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Fundamental Studies of Chemical Stability and Carrier Process in Hybrid Perovskite Materials

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ABSTRACT

FUNDAMENTAL STUDIES OF CHEMICAL STABILITY AND CARRIER PROCESS IN HYBRID PEROVSKITE MATERIALS

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Department of Chemistry and Biochemistry
Northern Illinois University, 2018
Prof. Tao Xu, Director

This dissertation comprehensively studies the optoelectronic properties of organic-inorganic hybrid perovskites to fundamentally answer their foundations of outstanding performance on solar cells, photodetectors, nanowire lasers and other optoelectronic applications. Specifically, a novel type of charge carrier-lattice interaction was discovered in perovskite methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$), where photoluminescence lifetime of photoinduced carriers is strongly dependent on the rotational frequency of CH$_3$NH$_3^+$, as modulated via substitution of hydrogens with deuterium atoms in the organic cation. In addition, two-dimensional Ruddlesden-Popper perovskite (CH$_3$NH$_3$)$_2$Pb(SeCN)$_2$I$_2$ was first synthesized and characterized in the field, and its photoluminescence properties were systematically examined. The existence of intensive photoluminescence peak with small full width at half maximum (35.8 nm) along with clearly observed photoluminescence decay kinetics (4.6 ns) indicates a highly homogeneous band structure and distinctive semiconductor properties of this material. By contrast, thiocyanate-based perovskite counterpart (CH$_3$NH$_3$)$_2$Pb(SCN)$_2$I$_2$ showed much broader photoluminescence peak (full width at half maximum: 171.1 nm) with no detectable time-resolved photoluminescence, thus signifying the negative impact of sulfur atom on the optoelectronic function of such material.
Moreover, it was found that the moisture stability of CH$_3$NH$_3$PbI$_3$ is significantly enhanced after incorporating divalent anion Se$^{2-}$ into the material lattice. 10% w/w PbSe doped CH$_3$NH$_3$PbI$_3$ films were chemically stable after 72 hrs of aging in 100% humidity at 40 °C, while pristine CH$_3$NH$_3$PbI$_3$ film was completely degraded after only 30 min. of aging under the same condition. As PbSe doped CH$_3$NH$_3$PbI$_3$ films maintained the perovskite structure, a top power conversion efficiency of 10.4% with 85% retention after 624 hours of aging in ambient air was achieved on an unencapsulated 10% w/w PbSe doped CH$_3$NH$_3$PbI$_3$ solar cell, in contrast to 16% retained power conversion efficiency after 432 hrs of aging on CH$_3$NH$_3$PbI$_3$ cell. Meanwhile, the incorporated Se$^{2-}$ also effectively suppressed iodine diffusion in solar cell, thereby leading to greatly improved chemical stability of the silver electrodes. To explore chemical pathways that can additionally enable greater thermal stability of perovskite materials, which is another crucial factor required for environmental stability of photovoltaics under operating conditions, isotropic Cs$^+$ cation was doped into CH$_3$NH$_3$PbI$_3$ structure for heat stress tests, where perovskite (CH$_3$NH$_3$)$_{0.95}$Cs$_{0.05}$PbI$_3$ thin film showed increased thermal stability up to 200 °C, at which pristine CH$_3$NH$_3$PbI$_3$ thin film was completely decomposed to PbI$_2$. As a bonus, (CH$_3$NH$_3$)$_{0.95}$Cs$_{0.05}$PbI$_3$ perovskite single crystal exhibited prolonged carrier lifetime in comparison with pristine CH$_3$NH$_3$PbI$_3$ counterpart, which can be one of the reasons responsible for the superior photovoltaic performance witnessed on Cs$^+$-doped perovskite solar cells.

To further evaluate the effects of alkali metal ion on the physical properties and optoelectronic performance of perovskite materials, ultraviolet (UV) photodetectors based on formamidinium lead chloride (HC(NH$_2$)$_2$PbCl$_3$) perovskite nanorods were fabricated. It was found that HC(NH$_2$)$_2$PbCl$_3$ nanorods grown with LiCl additive displayed much enhanced photocurrents
under UV illumination. Most importantly, LiCl:HC(NH$_2$)$_2$PbCl$_3$ photodetector exhibits unprecedented distinguishability towards 254-nm and 365-nm UV photons with temporally varying intensities, as in the form of bipolar photocurrents/photovoltages with periodically oscillating amplitudes. Such discovery in perovskite optoelectronics will realize ciphering, acquisition and decoding of optical information embedded in UV photons, and will contribute to the development of novel communication technology.
FUNDAMENTAL STUDIES OF CHEMICAL STABILITY AND CARRIER PROCESS IN HYBRID PEROVSKITE MATERIALS

BY

JUE GONG
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A DISSERTATION SUBMITTED TO THE GRADUATE SCHOOL IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY

Doctoral Director:
Tao Xu
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Certain tables and figures in this dissertation have been published previously, as follows:

Figure 1-1, Figure 2-2-3b, Figure 3-2-2 and Figure 3-2-3 appear in J. Gong et al. (2018), *Journal of Energy Chemistry*, 27(4), 1017-1039, doi: 10.1016/j.jechem.2017.12.005. Figures 2-1-1 – 2-1-20, Figures 2-1-22 – 2-1-24 and Tables 2-1-1 – 2-1-3 appear in J. Gong et al. (2016), *Journal of Physical Chemistry Letters*, 7(15), 2879-2887, doi: 10.1021/acs.jpclett.6b01199. Figures 3-1-1 – 3-1-23 and Tables 3-1-1 – 3-1-4 appear in J. Gong et al. (2018), *Advanced Materials*, 30(34), 1800973, doi: 10.1002/adma.201800973.
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1. INTRODUCTION

Metal halide perovskites (structural formula: ABX₃, A=CH₃NH₃⁺ (MA⁺), HC(NH₂)₂⁺ (FA⁺) and/or Cs⁺, B=Pb²⁺ and/or Sn²⁺, X=I⁻, Br⁻ and/or Cl⁻, with perovskite structure shown in Figure 1-1) have risen as a class of prominent light absorbers that demonstrated exceptional photovoltaic (PV) performance in solar cells within the past ten years, in which the record power conversion efficiency (PCE) of single-junction perovskite solar cells has rapidly attained 23.3% in 2018 [1] from original 3.8% in 2009 [2], corresponding to the fastest evolution in the history of solar cell research, as shown in Figure 1-2. Characteristically, the majority of the high-efficiency solar cells adopt perovskite methylammonium lead iodide CH₃NH₃PbI₃ (MAPbI₃) as the light-harvesting active material. [3-7] Crucially, the outstanding performance of MAPbI₃ cells stems from the superior charge carrier properties of the perovskite material, such as long carrier lifetimes (up to 3 ms) [8-11], large carrier diffusion lengths (up to 650 μm under intense light, and 3 mm in weak light) [8,12-15] and phenomenal charge mobility (greater than 100 cm²V⁻¹s⁻¹) [12,13,16,17], which are widely thought to arise from the beneficial electronic interaction between A-site organic cation—MA⁺, and photoinduced charge carriers in PbI₃⁻ inorganic lattice. Nevertheless, the detailed optoelectronic origin associated with such organic-inorganic interaction has not been clearly explained. In addition, there are increasing studies that indicate formidable PV performance on fully inorganic Cs⁺-based perovskite solar cells [18-22], seemingly contradicting the established observations where anisotropic MA⁺ is indispensable for good optoelectronic properties. Therefore, it is imperative to elucidate the underlying photophysical mechanisms that
govern the electrostatic interplays between photocarriers and MA\(^+\)/Cs\(^+\) cations, so as to synergistically address the root cause of stunning performance in perovskite solar cells.

