}, but also show poor thermal stability at the working temperature⁸ (85°C). The most commonly employed PSCs material CH₃NH₃PbI₃ (MAPbI₃) was shown to be intrinsically thermal-unstable⁸. In order to fight against the moisture instability alone, various strategies have been developed, including device encapsulation⁹, surface passivation¹⁰, but little improvement has been achieved. As a result, replacing MA cations seems inevitable^{8,11-13}.

Although the replacements of various cations have been experimented, such as formamidine (FA)^{14,15}, hydrazine (HA)¹⁶ and many others¹⁷, still none resolves the stability issue. This may be attributed to the hydrophilic nature of these cations^{10,18}. Therefore, the hydrophobic structure has been selected and introduced into perovskite structure to enhance their water resistance in some recent attempts¹⁹⁻²⁴. In this regard, a three-membered ring based aziridinium lead iodide has been simulated²⁵, which showed a theoretical bandgap as low as 1.49 eV and good water resistance. Yet, due to the

extreme toxicity of aziridine²⁶, it is impractical to apply to the real devices. Although such toxicity can be eliminated by applying a four-membered azetidinium ring-based perovskite AzPbI₃, it raises up the bandgap to 2.15eV, which is significantly higher than that of both MAPbI₃ and FAPbI₃, resulting in a low PCE of less than 1%^{27,28}. Moreover, the structure of AzPbI₃ is extremely distorted²⁷, because of the severe strain in the four-membered azetidine rings, which aggravates the thermal instability.

Based on these developments, a novel five-membered pyrrolidinium ring-based perovskite PyPbI₃ was synthesized in our previous attempt²⁹, to release the strain in Az cations. Such structure was proved to be highly ordered and moisture stable²⁹, offering a possible solution to the long-standing moisture instability problem. However, the thermal stability of PyPbI₃ remains uncertain, which is imperative, crucial, and needs to be investigated.

It is, therefore, the purpose of this study, to resolve the stability problems in MAbased perovskites, by investigating the thermal stability of PyPbI₃. Based on the results of in-situ X-Ray Diffraction (XRD), UV absorption and photoluminescence, we were able to uncover the thermal stability of PyPbI₃, which remains intact up to 135°C, as well as to confirm the smaller bandgap of PyPbI₃ (1.80 eV), than that of AzPbI₃ (~2.15 eV). In addition, PyPbI₃ was found to possess endured moisture resistance after exposing in ambient air for 4 months. These results not only make PyPbI₃ a promising candidate for photovoltaics, but also present a possible solution to the long-standing stability problem of perovskite solar cells.

3.2. Experimental

3.2.1. Film formation

1 millimole of pyrrolidinium hydroiodide (98%, TCI) and 1 millimole of lead iodide (99.999%, Sigma) were dissolved in 1ml DMF (99.99%, Sigma), respectively. Drop casting method and spin coating method were adopted to fabricate the perovskite thin films. After annealing at 120°C for 40 minutes, polycrystalline films were obtained from both methods. The structure was confirmed via P-XRD (**Figure S3.1**) and H-NMR spectra (**Figure S3.2**).

3.2.2. In-situ XRD measurement

X-Ray Diffraction (XRD) patterns of polycrystalline film were collected using a Bruker-AXS D8 DISCOVER X-ray diffractometer with CuK α 1 radiation (λ = 1.79026 Å) in the range of 8–78° (2 θ) with a step size of 0.002° and a time setting of 0.1 s per step. For in situ XRD experiments, the films were placed in a sample chamber armed with a temperature-control stage. The thermal XRD patterns were collected every 30 minutes.

3.2.3. Characterization

UV-vis spectra were acquired from thin film samples at room temperature using a Cary 5000 Spectrophotometer. The Tauc plot was used to estimate the bandgap of the material. The photoluminescence test is conducted by Ar-ion laser (excitation wavelength=514.5 nm) at room temperature from Melles Griot (35LAP431208) at a power of 130mW with a repetition rate of 50 Hz. The PL signals were collected using a liquid N₂-cooled silicon CCD. Scanning electron microscopy was carried out on a JEOL JSM-7000F instrument operating at a 0.1 - 5.0 kV landing voltage.

A Nicolet 6700 FT-IR Spectrometer was used to acquire the FTIR spectra in the wavenumber range of 500–4500 cm⁻¹ with a resolution of 1 cm⁻¹ in DRIFT mode, dispersing the powdered samples in dry KBr powder.

TGA measurements on the PyPbI₃ samples were performed using a Netzsch 409 PC Luxx station, with a temperature range from ambient to a maximum of 1600 Celsius.

3.3. Results and discussion

To investigate the thermal stability of PyPbI₃, in situ XRD with high temperature stage was employed. The initial temperature was set up at 40°C, and gradually increased to 135°C. The temperature was held for 30 min for each stage. As shown in **Figure 3.1**, no obvious change was observed in XRD patterns for all stages, which indicated the thermal stability of PyPbI₃. In addition, TGA measurement was also taken to evaluate



the thermal stability of PyPbI₃, as illustrated in Figure S3.3.

Figure 3.1 In-situ thermal XRD of PyPbI₃.

Moreover, the XRD test also confirmed the long-term moisture resistance of PyPbI₃ on a thin film sample which has been exposed in humid environment for 4 months. Such test is still of huge significance for the enduring stability even though the moisture stability of PyPbI₃ has been previously tested via dripping into water for 30 min²⁹. No decomposition was found in their XRD patterns, as indicated in **Figure 3.2** which presented excellent moisture resistance of PyPbI₃. These results prove that PyPbI₃ is stable not only at high temperature way above working condition, but also in moisture environment for an extensive period of time.



Figure 3.2 XRD patterns of PyPbI₃ before (black) and after (red) exposed in ambient for 4 months.

To further ensure the suitability of PyPbI₃ in photovoltaic application, the bandgap needs to be determined, which is given by UV absorption and steady-state photoluminescence (PL) tests. The onset of absorption spectra located at 660 nm, which reveals a bandgap of the material at 1.80 eV as derived from the Tauc plot, with an absorption coefficient of more than 10⁴, as shown in **Figure 3.3**. Such result is consistent with the photoluminescence result (**Figure 3.4**), which indicated the bandgap value of PyPbI₃ (~1.80 eV) is, indeed, significantly lower than that of AzPbI₃ (~2.15



eV), making it more promising for photovoltaic applications.

Figure 3.3 UV absorption and the Tauc plot (inset) of PyPbI₃ thin film.



Figure 3.4 Steady state photoluminescence (PL) result of PyPbI₃.



Figure 3.5 SEM image of the PyPbI₃ thin film.

Other than bandgap, another important factor that influences the device performance is the film morphology, which was detected by field emission SEM (JEOL JSM-7000F), as shown in **Figure 3.5**. Clearly, PyPbI₃ thin film consists of many large grains, with an average size of $2-3\mu m$, which is comparable to that of other literatures^{4,27,30}.

The defect density and the conductivity of the crystal were found to be 2.3×10^{16} cm⁻³ and 0.0177 (ohm·cm)⁻¹, respectively, following the method of literature^{31,32}. The value is comparable to that of MA-based perovskites³³.

As demonstrated, PyPbI₃ has presented exceptional thermal stability and long-term moisture resistance, which is in sharp comparison to the literature, where the usual MA and FA based perovskites show neither moisture resistance nor thermal/phase stability. Obviously, for practical solar cell applications, the PyPbI₃ structure is much favourable due to its outstanding thermal/moisture stability.



Figure 3.6 Packing image of the infinite [PbI₃⁻]_n chains highlighting the interchain I-I distances. Lead black and iodine purple.