In the meantime, stability issues have seriously hindered the continuous development of PV technology based on perovskite solar cells. From the chemical perspectives, MAPbI\(_3\) severely suffers from weak moisture stability where MAI is dissolved by humidity in the air, thus causing decomposition of perovskite into PbI\(_2\). [23-27] Moreover, MAPbI\(_3\) experiences similar structural degradation at elevated temperatures, in which MAI is thermally evaporated from the perovskite lattice that results in loss of light absorption and consequent deterioration of solar cell performance. [23,28-30] As such, it is of great importance to compositionally modify MAPbI\(_3\) for enhanced chemical stability through strengthening electrostatic attraction between A-site cations and anionic frameworks, while simultaneously preserving its excellent carrier properties for phenomenal solar cell performance.

![Figure 1-1. Crystal structure of metal halide perovskites [23]. © 2017 Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Reprint with permission of Elsevier from ref. [23].](image)

Here, this dissertation presents electron-roto interaction, a novel type of electron-lattice interaction discovered in solid-state hybrid lead iodide perovskites between photogenerated free Pb\(^{2+}\) and/or Sn\(^{2+}\) I\(^-\), Br\(^-\) and/or Cl\(^-\).
electrons and rotational MA$^+$ cations, whose rotational frequencies are modulated via isotopic substitution of hydrogens on ammonium and/or methyl groups with deuterium atoms, with carrier lifetimes of perovskite materials showing distinctive trend as CH$_3$NH$_3$PbI$_3$ > CH$_3$ND$_3$PbI$_3$ ≈ CD$_3$NH$_3$PbI$_3$ > CD$_3$ND$_3$PbI$_3$. [31] Since isotope effects do not vary the chemical nature (e.g. molecular dipole moment, electronic wavefunctions) of MA$^+$, and instead, only its physicality is altered, this finding unambiguously reveals the significant impact of MA$^+$ reorientation motions on the electrostatic interplay between MA$^+$ cations and free carriers in inorganic PbI$_3$ framework. Additionally, mixed-cation MA$_{0.95}$Cs$_{0.05}$PbI$_3$ perovskite single crystals exhibit much longer carrier lifetimes compared with pristine MAPbI$_3$ counterparts, despite reduced static photoluminescence intensities. [23] To address the effects of anions on the optoelectronic functions of perovskite materials, two-dimensional (2D) Ruddlesden-Popper (MA)$_2$Pb(SeCN)$_2$I$_2$ layered perovskite is synthesized and systematically studied, where it exhibits sharp static photoluminescence peak with small full width at half maximum (FWHM) of 37.1 nm and notably observed carrier lifetime of 4.6 ns, contrasting with the previously reported (MA)$_2$Pb(SCN)$_2$I$_2$ [32-36], a structural analogue that shows broad static photoluminescence peak (FWHM: 171.1 nm) with no detectable photoluminescence lifetime. Most importantly, 10% w/w PbSe doped MAPbI$_3$ film exhibits >140-fold of moisture stability as compared to pristine MAPbI$_3$ film, as indicated from time-dependent optical reflectance studies. Unencapsulated solar cell device based on 10% w/w PbSe:MAPbI$_3$ retained 70% of initial PCE of 10.4% after 700 hours of aging in ambient air; while pristine MAPbI$_3$ cell retained only 16% of original performance after 432 hrs of aging under the ambient condition. [37] At the end, LiCl-assisted solution-grown FAPbCl$_3$ nanowires display notably enhanced photocurrents under ultraviolet (UV) illuminations, in comparison to pristine FAPbCl$_3$
nanostructures grown without LiCl additive. Furthermore, it is also the first time in the field that perovskite-based UV photodetector exhibits temporal current direction switching in response to alternating current (AC) powered 254-nm UV photons, thereby signifying the high photoelectric sensitivity and subtle material band structures of FAPbCl₃. This dissertation provides insightful and vital guidelines that will further foster improvements in both material properties and device performance of hybrid perovskites.

Figure 1-2. Record efficiency chart of research solar cells, where red-yellow dots in dashed square refers to the best efficiencies of perovskite solar cells achieved in recent years. Source: National Renewable Energy Laboratory [1].
2. CHARGE CARRIER DYNAMICS IN PEROVSKITE MATERIALS

Different from conventional inorganic semiconductors (e.g. Si, GaAs, CdTe, etc.), perovskite materials simultaneously consist of cationic A\(^+\) and anionic BX\(_3\)^- sublattices, [38] where A\(^+\) cation is electrostatically pinned in the cuboctahedral lattice void formed by the BX\(_3\)^- framework, [31,39-42], as shown in Figure 1-1. Therefore, it is necessary to compositionally alter only one of the sublattices while keeping the other structural component intact, so as to isolate any changes in the optoelectronic properties of perovskite materials that are exclusively associated with the modifications.

2.1. Electron-Rotor Interaction in Methylammonium Lead Iodide Perovskites

To probe the electrostatic interactions between cationic MA\(^+\) and photoinduced electrons in the PbI\(_3\)^- framework that may give rise to dynamical perturbation of photocarriers in the conduction band (mainly formed by Pb 6\(p\) atomic orbitals [43-45], with schematic illustration depicted in Figure 2-1-1), isotopic CH\(_3\)NH\(_3\)PbI\(_3\) and CH\(_3\)ND\(_3\)PbI\(_3\) thin films were first synthesized from respective CH\(_3\)NH\(_3\)/PbI\(_2\) and CH\(_3\)ND\(_3\)/PbI\(_2\) precursor solutions, with experimental procedures detailed in Chapter 6—Materials and Methods. The pure nature of isotopic CH\(_3\)NH\(_3\)I and CH\(_3\)ND\(_3\)I compounds were unambiguously determined by their mass spectra (Figure 2-1-2), and by nuclear magnetic resonance (NMR) spectra with dimethylsulfoxide-d6 ((CD\(_3\))\(_2\)S=O, DMSO-d6, Cambridge Isotope Laboratories, Inc.) being the solvent, as respectively shown in

---

Figure 2-1-3 and Figure 2-1-4. The existence of water is due to the hygroscopic DMSO-d6, as confirmed by the NMR spectrum of blank DMSO-d6 in Figure 2-1-5, and therefore will not affect the isotopic natures of deuterated MAI salts.

Figure 2-1-1. Schematic illustration of MA⁺ rotational motions and their effects on the electrons in perovskite conduction band. [31] © 2016 American Chemical Society. Reprint with permission granted by American Chemical Society from ref. [31].

Figure 2-1-2. Mass spectra of CH₃NH₃I (black), CH₃ND₃I (red), CD₃NH₃I (blue), and CD₃ND₃I (pink) displayed from 15 to 225 m/z.
Figure 2-1-3. $^1$H NMR spectrum of CH$_3$NH$_3$I in DMSO-d$_6$. [31] © 2016 American Chemical Society. Reprint with permission of American Chemical Society from ref. [31].

Figure 2-1-4. $^1$H NMR spectrum of CH$_3$ND$_3$I in DMSO-d$_6$. [31] © 2016 American Chemical Society. Reprint with permission of American Chemical Society from ref. [31].
Figure 2-1-5. \(^1\)H NMR spectrum of blank DMSO-d6 without dissolved MAI compound. [31] © 2016 American Chemical Society. Reprint with permission of American Chemical Society from ref. [31].

Importantly, the prepared CH\(_3\)NH\(_3\)PbI\(_3\) and CH\(_3\)ND\(_3\)PbI\(_3\) thin films showed superior crystallinities and similar surface morphologies, where these perovskite films exhibit distinctive diffraction peaks at around 14.3° and 28.6° of 2θ angles that respectively refer to (110) and (220) crystallographic orientations [46-50], as evidenced by X-ray diffraction (XRD) patterns shown in Figure 2-1-6. Also, both thin film samples are featured with large grains with micrometer sizes and high surface coverages, as clearly seen in the scanning electron microscopy (SEM) images in Figure 2-1-7. The high qualities of both perovskite samples thus demonstrate the comparability of optical and electronic properties observed in the following material studies.
To understand the isotope effects of MA\(^+\) on the light absorptions of perovskite materials, UV-Vis absorption spectroscopy was performed on CH\(_3\)NH\(_3\)PbI\(_3\) and CH\(_3\)ND\(_3\)PbI\(_3\) thin films.

Figure 2-1-8 shows the ultraviolet-visible (UV-Vis) absorption spectra of CH\(_3\)NH\(_3\)PbI\(_3\) and
CH$_3$ND$_3$PbI$_3$ thin films, where their absorption onsets nearly overlap and occur at around 787 nm and 788 nm respectively, thereby corresponding to a 1.58-eV bandgap for CH$_3$NH$_3$PbI$_3$, and a 1.57-eV gap for CH$_3$ND$_3$PbI$_3$. [31]

Figure 2-1-8. UV-Vis absorption spectra of regular CH$_3$NH$_3$PbI$_3$ and isotopic CH$_3$ND$_3$PbI$_3$ thin films. [31] © 2016 American Chemical Society. Reprint with permission of American Chemical Society from ref. [31].

Previous studies showed that the bandgaps of semiconductors can be influenced by isotope effects when the isotope atoms constitute materials’ electronic structures. For instance, replacing Cu-63 with Cu-65 and/or Cl-35 with Cl-37 in CuCl crystals notably altered the optical bandgaps through electron-phonon interactions due to mass-induced change in lattice dynamics.[51] Electron-phonon coupling induced by isotopic effect is also shown to profoundly manipulate optoelectronic properties of conducting polymers, which have varied optoelectronic responses when hydrogen atoms on the main chains or side chains are replaced by deuterium atoms.[52] However, for organic-inorganic hybrid perovskite materials, the bandgap is mainly determined by the anionic Pb-I lattice since the generation, transport and recombination of photocarriers all exclusively occur in the inorganic PbI$_3^-$ framework.[31] As such, substitution of hydrogen with
deuterium in the organic MA\(^+\) does not alter the excitation energy of valence electrons, where the electronic excitation is *de facto* constituted by a major transition of electrons from the I 5\(p\) to Pb 6\(p\) orbital, with minor contribution from the Pb 6\(s\) to Pb 6\(p\) orbital.[53-56] In detail, electronic transition from I 5\(p\) to Pb 6\(p\) does not involve a change in the angular momentum quantum number (l=1), while the transition from Pb 6\(s\) to Pb 6\(p\) conserves the principal quantum number (n=6); therefore, perovskites CH\(_3\)NH\(_3\)PbI\(_3\) and CH\(_3\)ND\(_3\)PbI\(_3\) have the measured small bandgaps (~1.57 eV) and thus excellent light absorption as previously illustrated in Figure 2-1-8, which is in good agreement with CH\(_3\)NH\(_3\)PbI\(_3\) energy gaps reported elsewhere[6,57-60].

We then perform studies of incident photon-to-current efficiency (IPCE) to investigate the optoelectronic profiles of both CH\(_3\)NH\(_3\)PbI\(_3\) and CH\(_3\)ND\(_3\)PbI\(_3\) thin films, as illustrated in Figure 2-1-9. It can be clearly seen that the IPCE spectra of fabricated solar cell devices based on CH\(_3\)NH\(_3\)PbI\(_3\) and CH\(_3\)ND\(_3\)PbI\(_3\) closely overlap with each other. The comparable IPCE spectra of CH\(_3\)NH\(_3\)PbI\(_3\)- and CH\(_3\)ND\(_3\)PbI\(_3\)-based cells indicate that the deuterated MA\(^+\) does not affect the generation and subsequent collection of photocarriers at cathodes (gold) and anodes (fluorine doped tin oxide, FTO) of the devices. This is consistent with the fact that the photogenerated electron-hole pairs solely occur in the anionic PbI\(_3^-\) lattice and is therefore expected to be independent of MA\(^+\). [31]
In addition, we used terahertz (THz) spectroscopy to investigate the influence of isotope effect of MA$^+$ on the charge carrier mobility in CH$_3$NH$_3$PbI$_3$ and CH$_3$ND$_3$PbI$_3$ thin films. As shown in Figure 2-1-10, both perovskite materials demonstrate nearly constant real-part photoconductivity between spectral range of 0.3 to 1.25 THz with negligible imaginary-part photoconductivity, thereby implying a large charge carrier scattering frequency. [61] Such scattering of photocarriers in lead halide perovskites is likely dominated by the carrier-optical phonon interaction that is usually responsible for the effective hot-phonon bottleneck and slow hot carrier cooling, [62-66] which may in some way address the outstanding PV performance of lead-based perovskite solar cells. This frequency-independent photoconductivity (in the low-THz frequency region) is also in agreement with the reported measurements on different perovskite films. [67,68] Considering the similar photocarrier densities due to the identical excitation conditions, the comparable photoconductivity of CH$_3$NH$_3$PbI$_3$ and CH$_3$ND$_3$PbI$_3$ thin films suggest similar carrier mobility in these two films. [31] This phenomenon agrees with the fact that carrier mobility is primarily
determined by carrier-optical phonon interactions, electron-hole Coulomb interactions, and effective masses of carriers, which are all indigenous to the inorganic PbI$_3^-$ framework. Therefore, the carrier mobility measured by the THz study is expected to be independent of the organic MA$^+$. [31]

Figure 2-1-10. Terahertz spectra of CH$_3$NH$_3$PbI$_3$ (red) and CH$_3$ND$_3$PbI$_3$ (blue) thin films. [31] © 2016 American Chemical Society. Reprint with permission of American Chemical Society from ref. [31].

To elucidate whether isotopic CH$_3$ND$_3^+$ affects the PV performance of solar cell devices as compared to pristine CH$_3$NH$_3^+$, photocurrent density-voltage (J-V) characteristics were subsequently studied on CH$_3$NH$_3$PbI$_3$ and CH$_3$ND$_3$PbI$_3$-based devices. Figure 2-1-11 displays the J–V curves of devices based on CH$_3$NH$_3$PbI$_3$ and CH$_3$ND$_3$PbI$_3$ thin films. Note that these cells were prepared under inert atmosphere inside a glovebox to ensure no replacement of deuterium with hydrogen from water. Also, all solvents used in perovskite precursor solutions (γ-Butyrolactone, diethyl ether and 1-methyl-2-pyrrolidinone, see Chapter 6 for details) do not contain active hydrogens, which again ensures the isotopic nature of MA$^+$. [31] With both cells showing comparable PV performance, the champion CH$_3$NH$_3$PbI$_3$ cell exhibits a PCE of 17.15%
with a short-circuit photocurrent density \( (J_{sc}) \) of 21.57 mA/cm\(^2\), open-circuit voltage \( (V_{oc}) \) of 1.06 V and fill factor (FF) of 0.75. By contrast, the best CH\(_3\)ND\(_3\)PbI\(_3\) device yields a PCE of 16.27%, as characteristic of 21.22 mA/cm\(^2\), 1.05 V and 0.73 as \( J_{sc} \), \( V_{oc} \) and FF, respectively. The slight difference in the PV performance between the champion CH\(_3\)NH\(_3\)PbI\(_3\) and CH\(_3\)ND\(_3\)PbI\(_3\) devices are on par with a statistical comparison based on 8–10 devices fabricated from each material, as summarized in Table 2-1-1. In the meantime, it is evident that both devices exhibit noticeable J-V hysteresis that is commonly observed for CH\(_3\)NH\(_3\)PbI\(_3\)-based solar cells, as potentially due to slow dynamic processes of capacitive currents, charge trapping and de-trapping at interfaces and perovskite grain boundaries, perturbation of band structures due to ferroelectric polarization and ion migration. [69-78] In fact, asymmetric MA\(^+\) itself contributes to built-in electric field inside perovskite structure as due to the anisotropic localization of the monocationic charge on ammonium groups of MA\(^+\) cations, which remarkably results in the ferroelectric polarization and iodine migration of the perovskite systems, and thus the hysteretic solar cell performance. [79-81]

![Figure 2-1-11. J-V curves of solar cell devices based on pristine CH\(_3\)NH\(_3\)PbI\(_3\) and isotopic CH\(_3\)ND\(_3\)PbI\(_3\) perovskites under AM1.5 one-sun illumination. [31] © 2016 American Chemical Society. Reprint with permission of American Chemical Society from ref. [31].](image-url)
Table 2-1-1
Statistic summary of PV parameters based on 8-10 solar cell devices of CH$_3$NH$_3$PbI$_3$ and CH$_3$ND$_3$PbI$_3$ perovskites. [31] © 2016 American Chemical Society. Reprint with permission of American Chemical Society from ref. [31].