Table 3.1 Comparison of lattice parameters in various references.			
Sample	MAPbI3 ^{34,35}	FAPbI ₃ ³⁶	PyPbI ₃ ²⁹
Space group	Pm3m	Pm3m	P6 ₃ /mmc
Crystal system	Cubic	Cubic	Hexagonal
Lattice parameter	a=6.276(4) Å	a=6.3620(8) Å	a=9.3117(5) Å
	V=247.1(0.4) Å ³	V=257.51(5) Å ³	c=8.1080(4) Å
			V=608.84(7) Å ³

This superiority of bandgap and stability is attributed to the unique 1D structure of PyPbI₃, as illustrated in its single XRD patterns (**Figure S3.4**), which show hexagonal structure, with the PbI₂ inorganic chains arranged in a face sharing way and organic pyrrolidinium cations embedded between them. One huge benefit of this face sharing arrangement is that it results in a larger volume in the inorganic cage than 3D perovskite, as compared in **Table 3.1** and **Figure 3.6**, where the intramolecular force is weakened and imposes little constraint on the rotation of Py cation. As a result, organic cation is free to move in the cage and leads to 12-fold dipole orientations even at room temperature, as verified by our single crystal XRD²⁹ and FTIR (**Figure S3.5**) results.

Therefore, room temperature phase of PyPbI₃ remains at the working temperature.

The superb moisture resistance of PyPbI₃ can be attributed to its unique ring structure, which is composed of pyrrolidinium cations. The hydrophobic nature of these cations stops the invasion of water molecules^{13,19}, thus improves the moisture resistance of the perovskites.

Although the PyPbI₃ only device is still under development, promising results were already obtained from PyPbI₃ containing FAPbI₃ devices involving a PCE of 19.2%, in addition to much enhanced stability.

3.4. Conclusions

To summarize, ring based pyrrolidinium lead iodide was synthesized and investigated. The newly fabricated PyPbI₃ exhibits not only outstanding moisture resistance after exposing in air for 4 months, but also excellent thermal stability up to 135°C, which is significantly higher than the phase transformation temperature of commonly employed MAPbI₃. In addition, PyPbI₃ also possess a suitable bandgap of 1.80 eV, which enables a theoretical PCE above 26%, as estimated by the Shockley–Queisser's limit. Given that no phase transformation was found in PyPbI₃ at perovskite working temperature, it will be of great potential to replace the existing perovskite structures for solar cell application, not only with both the required stability and desired PCE, but also with stable device performance.

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Chapter 4

An Environmentally Stable Organic–Inorganic Hybrid Perovskite Containing Py Cation with Low Trap-State Density

Author contributions: Conceptualization, methodology, investigation, writing original draft preparation, me; writing—review and editing, Ryan T. Wang & Lory W. Yang & Elton E. Liu.; supervision, project administration, Dr. Gu Xu. All authors have read and agreed to the published version of the manuscript. This chapter is published in *Crystals*, 2020.

4.1. Introduction

With the growing demands for renewable energy, photovoltaics (PV) becomes a popular research area [1,2]. Among all PV materials, organic–inorganic hybrid perovskite (OIHP) has attracted much interest in recent years. In general, OIHP has a formula of ABX₃, where A represents monovalent cations, B for metals (e.g., Pb) and X for halides. Methylammonium lead iodide, with a chemical formula of MAPbI₃, has been considered one of the most important OIHP materials [3]. It has been studied and reported that MAPbI₃ has many superior properties including long diffusion length [4,5], tunable bandgap [6,7] and high defect tolerance [8], which results in the rapid development of its power conversion efficiency (PCE) from 3.8% to 25.2% [9] within only ten years, making OIHP one of the most promising PV materials.

Despite their excellent performance in terms of energy efficiency, the lifetime of the fabricated perovskite solar cell (PSC) is far from ideal [10]. For example, an unencapsulated PSC device would lose 10%–30% of its initial PCE within only several days in ambient conditions [11]. Comparing that with other already commercialized PV materials such as silicon, which has a lifetime of more than 25 years [12], the much shorter lifetime of PSCs confines them as a lab-scale product.

In order to fight against the MAPbI₃ instability problems, numerous methods have been attempted. Although strategies such as interface engineering [13–15] and doping [7,16,17] were shown to improve the environmental stability of MAPbI₃ effectively, they did not enhance the lifetime to any appreciable level, as MAPbI₃ is intrinsically unstable [10,18].

In this regard, replacing the unstable MA cations seems inevitable. In 2014, formamidinium lead iodide (FAPbI₃) [19] was introduced to improve the stability of PSC, but despite the enhanced thermal stability, they suffered severe moisture and phase instability issues [20]. Incorporating small inorganic cations such as cesium (Cs) to form the perovskite structure was also reported in 2015 [21], and the formed CsPbI₃ exhibited improved moisture and thermal stabilities, yet its phase was not stable at room temperature [22]. Most recently, ring-based molecules with a strong hydrophobic nature were considered as an alternative in replacing the conventional unstable MA molecule. In 2017 [23], a four-membered ring-based azetidine (Az) molecule was introduced into the perovskite crystal structure to form AzPbI₃. According to the results, the AzPbI₃ exhibited excellent moisture stability. However, the structure of AzPbI₃ was highly distorted, and its bandgap was not ideal (~2.15 eV). Chao et al. (2018) [24] simulated a three-membered ring-based perovskite, namely aziridinium lead iodide (AzPbI₃). Their results indicated that such perovskite exhibited a low bandgap of 1.49 eV, as well as enhanced structural stability compared with MAPbI₃ and FAPbI₃ in terms of the formation enthalpy. A major issue for AzrPbI₃ was that the aziridine molecule was highly toxic, which made it not practical for application. We thus reported in our previous work [25] a five-membered ring-based pyrrolidine (Py) molecule could be used to form a new perovskite pyrrolidinium lead iodide (PyPbI₃). The PyPbI₃ not only exhibited a lower bandgap (~1.80 eV) than AzPbI₃, but also showed good water- and high-temperature-resistance [9], providing a possible answer to the long-term PSC instability problem. However, the phase stability of PyPbI₃, equally important to the moisture and thermal stability, remains unknown. Moreover, other properties such as defect states, which affect the perovskite PV performance significantly, also need further investigation.

It is, therefore, the purpose of the current report to investigate the phase stability of PyPbI₃. The results of our stability measurements showed that PyPbI₃ exhibited only one phase in an ambient environment, indicating its excellent phase stability. The optical properties and morphology of the PyPbI₃ film were also evaluated. By conducting the space-charge-limited currents (SCLC) measurement in a capacitor-like device, we revealed that PyPbI₃ demonstrated a low trap-state density of ~ 2.3×10^{16} cm⁻³, which is comparable to that of MAPbI₃. Our results indicate that PyPbI₃ is an environmentally stable OIHP material with great potential to be employed in perovskite PV applications.

4.2. Materials and methods

4.2.1. Materials

N,N-Dimethylformamide (DMF, 99.99%) and PbI₂ (99.999%) were purchased from Sigma-Aldrich. Pyrrolidine hydroiodide (PyI, 98%) was purchased from TCI America.
4.2.2. Film Formation and Device Fabrication

The film was fabricated via a simple drop casting method. First, the ITO substrate was sequentially washed with distilled water and ethanol, two times with each. After 20 mins of UV–O₃ treatments, 80 μ L of PyI (80 mg) and PbI₂ (60 mg) in a DMF solution were drop cast on the substrate. The fabricated films were next annealed on a hot plate at 120 °C for 30 mins in air. In the capacitor-like device, the metal electrode was further deposited by thermal evaporation of gold under a pressure of 5 × 10⁻⁵ Pa.

4.2.3. Characterizations

Powder XRD measurements were conducted on a Bruker D8 DISCOVER diffractometer (Bruker Corporation, Billerica, Massachusetts, USA). The steady state photoluminescence (PL) measurement was taken at room temperature with an excitation wavelength of 514.5 nm. The film morphology image was taken by a FEI Magellan 400 XHRSEM scanning electron microscope (SEM) (FEI Company Magellan[™] XHR, Midland, ON, Canada). The current density–voltage characteristics of the devices were obtained using a Keithley 2400 source-measure unit. The light intensity was calibrated using a KG-5 Si diode.