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<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
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<td>CH$_3$NH$_3$PbI$_3$</td>
<td>21.58 ± 0.39</td>
<td>1.060 ± 0.006</td>
<td>0.742 ± 0.015</td>
<td>16.96 ± 0.48</td>
</tr>
<tr>
<td>CH$_3$ND$_3$PbI$_3$</td>
<td>21.24 ± 0.44</td>
<td>1.039 ± 0.018</td>
<td>0.716 ± 0.011</td>
<td>15.81 ± 0.61</td>
</tr>
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For the CH$_3$ND$_3$PbI$_3$-based device, we examined its steady-state power output and corresponding current density, which were measured near the maximum power point under continuous light illumination, as shown in Figure 2-1-12. The measurement shows that the actual power output ($\sim$15.4%) and current density ($\sim$17.90 mA/cm$^2$) for deuterated device are close to its reverse-scan J-V curve. Because there is no significant change of charge carrier mobility between pristine and deuterated films, charge carrier recombination should potentially be the reason accounting for the slight but evident discrepancies in PV performance of CH$_3$NH$_3$PbI$_3$ and CH$_3$ND$_3$PbI$_3$ solar cells.

Figure 2-1-12. Stabilized PCE and current density of CH$_3$ND$_3$PbI$_3$-based solar cell device at maximum power point under AM1.5 one-sun illumination. [31] © 2016 American Chemical Society. Reprint with permission of American Chemical Society from ref. [31].
Time-resolved photoluminescence (TRPL) measurements were then conducted to examine charge carrier lifetimes in isotopic MAPbI₃ perovskites, as commonly exemplified to investigate the kinetics of carrier recombination in perovskite materials. [82-84] Strikingly, TRPL reveals a significant difference in carrier lifetimes of the CH₃NH₃PbI₃ thin film (~145 ns) and CH₃ND₃PbI₃ thin film (~91 ns), as shown in Figure 2-1-13a and Figure 2-1-13b. Meanwhile, insets display static photoluminescence (PL) spectra of perovskite thin films; PL peak positions of CH₃NH₃PbI₃ (770 nm) and CH₃ND₃PbI₃ (775 nm) thin films are close to each other, thus corroborating their nearly identical optical bandgaps. To rule out the effects of grain boundary on promoting carrier recombination in thin films, single crystals of both CH₃NH₃PbI₃ and CH₃ND₃PbI₃ were synthesized, with detailed experimental methods of single crystal synthesis given in Chapter 6. Clearly, the comparison of TRPL spectra between single-crystal CH₃NH₃PbI₃ (Figure 2-1-14a) and single-crystal CH₃ND₃PbI₃ (Figure 2-1-14b) echoes the results obtained from the thin-film study. Specifically, the carrier lifetime in CH₃NH₃PbI₃ single crystal (400 ns) is still much longer than that of CH₃ND₃PbI₃ single crystal (~135 ns). It is not surprising that single crystals generally have longer carrier lifetime than their corresponding thin films, because single crystals should exhibit much less nonradiative recombination from less trap state densities. [13,44] The high crystallinities of CH₃NH₃PbI₃ and CH₃ND₃PbI₃ crystal samples were unambiguously confirmed by SEM images of cleaved crystal surfaces (Figure 2-1-15) and synchrotron high-resolution XRD patterns acquired at Advanced Photon Source (Figure 2-1-16).
Figure 2-1-13. TRPL spectra of CH$_3$NH$_3$PbI$_3$ thin film (a), and CH$_3$ND$_3$PbI$_3$ (b) thin films. Inset: Static PL spectra. [31] © 2016 American Chemical Society. Reprint with permission of American Chemical Society from ref. [31].

Figure 2-1-14. TRPL spectra of CH$_3$NH$_3$PbI$_3$ (a), and CH$_3$ND$_3$PbI$_3$ (b) single crystals. Inset: Static PL spectra. [31] © 2016 American Chemical Society. Reprint with permission of American Chemical Society from ref. [31].
Figure 2-1-15. SEM images of cleaved surfaces on as-grown CH$_3$NH$_3$PbI$_3$ (a) and CH$_3$ND$_3$PbI$_3$ (b) single crystals, with inset showing the photographs of crystals. [31] No grain boundaries are found from the cleaved facets, thus signifying the highly crystalline nature of both samples. [85] © 2016 American Chemical Society. Reprint with permission of American Chemical Society from ref. [31].
Figure 2-1-16. Photographs and SEM cleaved surface images of synthesized CH$_3$NH$_3$PbI$_3$ (a, b) and CH$_3$ND$_3$PbI$_3$ (c, d) crystals, [31] where no grain boundaries are found, thus signifying the single crystalline nature of both samples. [85] © 2016 American Chemical Society. Reprint with permission of American Chemical Society from ref. [31].

The observed isotope effect of MA$^+$ on the carrier lifetime must be implemented through a mass-relevant interaction(s) between the MA$^+$ and the photo-induced carriers in the inorganic PbI$_3^-$ framework, because deuteration should not alter any steady-state electronic wave functions on the MA$^+$ or on PbI$_3^-$ framework. Hence, there can only be two possible mass-relevant properties to influence the interaction between MA$^+$ and the carriers in the PbI$_3^-$ framework, namely the vibrational and rotational modes of MA$^+$. Note that we eliminated the translational modes of MA$^+$ in our consideration because the cationic MA$^+$ is confined electrostatically by the surrounding anionic PbI$_3^-$ lattice. [86-88] As expected, the infrared study shows that the characteristic broad N-H stretching at ~3150 cm$^{-1}$ disappeared almost entirely in CH$_3$ND$_3$PbI$_3$ (Figure 2-1-17). At this point, we can say that (1) carrier lifetime may be related to the vibrational difference between N-H and N-D, or (2) carrier lifetime may be related to the total mass of the MA$^+$, because CH$_3$NH$_3^+$ is lighter than CH$_3$ND$_3^+$. We then need to either rule out or confirm the impact of vibrational modes in MA$^+$ on carrier lifetime. If the N-H vibrations have any strong impact on carrier lifetime, we should be able to see the difference between CH$_3$ND$_3^+$ and CD$_3$NH$_3^+$, while eliminating the impact due to overall mass of the MA$^+$, because CH$_3$ND$_3^+$ and CD$_3$NH$_3^+$ have the same mass.
Therefore, we further synthesized CD$_3$NH$_3$PbI$_3$ single crystal, which adds the same amount of mass to the organic cation when compared with the aforementioned CH$_3$ND$_3$PbI$_3$, while keeping the N-H vibration mode intact. Again, the purity of precursor CD$_3$NH$_3$I is determined by NMR spectrum and mass spectrum, as respectively shown in Figure 2-1-18 and Figure 2-1-2. The quality of the CD$_3$NH$_3$PbI$_3$ sample is further confirmed by SEM image of the cleaved crystal surface (Figure 2-1-19) and synchrotron high-resolution XRD pattern (Figure 2-1-16), with detailed experimental methods for synthesizing single crystals given in Chapter 6. As displayed in Figure 2-1-20a, CD$_3$NH$_3$PbI$_3$ single crystal exhibits a carrier lifetime of ~135 ns, very close to that of...
CH$_3$ND$_3$PbI$_3$ (~120 ns, see Figure 2-1-14b). These results suggest that the vibrational modes in -NH$_3^+$ or in the deuterated -ND$_3^+$, or in -CH$_3$, or in -CD$_3$ do not notably impact carrier lifetime. Instead, it is the overall mass of MA$^+$ that leads to the variation in carrier lifetime. To further verify the impact of MA$^+$ mass on carrier lifetime, we synthesized the fully deuterated single-crystal CD$_3$ND$_3$PbI$_3$ (see Chapter 6 for detailed method of single crystal growth), in which fully deuterated CD$_3$ND$_3$PbI$_3$ is isotopically authenticated through neutron diffraction since deuterium atoms have positive scattering lengths toward neutrons [89-92], thereby leading to high signal-to-background ratios, as demonstrated in Figure 2-1-21. Meanwhile, the purity of CD$_3$ND$_3$I precursor can be unambiguously confirmed by NMR spectrum and mass spectrum, as shown in Figure 2-1-22 and Figure 2-1-2, respectively. Figure 2-1-20b shows that the carrier lifetime of this fully deuterated CD$_3$ND$_3$PbI$_3$ single-crystal sample is only ~65 ns as measured by TRPL, which is much shorter than either CD$_3$NH$_3$PbI$_3$ or CH$_3$ND$_3$PbI$_3$ single crystals and confirms our hypothesis of the effect of MA$^+$ mass on carrier lifetime, where the highly crystalline nature of per-deuterated CD$_3$ND$_3$PbI$_3$ crystal is also comparable with other crystals as confirmed by SEM image of cleaved crystal surface and high-resolution XRD pattern, as shown in Figure 2-1-23 and Figure 2-1-16, respectively.
Figure 2-1-18. $^1$H NMR spectrum of CD$_3$NH$_3$I dissolved in DMSO-d6 [31] © 2016 American Chemical Society. Reprint with permission of American Chemical Society from ref. [31].

Figure 2-1-19. SEM image of cleaved surface and photograph (inset) of as-grown CD$_3$NH$_3$PbI$_3$ single crystal, [31] where no grain boundaries are found, thus indicating the highly crystalline nature of crystal sample. [85] © 2016 American Chemical Society. Reprint with permission of American Chemical Society from ref. [31].
Figure 2-1-20. TRPL spectra of CD$_3$NH$_3$PbI$_3$ (a), and CD$_3$ND$_3$PbI$_3$ (b) single crystals. Inset: Corresponding static PL spectra of single crystal samples. [31] © 2016 American Chemical Society. Reprint with permission of American Chemical Society from ref. [31].

Figure 2-1-21. Neutron time-of-flight diffraction pattern of CD$_3$ND$_3$PbI$_3$ single crystal at ambient conditions, where brown lines are calculated crystallographic planes of CD$_3$ND$_3$PbI$_3$. All diffraction peaks can be assigned to tetragonal CD$_3$ND$_3$PbI$_3$ structure.
Figure 2-1-22. $^1$H NMR spectrum of CD$_3$ND$_3$I dissolved in DMSO-d6. [31] © 2016 American Chemical Society. Reprint with permission of American Chemical Society from ref. [31].

Figure 2-1-23. SEM image of cleaved surface and photograph (inset) of as-grown CD$_3$ND$_3$PbI$_3$ single crystal, [31] where no grain boundaries are found, thus indicating the highly crystalline nature of crystal sample. [85] © 2016 American Chemical Society. Reprint with permission of American Chemical Society from ref. [31].
Clearly, to this point, we need to focus the search for the root cause of this isotope-induced carrier-lifetime variation on the rotational modes of MA\(^+\). According to the unit cell dimensions of MAPbI\(_3\) single crystals—(8.8310 Å × 8.8310 Å × 12.6855 Å at room temperature)—the concentration of MA\(^+\) cations is 10\(^{21}\)/cm\(^3\), which overwhelmingly outnumbers the intrinsic charge carrier density (about 10\(^{10}\) cm\(^{-3}\) under dark, [13] in the PbI\(_3\) framework) by 11 orders of magnitude. Even under our TRPL condition (excitation at 405 nm, 40 pJ/pulse, 200-µm spot size), the estimated initial carrier density is no more than 10\(^{14}\) cm\(^{-3}\), which is still 7 orders of magnitude lower than the number of MA\(^+\) rotors. As such, the time-dependent wave function of these “rarely” occurring photoinduced electrons in the PbI\(_3\) framework have a slight chance to overlap with the anisotropically positioned cationic charge on the neighboring MA\(^+\), if all the MA\(^+\) cations are randomly oriented but fixed in the PbI\(_3\) cages. In other words, due to the relatively low carrier concentration, the interaction between an electron in conduction band (Pb 6\(p\) orbitals) and the cationic side of a neighboring MA\(^+\) requires a rapid reorientation of this MA\(^+\) to have its positive charge pointed to the electron; this occurrence enhances the overlapping probability of their respective wave functions. Such a requirement apparently demands the rotational movement of the MA\(^+\). In fact, MA\(^+\) does experience rotational modes in the PbI\(_3\) framework, including a symmetric axial rotation along the C-N bond that does not alter the overall orientation of MA\(^+\); in addition, there are two asymmetric in-plane rotations, which spatially reorient the charge on MA\(^+\) with respect to the nearby carrier. Such interaction also requires a timely coupling. In fact, all these rotational modes occur at a time scale no longer than a few tens of picoseconds, which is 2~4 orders of magnitude faster than the carrier lifetime. Hence, the reorientation of MA\(^+\) is kinetically rapid enough to enhance the probability of transient overlap between the wave functions of
electrons in the conduction band and the positive charge on MA\(^+\). In this regard, the modulation of the rotational frequency of MA\(^+\) by isotope effect is a logical interpretation of the observed mass-dependent carrier lifetime. [31]

In general, carrier lifetime is closely associated with exciton binding energy and polaron trapping energy. In terms of excitons, larger binding energy generally leads to higher recombination rate partially owing to the stronger Coulomb interaction. Theoretically, we can estimate the exciton binding energy by the following equation, [31,93]

\[
E(b) = \frac{\mu}{m_0 \varepsilon_r^2} R_H
\]

where \(m_0\) is the free-electron mass, \(R_H\) is the Rydberg constant of a hydrogen atom (13.6 eV), \(\varepsilon_r\) is the dielectric constant of the material, \(\mu\) is the reduced effective mass of the exciton and is obtained by \((m_e m_h)/(m_e + m_h)\). Because the previous terahertz experimental results show that carrier-transport properties are almost completely unaffected by the isotope effect (which means that the carrier effective masses are not notably affected), the main factor that affects the exciton binding energy is the dielectric constant. We then conducted density functional theory (DFT) calculations of the dielectric constant for a MAPbI\(_3\) unit cell with the C-N axis of MA\(^+\) in different directions, with detailed theoretical calculation methods elaborated in Chapter 6. As listed in Table 2-1-2, the dielectric constants depend distinctly on the momentary directions of C-N axis with respect to crystallographic planes (namely, the orientations of MA\(^+\)). Thus, MA\(^+\) rotation changes the dielectric constants of the material and influences the exciton binding energy. However, since exciton binding energy in MAPbI\(_3\) has been experimentally measured to be very small (only about 10 meV or less at room temperature), free charge carriers are directly generated upon light
absorption at ambient condition. [82,94] Therefore, the dielectric-induced variation (less than a factor of two according to the abovementioned equation and Table 2-1-2) in exciton binding energy is still less than kT (25.7 meV at room temperature). Hence, the MA⁺ rotation-induced effect on exciton binding energy should not have any large impact on carrier lifetime. Nonetheless, our calculation still manifested a strong correlation between rotor orientation and dielectric constants in solid-state materials.