4.3. Results

4.3.1. Fabrication and Characterizations of the Perovskite Film

The PyPbI₃ film was fabricated by employing a simple drop casting method as illustrated in **Figure 4.1** (Details shown in experimental section), following the methods reported in our previous work [9]. The thickness of the formed film was measured as 1500 nm by a profilometer. To investigate the crystal structure of the film, we conducted powder XRD measurements. The results are shown in **Figure 4.2**, and suggest the formation of PyPbI₃ in the film [9]. The relatively low intensity of the first peak could be attributed to the texture in the powder film.



Figure 4.1 The schematic illustration of the PyPbI₃ film fabrication process.



Figure 4.2 XRD results of the fabricated PyPbI₃ film.

The optical property of the PyPbI₃ film was evaluated via steady state photoluminescence (PL) measurement. The excitation wavelength adopted in this study was 514.5 nm. The PL result is shown in **Figure 4.3**, which shows a peak at around 600 nm, exhibiting a blue shift compared to our previous results [25]. This could be attributed to the different thickness of the perovskite film (in this work 1500 nm), leading to a change of its absorption property, as reported in the literature [26–28]. The relatively broad emission characteristic of the peak further indicates that the structure type of PyPbI₃ belongs to 1D perovskite [29]. In addition, the PL luminescence of PyPbI₃ remained the same after one hour in ambient conditions, which indicated its good moisture stability.



Figure 4.3 Steady state PL curve of PyPbI₃.

The morphology of the film was studied via field emission scanning electron microscope (SEM). As shown in **Figure 4.4**, the film consisted of many grains of micrometer sizes and had low grain boundary coverage area, which is comparable with that of MAPbI₃[30].



Figure 4.4 Planar SEM image of PyPbI₃.

4.3.2. Trap-State Density of the PyPbI₃ Film

To investigate the defect states in PyPbI₃ film, SCLC measurements were taken. We fabricated capacitor-like devices following steps shown in the experimental section. The structure of the device is illustrated in **Figure 4.5**, and was composed of ITO/PyPbI₃/Au. From the current density–voltage (J-V) curve shown in **Figure 4.5**, it can be observed that the J-V response is ohmic at low voltage. Upon reaching the intermediate voltage, the defect states are filled by the injected charge carriers (refers to TFL), resulting in a linear relationship between the voltage (V_{TFL}) and the density of defect states (N_{DEF}). Following the methods mentioned in previous reports (N_{DEF} = 2 $\epsilon\epsilon_0V_{TFL}/eL^2$)[11], ϵ_0 is the vacuum permittivity, ϵ (~4.90, determined by RUFUTO 871) is the dielectric constant of PyPbI₃, L (~1500 nm) is the thickness of the perovskite film, and e is the elementary charge. The defect density was estimated to be 2.3 × 10¹⁶ cm⁻³, which is comparable to that of MAPbI₃ (~10¹⁶ cm⁻³), indicating a low trap-state density in the polycrystalline film of PyPbI₃. The origin of the trap-states in PyPbI₃ was assumed to be located at the grain boundaries, as suggested in the literature [31].



Figure 4.5 Current–voltage curves of the devices adopting the as-illustrated configuration. Inset: Device scheme of ITO/perovskite/Au.

4.3.3. Stability Measurements of the PyPbI₃ Film

To investigate the phase stability of PyPbI₃, a set of stability measurements was conducted. According to previous reports on MAPbI₃ and CsPbI₃, the perovskite phase transition was triggered by either raising humidity [18,32] or temperature [22]. We therefore conducted the phase stability measurements in two different environments. First, we evaluated the phase stability of PyPbI₃ in moisture with a relative humidity (RH) of ~50%. The formed film was kept in a desiccator for one week. The results are illustrated in **Figure 4.6**. As can be observed, after one week in an ambient environment, the XRD patterns of PyPbI₃ remained unchanged, indicating the moisture and phase stabilities of PyPbI₃.



Figure 4.6 Initial XRD results of PyPbI₃, and results after one week in ambient conditions with a RH of 50%.

Next, we raised the temperature of the environment. The fabricated film was placed on a hot plate at a temperature of 85 °C for 6 hours. From the XRD results (**Figure 4.7**), a tiny peak appeared at around 14.78°, corresponding to the PbI₂ peak. The PbI₂ peak was assumed to be originated from the surface of the PyPbI₃ film, as suggested in literature [33]. Apart from that, we did not observe any other unknown diffraction peak. In addition, previous TGA measurements [9] further indicated the thermal stability of PyPbI₃, which is consistent with our XRD results.



Figure 4.7 XRD results of PyPbI₃ initial and after 6 hours with T = 85 °C.

4.4. Discussion

The above stability measurement results indicate that PyPbI₃ is highly phase-stable. Combining it with previous results, we can therefore conclude that PyPbI₃ exhibits excellent environmental stability compared to MAPbI₃. The results are further summarized in **Table 4.1**. We also explored the reasons for the enhanced environmental stabilities found in PyPbI₃. The excellent moisture resistance of the perovskite can be attributed to the strong hydrophobic nature of its pyrrolidine rings [9], which can repel the invasion of water molecules, as demonstrated in **Figure 4.8**. The high thermal stability can be related to the greater molecular weight of the Py molecules (71 g/mol) compared to the MA molecules (31 g/mol), as the former molecule is less volatile[11].

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Table 4.1 Comparison of five OIHPs comparing moisture, thermal and phase stabilities.						
Formula	MAPbI ₃	FAPbI ₃	CsPbI ₃	AzPbI ₃	PyPbI ₃	
Moisture stability	Bad [18]	Bad [31]	Regular [21]	Good [23]	Good [25]	
Thermal stability	Bad [34]	Regular [19]	Regular [35]	N/A	Good [9]	





Figure 4.8 Schematic illustration of water-repelling mechanism in PyPbI₃. The top five-membered ring stands for the Py molecule, and structure beneath represents PyPbI₃ perovskite.

4.5. Conclusions

In conclusion, a five-membered ring-based perovskite PyPbI3 was synthesized and its properties were characterized. The trap-state density of the polycrystalline PyPbI₃ film was calculated to be 2.3×10^{16} cm⁻³. The stability measurements reveal that PyPbI₃ is an environmentally stable perovskite, which shows great potential for employment in PSCs to resolve their long-term instability problems. In the future, it will be of great significance to fabricate and investigate the PyPbI₃-only solar cell device.

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Chapter 5

Promoting thermodynamic and kinetic stabilities of FA-based perovskite by in-situ bilayer structure

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5.1. Introduction

Organic-inorganic hybrid perovskite solar cell (PSC) has been widely considered as a promising candidate for the next generation of photovoltaics, due to its excellent absorption property¹, long diffusion length^{2,3}, etc. As a consequence, the power conversion efficiency (PCE) of PSCs has been improved drastically from 3.8% to 25.2%⁴, within one decade of its original report in 2009⁵.

However, the perovskite materials suffer severe moisture^{1,6}/thermal⁷ /photo⁸ instability problems, which hinder their commercialisation. The commonly employed methylammonium (MA)-based MAPbI₃ has been proved to be thermally unstable intrinsically⁷. As a result, formamidinium (FA)-based FAPbI₃ has been suggested to replace MAPbI₃ due to its better thermal stability^{8,9} and smaller bandgap (~1.48 eV, compared to 1.55 eV of MAPbI₃). However, the FA-based perovskites suffer undesirable phase instabilities¹⁰⁻¹³, viz., FAPbI₃ may spontaneously be transformed from the black colored photo-active α -phase, which is thermodynamically unstable, to the yellow colored photo-inactive δ -phase, which is thermodynamically stable, in ambient environment, which in turns stops the photovoltaic function, thereby impeding its development for practical applications.