Table 2-1-2
Dielectric constants for MAPbI₃ when MA⁺ is pointing to different crystallographic orientations. Note that for a non-perfect isotropic structure (room temperature MAPbI₃ is in tetragonal structure [13,47,85]; therefore, only two crystallographic directions have the identical chemical environments), its dielectric constant is a second-order tensor; therefore, the dielectric constant is a 3-by-3 matrix, with the averaged diagonal dielectric constants given in the last row.) [31] © 2016 American Chemical Society. Reprint with permission of American Chemical Society from ref. [31].

<table>
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<th></th>
<th>100</th>
<th>110</th>
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<td>25.800</td>
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<td></td>
<td>16.600 (averaged)</td>
<td>23.406 (averaged)</td>
<td>25.659 (averaged)</td>
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With the impact of excitons shown to be negligible on the carrier lifetime of MAPbI₃, we need to identify the root cause of deuteration-induced variation in carrier lifetime by investigating the polaron trapping effect that can lead to shallow traps in semiconductors. [95-97] On escaping from being bound with a hole in a polarizable semiconductor, a conduction electron attracts/repels multiple lattice cations/anions in its proximity via electrostatic interaction, leading to an electron-multi-ion entity called a polaron. [98] Apparently, high hole mobility facilitates the polaron formation because the corresponding electron can overcome the recombination and interact with its neighboring lattice ions. In this manner, a shallow trap forms near the edge of the conduction
band, in which the conduction electron can relax without recombination, leading to extended carrier lifetime. [99-102] In the case of MAPbI₃ single crystals, due to their excellent hole mobility [13, 103] and low exciton binding energy, [82] the photo-induced electron can readily overcome recombination so as to interact with neighboring lattice ions. Recent theoretical work also implies that carriers in perovskite might be associated with polarons. [39,104-106] In particular, the rapid picosecond in-plane rotations of MA⁺ enable quick spatial reorientation of the cationic charge, so as to overlap their wave function with that of the free electron, forming a stably shallow trap that extends carrier lifetime. Note that the MA⁺ cannot be a recombination center due to its poor electron affinity. In contrast, heavier CH₃ND₃⁺, CD₃NH₃⁺, and CD₃ND₃⁺ suffer from retarded rotation so as to decrease the probability of electrostatic overlap with the free electron; therefore, we observe shorter carrier lifetimes of deuterated perovskites. From the evidence, it is desirable to elucidate the dynamical relationship between MA⁺ orientations that are manifested as crystallographic planes and polaron trapping energies.

We conducted DFT calculations on the different polaron trapping energies when the C-N axis respectively points to the three representative crystallographic planes [100], [110], and [111] in a MAPbI₃ unit cell. The electronic structures near the band edge of MAPbI₃ generally reflects the trapping states for photo-generated carriers, and therefore, we show the calculated density of states (DOS) near the band edges of CH₃NH₃PbI₃ with CH₃NH₃⁺ along different crystallographic directions. The results are shown in Figure 2-1-24 and summarized in Table 2-1-3. As can be seen, the DOS near the valence band edge depend significantly on the orientation of CH₃NH₃⁺, and the difference for CH₃NH₃⁺ along the [111]/[110] and [100] directions are especially remarkable. This means that the hole trapping states will depend strongly on the orientation of CH₃NH₃⁺ in
CH$_3$NH$_3$PbI$_3$. Furthermore, similar results also occur for the electron trapping states, as shown in Figure 2-1-24 (d)–(f) and Table 2-1-3. It can be seen that [110] corresponds to the greatest trapping energies for both electrons (225 meV) and holes (71 meV), whereas [100] corresponds to the smallest trapping energies for both electrons (117 meV) and holes (7 meV). Hence, faster rotation of MA$^+$ gives rise to a greater incidence of orienting the C-N axis along [110] direction, which is associated with the greatest polaron trapping energy for both electrons and holes, than the slow rotation of deuterated MA$^+$, taking into account the effect of anisotropic alignments of MA$^+$.

Figure 2-1-24. Calculated DOS of CH$_3$NH$_3$PbI$_3$ for valence bands (a-c) and conduction bands (d-f), with cationic side of CH$_3$NH$_3^+$ pointing toward different crystallographic directions. [31] © 2016 American Chemical Society. Reprint with permission of American Chemical Society from ref. [31].

Table 2-1-3

<table>
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<th>Crystallographic planes</th>
<th>Electron (meV)</th>
<th>Hole (meV)</th>
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<td>111</td>
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</table>
Therefore, the lightest CH$_3$NH$_3^+$ is more effective in trapping photoexcited electrons than any of its heavier isotopic counterparts; consequently, this results in the relatively longer carrier lifetime in CH$_3$NH$_3$PbI$_3$. To give a quantitative ratio of the in-plane rotational frequencies around the C-N axis of the four isotopes of MA$^+$, we use the rigid rotor model in quantum mechanics, and the estimated frequency ratio is $\nu$(CH$_3$NH$_3^+$) : $\nu$(CH$_3$ND$_3^+$) : $\nu$(CD$_3$NH$_3^+$) : $\nu$(CD$_3$ND$_3^+$) $\approx$ 1 : 0.85 : 0.85 : 0.76, with the assumption that they take on the same rotational quantum state (see Chapter 6 for detailed calculation). Apparently, the trend of the in-plane rotational frequencies of the four isotopes of MA$^+$ agrees well with the trend found in their carrier lifetimes, that is, $\tau$(CH$_3$NH$_3^+$) > $\tau$(CH$_3$ND$_3^+$) $\approx$ $\tau$(CD$_3$NH$_3^+$) > $\tau$(CD$_3$ND$_3^+$). Therefore, it is reasonable to state that the carrier lifetime in MAPbI$_3$ has strong dependency on the rotational frequency of the organic rotor MA$^+$, and such electron-rotor interaction is implemented via polaron formation involving the coupling between conduction electrons in the PbI$_3^-$ inorganic octahedral framework and the asymmetric cationic charges on the organic rotors.

2.2. MA$^+$, Cs$^+$ Alloyed Lead Iodide Perovskites with Prolonged Carrier Lifetimes

Different from stereotypical perception, non-polar Cs$^+$ cation with isotropic charge distribution is attributable to dynamic structural disorders that can consequently lead to longer carrier lifetimes in metal halide perovskites, [107-111] which is significantly discordant with the aforementioned delayed carrier recombination in lead iodide perovskites via asymmetric MA$^+$-induced polaron formation. Therefore, it is intriguing at a fundamental level to compare the optoelectronic properties of photoactive MAPbI$_3$ and α-CsPbI$_3$, which are the perovskite motifs

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frequently applied in solar cell applications. However, the black-phase $\alpha$-CsPbI$_3$ is not thermodynamically stable at room temperature due to its small Goldschmidt tolerance factor of $t<0.8$ ($0.9<t<1$ is required for optimal cubic perovskite structure) \cite{19,23,112-116} as caused by the small size of Cs$^+$ ($r=167$ pm \cite{117,118}), with $t$ defined as: \cite{114,116,119}

$$t = \frac{r_A^+ r_x}{\sqrt{2}(r_B^++r_x)}$$

where $r_A$, $r_B$ and $r_x$ stand for the radii of A-, B- and X-site ions, respectively. It is thus necessary to tune the Goldschmidt tolerance factor by adopting MA$^+/Cs^+$ co-cationed lead iodide systems for phase-stable perovskite materials, so as to investigate their photophysical origins. Mixed-cation MA$_{0.95}$Cs$_{0.05}$PbI$_3$ and pristine MAPbI$_3$ crystals were then synthesized from corresponding solutions with stoichiometric MAI, CsI and PbI$_2$ precursors by following method reported in works \cite{85,120}, with the photographs of prepared crystals shown in Figure 2-2-1 and detailed experimental procedures elaborated in Chapter 6. The single crystalline natures of the solution-grown perovskite MAPbI$_3$ and MA$_{0.95}$Cs$_{0.05}$PbI$_3$ crystals were evidenced by XRD patterns, as shown in Figures 2-2-2 a & b. Characteristically, as shown in Figure 2-2-2c, both crystal samples exhibited different preferred orientations, with the (400) plane of MA$_{0.95}$Cs$_{0.05}$PbI$_3$ shifted toward greater 2θ angle by 0.1˚ with respect to MAPbI$_3$, thus indicating the existence of Cs$^+$ that caused shrinkage of lattice spacing of the mixed-cation perovskite. Also, the splitting of (400) plane disappeared on MA$_{0.95}$Cs$_{0.05}$PbI$_3$ as relative to MAPbI$_3$, thereby suggesting the increase of structural symmetry due to the lattice incorporated Cs$^+$ cation. As shown in Figure 2-2-3a, MA$_{0.95}$Cs$_{0.05}$PbI$_3$ perovskite crystals grown from the same solution exhibit luminescence with peak intensities at around 770 nm, in contrast with the peak wavelength of around 780 nm for pristine MAPbI$_3$ crystals, thus indicating blue shifted optical bandgaps due to Cs$^+$ doping and agreeing
well with the fact that 100% cesium composition perovskite—α-CsPbI$_3$ has larger bandgap (~1.73 eV) than MAPbI$_3$ analogue (~1.57 eV).[19,47,121-124] By performing TRPL, it is evident that incorporation of Cs$^+$ can lead to prolonged bulk carrier lifetimes in MA$_{0.95}$Cs$_{0.05}$PbI$_3$ crystals as compared to pristine MAPbI$_3$ crystals. As shown in Figure 2-2-3b, MA$_{0.95}$Cs$_{0.05}$PbI$_3$ crystals exhibit remarkably longer slow-component carrier lifetimes ($\tau_2$, crystal #1: 129.4 ns, crystal #2: 160.1 ns) with respect to the pristine MAPbI$_3$ counterparts (crystal #1: 56.1 ns, crystal #2: 44.8 ns), despite slightly shorter fast-component carrier lifetimes ($\tau_1$, crystal #1: 3.0 ns, crystal #2: 2.3 ns) in comparison with MAPbI$_3$ (7.2 ns and 8.3 ns for crystals #1 and #2, respectively). This indicates a slightly increased surface trap-assisted carrier recombination, but largely delayed free carrier recombination process [125,126].

![Figure 2-2-1](image)

Figure 2-2-1. Photographs of a solution-grown pristine MAPbI$_3$ crystal (a) and mixed-cation MA$_{0.95}$Cs$_{0.05}$PbI$_3$ crystals (b). Both crystals are morphologically featured with distinctive crystallographic planes.
Figure 2-2-2. Structural comparison between MAPbI$_3$ and MA$_{0.95}$Cs$_{0.05}$PbI$_3$ single crystals. XRD patterns of pristine MAPbI$_3$ single crystal (a), MA$_{0.95}$Cs$_{0.05}$PbI$_3$ single crystal (b) and zoomed-in comparison of (400) planes (c).

Figure 2-2-3. Optoelectronic properties of hybrid lead iodide perovskite crystals. Static PL spectra (a) and TRPL spectra (b) of pristine MAPbI$_3$ crystals (black and red) and mixed-cation
MA$_{0.95}$Cs$_{0.05}$PbI$_3$ crystals (green and blue). [23] © 2017 Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Reprint with permission of Elsevier from ref. [23].

In fact, the clearly noticed fast-component PL decays of MA$_{0.95}$Cs$_{0.05}$PbI$_3$ crystals justify the much lower static PL intensities observed in Figure 2-2-1a as due to smaller PL quantum yields [127], since the applied 405-nm excitation light (method of PL experiments detailed in Chapter 6) can only illuminate the shallow crystal surfaces as due to small penetration depths. [32,128] Nevertheless, the greatly prolonged carrier lifetimes in MA$_{0.95}$Cs$_{0.05}$PbI$_3$ perovskites are expected to have positive effects on solar cell performance based on Cs$^+$/MA$^+$ mixed-cation perovskites, as proven in many works reported elsewhere [29,129,130].

2.3. Effects of A-Site Cations on the Carrier Dynamics of Bromide Perovskites

Although the (MA$^+$, Cs$^+$)PbI$_3$ alloyed lead iodide perovskites have been demonstrated to possess longer charge carrier lifetime in comparison with pristine MAPbI$_3$ system, it is still not completely clear how each type of A-site cation affects the charge recombination dynamics of perovskite materials based on halide anions other than iodide. Also, it is worth noting that the TRPL spectra mentioned in previous context only measure the emitted photons at their peak-intensity wavelengths, which inevitably overlook the entire PL decays over the whole spectral regions. Therefore, a more thorough TRPL study was further performed with a streak camera on bromide perovskites structured with different A-site cations, in order to more explicitly examine the overall time-dependent variation of photon counts across the entire spectral windows [38]. As shown in Figure 2-3-1, MAPbBr$_3$ single crystal has a PL lifetime of ~1 ns by integrating photon intensities from 450 to 600 nm, while FAPbBr$_3$ has an integrative PL lifetime of ~750 ps from 450 to 600 nm, as shown in Figure 2-3-3; in the meantime, CsPbBr$_3$ exhibits a much shorter PL lifetime
of ~500 ps from 450 to 600 nm (Figure 2-3-5). Such PL lifetimes were extrapolated from respective PL decay curves at 1/e (~0.368) of maximum PL intensities [131]. The comparability of observed PL lifetimes is convincing in terms of the highly crystalline natures of perovskite crystal samples, as indicated through the strongly preferred crystallographic orientations shown in XRD patterns of Figure 2-3-2, Figure 2-3-4 and Figure 2-3-6. The trend of PL lifetimes (MAPbBr$_3$ > FAPbBr$_3$ > CsPbBr$_3$) closely agrees with hot PL lifetimes observed in previous report [11], which arise from the dynamic disorders of organic cations MA$^+$ and FA$^+$. 

Figure 2-3-1. Charge carrier dynamics of MAPbBr$_3$ single crystal. (a) TRPL spectrum of MAPbBr$_3$ measured from 0 to 1.8 ns with streak camera. (b) Corresponding PL decay curves as integrated over the entire spectral region from 450 to 600 nm, with blue, purple and red curves respectively referring to decays under increased excitation intensities.
Figure 2-3-2. XRD pattern of the MAPbBr$_3$ single crystal, where only three crystallographic orientations—(002), (003) and (004) are observed, thus indicating the single-crystalline nature of crystal sample. The assignment of crystallographic planes closely matches previous reports [85,107,132].

Figure 2-3-3. Charge carrier dynamics of FAPbBr$_3$ single crystal. (a) TRPL spectrum of FAPbBr$_3$ measured from 0 to 1.8 ns with streak camera. (b) Corresponding PL decay curves as integrated over the entire spectral region from 450 to 600 nm, with blue, purple and red curves respectively referring to decays under increased excitation intensities.
Figure 2-3-4. XRD pattern of the FAPbBr₃ single crystal, where only three crystallographic orientations—(002), (003) and (004) are seen, thus indicating the single-crystalline nature of crystal sample. The assignment of crystallographic planes closely matches previous reports [107,132].