In order to fight against the FAPbI₃ phase instability problem, numerous efforts have been made, such as doping¹⁴⁻¹⁶, strain engineering¹⁷⁻¹⁹, etc. Among them, interfacial modification has attracted lots of interests²⁰⁻²². It was found that functionalizing perovskite surface by small molecules^{16,23-25} or two-dimensional (2D) perovskites²⁶⁻²⁸ can effectively stabilize the FA-based black perovskite phase, without affecting its photovoltaic performance. Most recently, 1D/3D bilayer PSCs show great potential to be employed as an alternative approach for the development of both highly efficient and stable PSCs, due presumably to their superior moisture stability²⁹⁻³², self-healing property³³, and thermodynamic reliability^{34,35}. However, the influence of the stacking 1D perovskites on the phase transition behavior of the 3D perovskite layer remains unknown. For instance, the formed 1D perovskites may behave only as a protective layer, to prevent the invasion of water molecules. It might also affect the 1D/3D bilayer structure through its thermodynamic and kinetic reliabilities.

In the meantime, attempts have been made to unravel the cause of FAPbI₃ phase stability improvement^{13,36-38}, in order to develop appropriate strategies to resolve this long-term instability problem. It was recently found that the system energy^{36,37} and entropy^{38,39} may play a key role in stabilizing the perovskite black phase. However, it is far from satisfactory to just make a mere comparison between the states of perovskite before and after the phase transition, while ignoring the variation path of above-mentioned parameters during the transition process, e.g., the phase transition activation barrier has been absent thus far.

It is therefore the purpose of the current report, to present a facile strategy to enhance the FA-based perovskite phase stability and photovoltaic performance, as well as to investigate the effect of 1D perovskites on the phase transition behavior of 3D perovskites, from thermodynamic and kinetic perspectives, through in-situ 1D/3D perovskite bilayer structure. Based on the previous reports of 1D PyPbI₃³⁰, which was first found to be moisture and thermodynamically stable³⁵, and later used as a promising 1D material to enhance the stability and PCE of MAPbI₃⁴⁰, a thin layer of PyPbI₃ has been employed during the fabrication of a 1D/3D FA-based PSC architecture. By employing kinetic measurements and first-principle calculations, we obtained the phase transition activation barrier and the formation energy difference (ΔE) between the α and δ phases for the perovskite phase transition. Considering the temperature dependence of the activation barrier, which has been well observed but not accounted for in the literature³⁹, our phenomenological analysis reveals that the activation barrier was improved after the formation of such 1D/3D structure, indicating that the phase transition in 1D/3D perovskites is suppressed kinetically. In addition, the thermodynamic energy difference of FA-based perovskite decreases after the stacking of 1D PyPbI₃, indicating a reduced driving force for α -to- δ phase transition. As a result, the phase stability of perovskites was enhanced simultaneously in terms of both thermodynamics and kinetics, as confirmed by stability measurements. In addition, the photovoltaic performances of 1D/3D bilayer PSCs are also enhanced, with the champion device showing a PCE of 19.62%, V_{oc} of 1.08 V, J_{sc} of 24.38 mA/cm², and FF of 0.73. Our results indicate that such strategy could be a better choice for the simultaneous improvement of stability and photovoltaic performance.

5.2. Results and discussion

5.2.1. Fabrication and characterization of perovskite thin films

The single crystal of 1D pyrrolidinium lead iodide, with a formula of PyPbI₃, was synthesized successfully via anti-solvent vapor-assisted crystallization (AVC) method (details available in supplementary information). The crystal structure of PyPbI₃ consists of 1D chains of face-sharing [PbI₃]⁻ octahedra with six organic pyrrolidine cations (Py⁺) arranged hexagonally around the chain, as illustrated in **Fig. 5.1**a-c. Single-crystal XRD results³⁰ reveal that PyPbI₃ crystallizes following hexagonal space group P6₃/mmc in high purity, as confirmed by the comparison of experimental and calculated XRD patterns in **Fig. 5.1**d. In the following experiments, 1D PyPbI₃ crystal were synthesized on top surface of the 3D perovskite film (structure of 1D/3D perovskite film illustrated in **Fig. S5.2**) via in-situ growth method according to the procedure mentioned in the previous 1D/3D works³² (**Fig. S5.3**) (see Methods for details).



Figure 5.1 (a) Crystal structure of 1D pyrrolidinium lead iodide (PyPbI₃), viewed (b) along b axis and (c) along c axis. (d) Normalized XRD data for calculated 1D, experimental 1D (PyI=120 mg/mL), 3D and 1D/3D films (PyI=10 mg/mL). Stability test of controlled 3D and 1D/3D films:
(e) Normalized XRD pattern changes before and after 5-day storage under ambient conditions with a relative humidity of 50 ± 5%; * and # for perovskite α phase and δ phase, respectively. (f) Photographs of perovskite films during 25-day storage in ambient with a relative humidity of 50 ± 5%. (g) UV-vis spectra of pristine 3D and 1D/3D films before and after 5-day under ambient conditions.

To study the crystal structure of the 1D/3D perovskite film, X-ray diffraction (XRD) measurements were performed. As shown in **Fig. 5.1**d, the peak detected at 10.98° in the 1D/3D perovskite film could be attributed to (100) reflections of 1D PyPbI₃³⁰, indicating that a 1D/3D perovskite bilayer structure was successfully constructed. The seemingly 'weak' XRD pattern of 1D PyPbI₃ is attributed to the fact that, the 1D/3D films were fabricated adopting a low concentration of PyI solution, which would be obviously much more evident should higher concentration be incorporated.

Furthermore, perovskite films treated with 0, 5, 10 and 15 mg/mL of pyrrolidinium hydroiodide (PyI, chemical structure shown in **Fig. S5.4**) isopropanol (IPA) solution were fabricated. As illustrated in **Fig. S5.5**, with the increased concentration of PyI solution, the intensity of (100) peak for PyPbI₃ increases, and as a consequence, there will be more PyPbI₃ generated on the perovskite surface. Following the literature^{22,41}, an excessive PbI₂ phase (diffraction peak at 12.6 °) was introduced to enhance the efficiency. For all the samples, the characteristic peaks (e.g. 13.8 ° and 24.2 °) are related to the 3D perovskite^{13,36}.

To investigate whether the 1D/3D structure perovskite films exhibit a better phase stability than the 3D perovskite films, all the prepared films were stored under ambient conditions with a relative humidity (RH) of approximately $50 \pm 5\%$. Fig. 5.1e shows the corresponding XRD patterns measured before and after 5 days in ambient conditions. The pristine 3D perovskite film degraded into photo-inactive δ -phase (e.g. at 11.7° , #) after 5 days in air. In contrast, the 1D/3D perovskite film illustrated a retarded black-to-yellow phase transition with only a tiny peak appeared at 11.7° after 5 days, as demonstrated in Fig. 5.1e and Fig. S5.7. The photographs of degraded 3D and 1D/3D perovskite films are presented in Fig. 5.1f. The color of the 3D film changed from black to yellow after stored in air for 5 days, while the 1D/3D film remained intact in black even after 25 days. Fig. 5.1g illustrates the UV-vis absorption spectra for those films. For the 1D/3D perovskite film, a slight red shift in the absorbance onset was observed after 5 days in air. This could be ascribed to the increase of defect states in the aged film,

which reduces its bandgap. In contrast, the pristine 3D perovskite film exhibited a drastic decrease of light absorbance over the whole visible range after 5 days.

5.2.2. Kinetic and thermodynamic analyses of perovskite phase transition process

To better understand the reason for the improved phase stability in 1D/3D perovskites, the phase transition process has been analyzed in terms of thermodynamics and kinetics. In particular, kinetic parameters such as activation energy barrier, E_a , can be extracted by measuring the transformed fraction of the transition process at various stages.



Figure 5.2 Kinetic data for pristine 3D and 1D/3D films. (a) XRD patterns for 3D and (b) 1D/3D films showing different stages of the perovskite α-to-δ phase transition at 298K with a relative humidity of 85 ± 5%. (c) Corresponding x(t) plots for 3D and 1D/3D films at different temperatures. (d) Qualitative description of the data of 2c, for the relationship between the activation barrier E_a and the temperature T, of 3D and 1D/3D perovskites, respectively.

Hence in our experiments, the strongest peak $\approx 11.7^{\circ}$ scattered from (010) plane of the δ phase, was tracked to determine the transformed fraction via in-situ XRD technique. The data were recorded every ~15- 30 minutes at 273 K, 298 K and 308 K with RH= 85 ± 5%, respectively. **Fig. 5.2**a, b shows the XRD plots of 3D and 1D/3D perovskite films measured at several critical time moments, taken from the 298 K samples (detailed XRD plots for all temperatures were shown in **Fig. S5.8**, **S5.9**). We define A(t) as the integrated scattering intensity of the (010) peak at different time t, and thus the transformation fraction *x* can be expressed by the following equation:

$$x(t) \equiv \frac{A(t)}{A(t_{end})}$$

where the A(0)=0 and A(end)=1, since there is no δ phase at t=0, and we define the time t_{end} when the peak intensity stops increasing. By employing in-situ XRD data measured over time and temperature, the *x*(t) plots for 3D and 1D/3D perovskite films as a function of time could be constructed, as shown in **Fig. 5.2**c. As the activation energy barrier is apparently depending on the temperature (Non-Arrhenius) and involving multiple steps³⁹, viz., the activation barrier increases at elevated temperature, as shown in **Fig. 5.2**d, which has been widely reported but yet to be accounted for. Therefore, it is illustrative, at least phenomenologically, to employ Taylor series expansion of the activation barrier, $E_a = E_a^{0} + a_1^*(T-T_0) + a_2^*(T-T_0)^2$, around the temperatures under the investigation (e.g., $T_0 \sim 300$ K). Numerical fitting of the E_a equation can be done by

ignoring the thermodynamic factor as the first approximation⁴², viz., (attempting frequency)⁻¹*exp(E_a/kT)= (transition time), obtainable from **Fig. 5.2**c at RH=85%. It was found that the leading term alone, E_a^{0} , increases from 0.680 to 0.775 eV, as shown in **Fig. 5.3**b, with the additional enhancement of a_1 *(T-T₀) and a_2 *(T-T₀)², where a_1 increases from 0.0033 to 0.0059 eV/K, and a_2 from 3.58*10⁻⁶ to 1.09*10⁻⁵ eV/K², for 3D and 1D/3D films, respectively, leading to an overall enhancement of lifetime by 30-40 times.



Figure 5.3 (a) DFT-computed energy difference between α and δ phase FA-based perovskite with and without a 1D PyPbI₃/perovskite interface. (b) The thermodynamic and kinetic analysis of 3D perovskite and 1D/3D perovskite phase transition process.

To understand the acquired phase stability from the thermodynamic perspective, we further estimated the formation energy of α and δ phase of 3D and 1D/3D perovskite, respectively, by employing the density functional theory (DFT)-based first-principle calculations (details shown in the experimental section). The resulting formation energy

difference (ΔE) between the α and δ phases of the two structures were illustrated and compared in Fig. 5.3a. The calculated ΔE with the presence of the 1D PyPbI₃ at the interface for a single unit cell was found to be -0.04 eV, which is higher than the 1Dfree case (ΔE = -0.16 eV), indicating the driving force of $\alpha \rightarrow \delta$ phase transition has been significantly reduced in our 1D/3D perovskites. Combining the calculation with the E_a results (summarized by Fig. 5.3b), we have now a more complete picture for the improved phase stability in 1D/3D FA-based perovskite. According to the usual kinetics theory⁴², the transition rate can be described by $v_0^*\sinh(\Delta G/kT)^*\exp(-E_a/kT) \approx$ $v_0^* \Delta G/kT^* \exp(-E_a/kT)$ when $\Delta G \sim kT$, where v_0 is the attempting frequency, ΔG the Gibbs free energy difference ($\sim \Delta E$ here), and E_a the activation barrier. This indicates that, the stability, or the lifetime, which is related to the inverse of the transition rate, is mainly determined by the kinetics, rather than the thermodynamics, as the former is exponential. In other words, the transition can be effectively stopped by a large enough E_a regardless of the sign of ΔG , viz., although the equilibrium is favored by the δ -phase, it may never be reachable under a large kinetic barrier. In addition, the reduction of ΔE (ΔG) may also impede thermodynamically the phase transition. For the 3D perovskite $(\Delta E = -0.16 \text{ eV})$, the ratio of δ/α phases can be estimated by $\exp(0.16/kT_0)$, which is about 600, while this value drops to ~ 5 for 1D/3D perovskite, exp(0.04/kT₀). The above results can also be confirmed by the XRD data in Fig. 5.2a and 5.2b, where the ratio of δ/α phases was indeed suppressed in the 1D/3D perovskite. Therefore, the dramatic enhancement of the stability here is not only attributed to the increased kinetic energy

barrier, but also caused by the reduction of the thermodynamic energy difference between the two phases, due in particular to the introduction of 1D PyPbI₃.



5.2.3. Optical properties and morphologies of perovskite films

Figure 5.4 Optical properties and morphological characterizations of 3D and 1D/3D films: (a) UV-vis spectra. (b) steady-state photoluminescence, (c) time-resolved photoluminescence spectra of 3D and 1D/3D films treated with PyI (10 mg/mL) on a SnO₂/ITO glass substrate. (d) SEM images of 3D and (e) 1D/3D films. (f) AFM images of 3D and (g) 1D/3D films.

To better understand the phase stability improvement, the possible effects of introducing 1D PyPbI₃ on the optical properties and morphologies were also examined. The UV-vis absorption results (**Fig. 5.4**a) show that the light absorption property of 1D/3D perovskite films was slightly enhanced in the wavelength range of 500-600 nm. As expected, the bandgap of bulk perovskite was not noticeably affected by stacking 1D PyPbI₃ layer, as verified by the Tauc plot (**Fig. 55.10**).

The steady-state photoluminescence (PL) of 3D and 1D/3D perovskite films was also measured. As shown in **Fig. 5.4**b, the PL peak of 1D/3D perovskite film located at 798 nm, which exhibited a slight blue shift compared to that of 3D ones (~800 nm).

The time-resolved photoluminescence (TRPL) measurements were carried out on glass/ITO/SnO₂/3D perovskite samples with and without 1D PyPbI₃. The wavelength of excitation light was 475 nm and the data were fitted by a two-component exponential function, as shown in **Fig. 5.4**c. The fast (τ_1), slow (τ_2) and average (τ_{av}) lifetime were calculated³¹ and summarized in **Table S5.3**. The average decay lifetime τ_{av} increased from 201.69 ns to 259.87 ns for 3D and 1D/3D perovskite films, respectively, indicating a reduced non-radiative recombination loss in 1D/3D films.

In addition, surface morphology of the 3D and 1D/3D perovskite films was investigated via scanning electron microscopy (SEM). The SEM images (**Fig. 5.4d**, e) reveal that the surface of 1D/3D perovskite films shows a smaller grain size than the 3D sample, which is consistent with the previous study³¹. The surface roughness of perovskite films was also measured by employing atomic force microscopy (AFM) (**Fig. 5.4f**, g). Apparently, the surface roughness, as well as the corresponding specific surface area have increased significantly after stacking 1D PyPbI₃, with the root mean square (RMS) roughness raised from 6.9 nm to 12.7 nm. The afore-observed morphological change of fabricated films suggests the formation of 1D perovskites on top of the absorption layer, in agreement with other 1D/3D works^{32,33}.



5.2.4. Photovoltaic performance and operational stability of PSCs

Figure 5.5 (a) J–V curve for the best performance of controlled and 1D/3D device (device statistics in the inset); (b) stabilized photocurrent measurement at the maximum power point (0.84 V) of 1D/3D PSCs, (c) corresponding EQE measurement and the integrated J_{sc} of 3D and 1D/3D PSCs, and (d) stability tests of unencapsulated PSCs without and with PyI (10 mg/mL) under ambient conditions (RH~65%).

In order to evaluate the photovoltaic performance of 1D/3D perovskite solar cell devices, we fabricated PSCs employing ITO/SnO₂/perovskite/spiro-OMeTAD/Ag configuration (**Fig. S5.11** inset). The box-chart of devices prepared with different concentrations of PyI solution is shown in **Fig. S5.11**, which reveals an optimized PyI concentration of 10 mg/mL. The PCE distribution of the 3D and 1D/3D PSC devices is

compared in Fig. 5.5a (distribution of photovoltaic parameters can be found in Fig. S5.12, Table S5.4, S5.5). The champion 1D/3D PSC exhibited an efficiency of 19.62%, with a short-circuit current density (J_{sc}) of 24.38 mA cm⁻², an open-circuit voltage (V_{oc}) of 1.08 V, and a fill factor (FF) of 0.73. The improved efficiency and V_{oc} of 1D/3D devices can be attributed to the surface passivation effect, i.e. the ammonium group of pyrrolidine molecules coordinates with the lead vacancy in 3D perovskite^{20.25}. The statistics of the PCE distribution for fabricated 1D/3D PSCs is demonstrated in Fig. 5.5a inset, which verifies a good reproducibility of the devices. Fig. 5.5b further confirms a stable power output for 1D/3D PSCs, which exhibited a stabilized photocurrent density and efficiency of 20.52 mA/cm² and 17.35% during maximum power point under one sun illumination for over 600 s. External quantum efficiency (EQE) spectra of 3D and 1D/3D PSCs is shown in Fig. 5.5c, and the integrated current density is 21.50 mA/cm², which is higher than that of the 3D device (21.14 mA/cm²).

Apart from the enhanced photovoltaic performance, one of the most concerned issues should be the devices environmental stability. To demonstrate the effect of 1D PyPbI₃ on the device stability, the measurement was conducted under simple/primitive testing conditions without encapsulation, in ambient RH of $65 \pm 5\%$ and 22 ± 3 °C, for all the possible duplications. It should also be mentioned that, although silver electrode might induce diffusion, both 3D and 1D/3D devices were fabricated using the same configuration, in order to make comparisons. As demonstrated in Fig. 5.5d, the unencapsulated 1D/3D devices maintained 94% of its initial efficiency after 3 days in

air, while the controlling 3D devices suffered a 22% loss. Remarkably, after 27 days, the 1D/3D devices can still retain 70% of their initial efficiency, while the PCE of 3D devices decays to nil after 12 days. These results indicate that the environmental stability of 1D/3D PSCs has been improved significantly.

5.3. Summary

In summary, we have investigated the effects of 1D perovskites on the phase stability of FA-based perovskites, from both kinetic and thermodynamic perspectives, by the construction of 1D PyPbI₃/3D perovskite bilayer structure. Incorporating the temperature dependence of the phase transition activation barrier, a phenomenological model has been developed. The results indicate that the activation barrier was enhanced under the presence of 1D PyPbI₃, resulting in a prolonged lifetime by 30-40 times. From the DFT calculation, the thermodynamic energy differences between α - and δ -phase were found to be -0.04 eV and -0.16 eV, for 1D/3D and 3D perovskites, respectively. Our results suggest that the inherent characteristics of 1D PyPbI₃, which are both kinetically and thermodynamically more reliable, may help stabilizing the black perovskite phase by improving its E_a and reducing ΔE . In addition, the championing 1D/3D structure PSC exhibited a PCE of 19.62%, which is among the highest in the related previous reports^{32,26,33}. This work exemplifies the importance of 1D/3D bilayer expected to stimulate other successful perovskite phase-stabilizing strategies in the near future.

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Chapter 6

Conclusions and outlooks

This thesis aims to improve the stability of perovskite solar cells, which is considered as the main obstacle for commercialization.

To replace the unstable protype MA cations, 5-membered hetero-cycles of pyrrolidine (C₄H₈NH), were introduced into the perovskite lattice to improve their moisture stability. We investigated the structural and optical properties of the new perovskite, pyrrolidinium lead iodide (PyPbI₃). It has been found that PyPbI₃ showed good moisture resistance and moderate bandgap of PyPbI₃ making it a promising perovskite PV material, which prompted us to further explore its thermal and phase stabilities, equally important as the water stability. The results indicated that the solution processed PyPbI₃ film is environmentally stable and exhibited no phase transition at working temperature.

Both efficiency and stability of PSC were enhanced via the in-situ 1D PyPbI₃/FAbased perovskite bilayer structure. Additionally, we also investigated the effects of 1D perovskites on the phase stability of FA-based perovskites, from both kinetic and thermodynamic perspectives, which leads to the development of the phenomenological model of perovskite phase transition. The results suggested that the inherent characteristics of 1D PyPbI₃ may be applicable to improve stability and efficiency of PSC.

Our works have attracted interests from the perovskite research community. The 1D/3D PSC work is introduced and highlighted by several review papers (*Chemical Society Review*, 2020, 49, 8235-8286; *Journal of Materials Research*, 2020, 35(16), 2166-2189.) as one of the most promising 1D/3D reports. Moreover, based on our finding, other works also employed 1D/3D method to enhance the lifetime and efficiency of FA-based PSC (*Energy& Environmental Science*, 2020, 13, 4344-4352) and MA-based PSC (*Energy Technology*, 2019, 1900918; *Nature Energy*, 2020, 5, 768-776). Apart from the 1D/3D interface engineering, the introduction of 1D Py-based perovskite also help to understand the fabrication of MAPbI₃ film (*Energy Technology*, 2020, 8, 2000148), as well as discover and investigate new perovskite materials (*Chemistry of Materials*, 2020, 32, 13, 5650–5663; *Dalton Transactions*, 2020, 49, 12767-12775; *RSC Advances*, 2020, 10, 1198-1203). Hopefully, the introduction of 1D perovskite research

The future research activities of perovskite PV may be divided into five main categories: toward theoretical efficiency, long term stability, large area coating, recycling technology and perovskite-based tandem technology. We believe that further development of 1D perovskites is necessary to improve PSC's efficiency and lifetime. It is also important to develop low-cost large area coating methods such as blade coating, slot-die coating, stamping and spray coating. In addition, the solution used for the spincoating method is limited for large area production, which means that coating solutions are required to be newly developed for large area coating. Recycling technology should be focused on avoiding lead waste, as lead is a toxic element. Effective collection and reuse of PbI₂ from damaged PSC is thus required to suggest full recyclability.

Although the single junction-based PSC still dominates the research community nowadays, it is believed that the perovskite-based tandem cells would attract more attention and investigation in the future, due possibly to the ease of their industrialization. In fact, many solar cell companies are now focusing on commercialization of perovskite-based tandem solar cells. The first volume manufacturing line for perovskite-on-silicon based tandem cell is expected to be completed in 2021, as reported by the Oxford PV company.

Appendix: Supporting materials

Supporting information for Chapter 2

Pyrrolidinium lead iodide from crystallography: a new perovskite with low bandgap and good water resistance

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1. Thin film synthesis

1m Mol of pyrrolidinium hydroiodide (98%, TCI) and 1m Mol of lead iodide (99.999%, Sigma) were dissolved in 1ml DMF (99.99%, Sigma), respectively. Drop casting method and spin coating were adopted to fabricate the perovskite films. After annealing at 120°C for 1-hour, polycrystalline films were obtained from both methods. We then extracted yellow needle-like single crystal from the drop casting film.

2. Powder X-ray diffraction study

X-ray powder diffraction (XRD) patterns of polycrystalline material were collected using a Bruker-AXS D8 DISCOVER X-ray diffractometer with CuK α 1 radiation (λ = 1.79026 Å) in the range of 8–78° (20) with a step size of 0.002° and a time setting of 0.1 s per step.

3. Single crystal X-ray diffraction study

Data-sets of hexagonal PyPbI₃ were collected using a Bruker APEX-II diffractometer equipped with a CCD detector (graphite-monochromatized Mo-K α radiation, $\lambda = 0.71073$ Å) at 297K. Data integration and cell refinement were performed using the Olex2 software.¹ The structure was analyzed by direct methods and refined using the XL (Sheldrick, 2008) software package.² All nonhydrogen atoms of the structure were refined with anisotropic thermal parameters, and the refinements converged for Fo² > 2 σ (Fo²). All the calculations were performed using SHELXTL crystallographic software package. Symmetry analysis on the model using PLATON revealed that no obvious space group change was needed. In the refinement, the commands EDAP and EXYZ were used to restrain some of the related bond lengths and bond angles. CCDC-1886890 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The experimental data and are given in table S2.1.

4. Optical properties tests

UV-vis spectra were acquired from thin film samples at room temperature using a DU 800 Spectrophotometer. The Tauc plot was used to estimate the bandgap of the material. The photoluminescence test is conducted by Ar-ion laser (excitation wavelength=514.5 nm) at room temperature from Melles Griot (35LAP431208) at a power of 130mW with a repetition rate of 50 Hz. The PL signals were collected using a liquid N₂-cooled silicon CCD.



Figure S2.1. Photographs of PyPbI3 before (left) and after (right) dipping in water

compound	(C ₄ H ₈ NH)PbI ₃
empirical formula	$C_4H_{10}NPbI_3$
formula weight	660.00
temperature	297К
wavelength	0.71073 Å
crystal system	hexagonal
space group	P63/mmc (No. 194)
unit cell dimensions	a= 9.3117(5) Å
	c= 8.1080(4) Å
volume	608.84(7) Å ³
Ζ	1.99992
density (calculated)	3.600 g·cm ⁻³
absorption coefficient	21.405 mm ⁻¹
Absorption (exp)	2.53, 23.57
Tmin, Tmax	
F(000)	564
crystal size	0.37*0.05*0.03 mm ³
θ range for data	2.526 to 30.433 °
collection	
index ranges	-13 <h<9< td=""></h<9<>
	-8 <k<13< td=""></k<13<>
	-11 <l<11< td=""></l<11<>
reflections collected	6688
independent reflections	384 (Rint = 0.0406)
refinement method	Full-matrix least-squares on F ²
data / restraints / parameters	384/0/21
goodness-of-fit on F ²	1.042
final R indices [I>2σ(I)]	0.0235
R indices (all data)	0.0589

Table S2.1. Crystal data and structure refinement for (C₄H₈NH)PbI₃

Reference

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Supporting information for Chapter 3

Pyrrolidinium containing perovskites of thermal stability and water resistance for photovoltaics

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Fig S3.2. H-NMR result of the PyPbI₃ product.



Fig S3.3. TGA curve of PyPbI₃. the product started weight dropping at 218°C, which indicates the original structure of PyPbI₃ remains stable even beyond 200°C. This is much higher than the phase transformation temperature of MAPbI₃, which is only around 55°C⁹. The weight loss then continues throughout the rest of the curve till 600 °C, where the PyPbI₃ decomposes completely.



Fig S3.4. Crystal structure of $(C_4H_8NH_2)PbI_3$; lead yellow, iodine purple, carbon black, nitrogen blue and hydrogen grey. Reprinted with permission from ref. 26.



Fig S3.5. The FTIR spectra of the PyPbI₃ thin film. No sharp bands appear at μ < 840 cm⁻¹ or μ > 3500 cm⁻¹, which means there is no water exist in the material. This is not surprising, considering that the PyPbI₃ product was annealed at 120°C to form the thin film. All the other bands in the spectra can be assigned unambiguously to the pyrrolidinium cations. Moreover, their broadness is a clear indication of their orientational disorder, which was also confirmed by our single crystal XRD results. Obviously, the vibrations of the Pb-I skeleton are not visible in the explored wavenumber range.

Supporting information for Chapter 5

Promoting thermodynamic and kinetic stabilities of FA-based perovskite by in-situ bilayer structure

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Materials. All the commercial materials were used as received without further purification, including pyrrolidinium hydroiodide (98%, TCI), SnO₂ (15% in H₂O colloidal dispersion, Alfa Aesar), ethanol (AR Beijing Chemical Works), HBr (48 wt.% in water, Sigma-Aldrich), HI (57 wt.% in water, Sigma-Aldrich), PbO (99.999%, Sigma-Aldrich), PbI₂ (99.999%, Sigma-Aldrich), CsI (99.90%, Aladdin Industrial Corporation), chlorobenzene (99.9%, Sigma-Aldrich), isopropanol (IPA, 99.99%, Sigma-Aldrich), N,N-dimethylformamide (DMF, 99.99%, Sigma-Aldrich), Dimethyl sulfoxide (DMSO, 99.9%, Sigma-Aldrich), Spiro-OMeTAD (Xi'an Polymer Light Technology Corp.), bis(trifluoromethane)sulfonimide lithium salt (99.95%, Aldrich), 4tertbutylpyridine (99.9%, Sigma-Aldrich), and ITO substrates. The $HC(NH_2)_2I$ and $HC(NH_2)_2Br$ were prepared according to procedure mentioned in previous work^{1,2}.

Film formation and device fabrication. The ITO substrate was sequentially washed with distilled water and ethanol, with two times each. The SnO₂ colloidal solutions (15% in H₂O) were further diluted by H₂O to 2.67%. After 20 mins of UV–O₃ treatments, the diluted SnO₂ solutions were spin-coated at 3000 rpm for 30 s on ITO substrates, and annealed on a hot plate at the displayed temperature of 150 °C for 30 min in ambient air. For the mixed A cation $FA_{0.9}Cs_{0.1}Pb(I_{0.92}Br_{0.08})_3$ (abbreviated as FAPbI₃ in the main text) metal halide perovskite layer, two-step spin coating method was adopted following previous report. In detail, 30 µL of lead iodide solutions were first spin-coated at 2300 rpm for 30 s and annealed at 70 °C for 1 min. Then, 80 µL of mixed cation precursor solutions were spin coated at 2000 rpm for 30 s. The as-fabricated films were then annealed at 150 °C for 45 min in air. After the perovskite annealing, 30 µL of PyI (in IPA) solutions were spin coated on top of the perovskite layer at 3000 rpm for 30 s, and annealed at 120 °C for 10 mins in ambient. Last, 30 µL Spiro-OMeTAD solution doped with LiTFSI and tBP was deposited at 3000 rpm for 30 s. The hole transport material (HTM) solution was prepared by dissolving 60 mg spiro-OMeTAD, 30 µL 4-tert-butylpyridine and 35 µL Li-TFSI/acetonitrile (260 mg mL-1) in 1mL chlorobenzene. Finally, 100 nm Ag was thermally evaporated as counter electrode under a pressure of 5×10^{-5} Pa on top of the hole transport layer to form the metal contact.

Characterization. The absorption spectra were recorded by Hitachi UH4150 spectrophotometer. X-ray diffraction (XRD) patterns were obtained using a Rigaku D/Max 2,200 with Cu K α as the X-ray source. Insitu X-Ray diffraction (XRD) patterns of the polycrystalline films were

collected using a Bruker-AXS D8 DISCOVER X-ray diffractometer with CuKal radiation (λ = 1.79026 Å) in the range of 5-25° (2 θ) with a step size of 0.0021 and a time setting of 0.1 s per step. The films were placed in a sample chamber armed with a temperature-control stage. The thermal XRD patterns were collected every several minutes. The films morphology was measured using a scanning electron microscope (SEM) (S4800). Atomic force microscope (AFM) was performed using Bruker Dimension 5000 Scanning Probe Microscope (SPM) in "tapping" mode. The current density-voltage characteristics of photovoltaic devices were obtained using a Keithley 2400 source-measure system. The photocurrent was measured under AM 1.5 G illumination at 100 mW/cm² using a Newport Thermal Oriel 91192 1000 W solar simulator. The light intensity was calibrated using a KG-5 Si diode. The effective area of each cell was 0.102 cm² defined by masks for all the photovoltaic devices discussed in this work. Current density-voltage measurements were carried out at room temperature. External quantum efficiencies (EQE) were determined on a solar cell quantum efficiency measurement system (QER) provided by Enli Technology Co., Ltd. A calibrated silicon diode with a known spectral response was used as a reference. Steady-state photoluminescence (PL) was obtained by using an FLS980 (Edinburgh Instruments Ltd) with an excitation at 465 nm. Transient-state photoluminescence (TRPL) was

measured by using an FLS980 (Edinburgh Instruments Ltd) with an excitation wavelength at 475 nm and an excitation density of 3.4×10^{14} cm⁻³.

First-principles study. We carried out DFT calculations using the Cambridge Serial Total Energy Package. The exchange-correlation energy was described using the revised Perdew-Burke-Ernzerhof exchange-correlation density functional (PBESOL)³ within the generalized-gradient approximation (GGA). A 400-eV plane-wave kinetic energy cutoff was chosen. The Brillouin zone was sampled with $3 \times 3 \times 2$, $3 \times 3 \times 2$, $2 \times 2 \times 3$, and $1 \times 1 \times 1$ Monkhorst–Pack grids, respectively, for FAPbI₃-hexagonal, FAPbI₃-trigonall, PyPbI₃ and their interfaces calculations. The structure of the supercell and the interface were further optimized to lower the mismatch factor. A 15 Å thick vacuum layer was used to avoid the interaction between top and bottom surfaces.

Johnson–Mehl–Avrami model. As Figure 5.2c exhibits classic phase transformation kinetics, the Johnson–Mehl–Avrami (JMA) model was employed to explore the perovskite phase transition process. Through x(t) plots, the phase transition activation energy E_a , were then extracted by

employing the below equation, which has previously been suggested in describing precursor-to-perovskite transition.

$$ln(t_{x2} - t_{x1}) = \frac{E_a}{RT} - lnk_0 + ln(\beta_{x2} - \beta_{x1})$$

where t_{xn} presents the time corresponding to x_n and E_a is the effective activation energy for the perovskite phase transition process. By applying the equation, the data was plotted as $\ln (tx_2 - tx_1)$ versus $1E^6/RT$ and the slope of the line equals E_a , as shown in Fig. S5.13. The phase transition activation energies of 3D and 1D/3D perovskite films were found to be -29.96 KJ/mol (~0.31 eV) and -90.46 KJ/mol (corresponds to ~-0.94 eV), respectively. However, the negative activation energy is un-physical. As shown in Fig. 5.2d, it is obvious that the activation energy should be positive. Therefore, we must consider the temperature dependence of E_a , and place it into the equation.

Single crystal synthesis of 1D PyPbI₃

The single crystal of PyPbI₃ was synthesized via commonly adopted antisolvent vapor-assisted crystallization (AVC) method⁴. First, 1M of lead oxide (PbO) were dissolved into 2.5 ml HI solution at 90 Celsius. Next, 1M of pyrrolidinium hydroiodide (PyI) salt were added and stirred for 15 mins. After cooling down to room temperature, the solution was filtered and transferred into an enclosed bottle and acetone as anti-solvent was added. After two weeks, the yellow needle-like single crystal of PyPbI₃ can be obtained. The photograph of synthesized single crystal was shown below in Figure S5.1.



Figure S5.1. Photograph of the needle-like PyPbI₃ single crystal.



Figure S5.2. Schematics of the thin film with 1D/3D bilayer structure.



Figure S5.3. The schematic illustration of perovskite film surface treatment process with PyI.



Figure S5.4. Chemical structure of PyI molecule, with carbon grey, nitrogen green and hydrogen blue.



Figure S5.5. XRD patterns of 1D/3D perovskite films treated with different PyI concentration.



Figure S5.6. FWHM of fabricated perovskite thin film with different PyI concentration of 2θ at 13.8° .



Figure S5.7. XRD patterns for 1D/3D and 3D perovskite films initial and under ambient for 5 days. Pink and light blue lines for 1D/3D and 3D initial; purple and blue lines for 1D/3D and 3D after 5 days.



Figure S5.8. In-situ XRD patterns of 3D perovskite films measured every 15-30 minutes at 273K (light blue), 298K (blue) and 308K (dark blue).



Figure S5.9. In-situ XRD patterns of 1D/3D perovskite films measured every 15-30 minutes at 273K (light pink), 298K (pink) and 308K (purple).



Figure S5.10. The Tauc plot of 3D and 1D/3D perovskite film with PyI (10 mg/mL) on a SnO_2/ITO glass substrate.



Figure S5.11. Box-chart for the efficiencies of PSCs fabricated using different concentration of PyI. Inset shows the 1D/3D PSC device structure.



Figure S5.12. J–V metrics of 1D/3D devices with different concentrations in comparison to the controlled 3D ones.



Figure S5.13. Plot constructed from JMA equation to extract E_a . The E_a of 3D and 1D/3D perovskite was determined to be -29.96 KJ/mol and -90.46 KJ/mol, respectively.

compound	$(C_4H_8NH_2)PbI_3$
empirical formula	$C_4H_{10}NPbI_3$
formula weight	660.00
temperature	297K
wavelength	0.71073 Å
crystal system	hexagonal
space group	P6 ₃ /mmc (No. 194)
unit cell dimensions	a= 9.3117(5) Å
	c= 8.1080(4) Å
volume	608.84(7) Å ³
Ζ	1.99992
density (calculated)	3.600 g·cm ⁻³
absorption coefficient	21.405 mm ⁻¹
Absorption (exp)	2.53, 23.57
Tmin, Tmax	
F(000)	564
crystal size	0.37*0.05*0.03 mm ³
θ range for data	2.526 to 30.433 °
collection	
index ranges	-13 <h<9< td=""></h<9<>
	-8 <k<13< td=""></k<13<>
	-11<1<11
reflections collected	6688
independent reflections	384 (Rint = 0.0406)
refinement method	Full-matrix least-squares on F ²
data / restraints / parameters	384/0/21
goodness-of-fit on F ²	1.042
final R indices [I> $2\sigma(I)$]	0.0235
R indices (all data)	0.0589

Table S5.1. Crystal data and structure refinement⁵ for PyPbI₃

	20 (Deg)	FWHM
0 mg/ml	13.86725	0.15943
5 mg/ml	13.87556	0.15749
10 mg/ml	13.88195	0.15939
15 mg/ml	13.86789	0.1512

Table S5.2. Peak center and full-width at half-maximum of (001)

reflection peak for α -phase perovskite; data obtained from Origin.

	A ₁	$\tau_1(ns)$	A_2	$\tau_2(ns)$	$\tau_{ave}(ns)$
Controlled	0.43	116.10	0.57	266.26	201.69
Passivated	0.31	135.72	0.69	315.65	259.87

 Table S5.3. Fitted data for TRPL measurement.

Table S5.4. Photovoltaic parameters of the optimized PSCs under one s	sun
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				PCE (%)	
	J_{sc} (mA/cm ²)	$V_{oc}(V)$	FF	Best	Average
3D PSCs	23.16	1.02	73.97	18.21	17.41
1D/3D PSCs	24.38	1.08	73.15	19.62	18.33

illumination (the concentration of PyI is 10 mg/ml).

				PCE (%)	
	J_{sc} (mA/cm ²)	$V_{oc}(V)$	FF	Best	Average
0 mg/ml	23.16	1.02	73.97	18.21	17.41
1 mg/ml	23.95	0.98	70.97	16.32	15.91
2 mg/ml	23.42	1.01	75.42	17.84	16.89
3 mg/ml	24.58	0.98	72.70	17.47	15.98
4 mg/ml	24.18	0.98	69.35	16.46	15.49
5 mg/ml	24.51	1.03	70.76	17.90	17.02
10 mg/ml*	24.38	1.08	73.15	19.62*	18.33
15 mg/ml	23.97	0.99	70.95	16.80	15.23
20 mg/ml	16.15	0.99	38.63	5.73	4.94

 Table S5.5.
 Photovoltaic parameters of PSCs treated with different

concentrations of PyI solution.

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