Figure 2-3-5. Carrier dynamics of CsPbBr₃ single crystal. (a) TRPL spectrum of CsPbBr₃ measured from 0 to 1.8 ns with streak camera. (b) Corresponding PL decay curves as integrated over the entire spectral region from 450 to 600 nm, with blue, purple and red curves respectively referring to decays under increased excitation intensities.
Figure 2-3-6. XRD pattern of the CsPbBr$_3$ single crystal, where prominent crystallographic orientations—(020), (040), (060) and (080) are seen, thus indicating the single-crystalline nature of the crystal sample. The assignment of crystallographic planes closely matches previous reports [107,133].

2.4. 2D Ruddlesden-Popper (MA)$_2$Pb(SeCN)$_2$I$_2$ Perovskite with Distinctive Optoelectronic Properties

From the chemistry perspectives, metal halide perovskites offer a unique platform to explore the effects of heteroatoms on the optoelectronic responses of compositionally modified structures. This is perfectly illustrated through the reduced material dimensionality via bulky butylammonium (C$_4$H$_9$NH$_3^+$, BA$^+$)/MA$^+$ co-cationed structures that form 2D Ruddlesden-Popper layered lead iodide perovskites (BA)$_2$(MA)$_n$Pb$_n$I$_{3n+1}$ ($n=1$, 2, 3, 4, 5, $\infty$), with BA$^+$ served as interlayer spacers. [134,135] Such practice of achieving 2D perovskites, although warrants tunable optical bandgaps and exciton binding energies through chemically adjusting the relative ratio of BA$^+$ and MA$^+$ cations, [23] does not change the fact that the electronic structures are still exclusively constituted by Pb and I electronic wave functions. Previously, pseudohalide thiocyanate-based lead iodide perovskite—(MA)$_2$Pb(SCN)$_2$I$_2$ (crystal structure shown in Figure 2-4-1) had attracted extensive attention owing to its remarkable moisture tolerance ability,
[32,136-139] as due to its SCN⁻ dangling groups that form hydrogen bonds with water molecules and thereby preventing the solvation of MA⁺ cations. Moreover, the SCN⁻ is thought to play a crucial role in affecting the electronic properties of valence band maximum (VBM) in (MA)₂Pb(SCN)₂I₂ perovskite with its S 3p atomic orbital [53]. It is therefore of great intrigue to coherently tune the valence electron properties in this class of 2D materials by substituting S with another chalcogen element. In this study, (MA)₂Pb(SeCN)₂I₂ was synthesized via a vacuum method that did not involve any high-temperature annealing, as thermal effects could result in structural decomposition to 3D MAPbI₃ (loss of SeCN⁻ composition) according to previous report [140]. The 2D phase of as-prepared (MA)₂Pb(SeCN)₂I₂ is unambiguously confirmed by XRD patterns in comparison with (MA)₂Pb(SCN)₂I₂, as shown in Figure 2-4-2a. Noticeably, the diffraction peaks of (MA)₂Pb(SeCN)₂I₂ were unanimously shifted to smaller 2θ angles and therefore indicated enlarged lattice spacing d (Figure 2-4-3) as due to Bragg’s law:
\[ 2d \sin \theta = n \lambda \]

where \( d, \theta, n \) and \( \lambda \) represent lattice spacing, diffraction angle, periodicity (positive integers) and wavelength of X-ray photons. The enlarged lattice spacing is justified through the larger size of Se atom (117 pm) in contrast with S (102 pm) and is comprehensively summarized for various crystallographic planes in Figure 2-4-3. Meanwhile, it is noticeable to witness multiple splitting of diffraction peaks, such as (411) plane at around 27.0° of 2\( \theta \) (Figure 2-4-2b), which hence signifies reduced structural symmetries as caused by the polyanion SeCN\(^-\) group. Characteristically, the existence of SeCN\(^-\) is confirmed by the transmittance dip at around 2094 cm\(^{-1}\) of FTIR spectrum in Figure 2-4-4, which is in good agreement with literature values [141]. Additionally, the transmittance dips at 939.16 cm\(^{-1}\), 1261.2 cm\(^{-1}\), 1421.28 cm\(^{-1}\), 1463.7 cm\(^{-1}\), 1490.7 cm\(^{-1}\), 1612.1 cm\(^{-1}\) and 3160 cm\(^{-1}\) refer to C-N stretch, CH\(_3\)-NH\(_3^+\) rock, symmetric CH\(_3\) bend, asymmetric CH\(_3\) bend, symmetric NH\(_3^+\) bend, asymmetric NH\(_3^+\) bend and N-H stretches. [44,86,142] Optical reflectometry was subsequently performed to characterize the light absorbing properties of the as-
prepared (MA)$_2$Pb(SeCN)$_2$I$_2$, as shown in Figure 2-4-5, where an onset between 500 and 600 nm was detected. This onset area is equivalent to a 2.04 eV direct bandgap, or a 1.82 eV indirect bandgap, as extrapolated from Tauc plots presented in Figure 2-4-6. In detail, the absorption coefficient ($\alpha$) in determining bandgaps is calculated through the following equation:

$$\alpha = \frac{(1 - \frac{R(\%)}{100})^2}{2 \times \frac{R(\%)}{100}}$$

in which $R(\%)$ stands for percentage of light reflected, and bandgap energies are extrapolated at $(\alpha h\nu)^2=0$ (direct gap) or $(\alpha h\nu)^{1/2}=0$ (indirect gap) through linearly fitting the onset portions of Tauc plots. It is worth mentioning that the obtained (MA)$_2$Pb(SeCN)$_2$I$_2$ energy gaps are considerably larger than the gaps for MAPbI$_3$ (~1.57 eV) as due to quantum confinement effects of 2D structures [134], agreeing well with the red color of as-synthesized (MA)$_2$Pb(SeCN)$_2$I$_2$ thin film as shown in Figure 2-4-5 inset, and are closely on par with reported energy gaps for (MA)$_2$Pb(SCN)$_2$I$_2$ [33,140].

Figure 2-4-3. Column chart that summarizes the lattice spacings of (MA)$_2$Pb(SeCN)$_2$I$_2$ (red) and (MA)$_2$Pb(SCN)$_2$I$_2$ (blue).
Figure 2-4-4. FTIR spectrum of 2D (MA)$_2$Pb(SeCN)$_2$I$_2$, where the assignments of transmittance dips and numbering ($\nu_x$) follows the previous reports [44,86,141,142].

Figure 2-4-5. Optical reflectance spectrum of as-prepared (MA)$_2$Pb(SeCN)$_2$I$_2$ thin film. Inset: photograph of the synthesized (MA)$_2$Pb(SeCN)$_2$I$_2$ thin film.
Static PL and TRPL were then conducted to characterize the optoelectronic properties of as-synthesized (MA)$_2$Pb(SeCN)$_2$I$_2$. As shown in Figure 2-4-7a, as-synthesized (MA)$_2$Pb(SeCN)$_2$I$_2$ (FWHM: 37.1 nm) stunningly exhibits an emission peak that is significantly narrower than (MA)$_2$Pb(SCN)$_2$I$_2$ (FWHM: 171.1 nm, Figure 2-4-7b), which thus suggests a highly homogeneous band structure on the SeCN-based 2D perovskite. Such homogeneous carrier recombination is echoed with clearly observed PL decay that is featured with 0.50 ns fast-component lifetime and 4.6 ns slow-component lifetime, as shown in Figure 2-4-8; in the meantime, synthesized (MA)$_2$Pb(SCN)$_2$I$_2$ did not exhibit noticeable TRPL signal, as shown in Figure 2-4-7b inset, and therefore signify the positive effects of SeCN group on the semiconductor properties of 2D perovskites.
To verify the authenticity of observed 2D (MA)$_2$Pb(SeCN)$_2$I$_2$ phase, (MA)$_2$Pb(SeCN)$_2$I$_2$ thin film was heated at 100 °C for 10 min. before again being measured on PL/TRPL. The thermally treated material surprisingly showed a secondary PL peak at 748 nm, in addition to the original 574 nm emission, in which the emission at 748 nm exhibits a much longer carrier lifetime of 74.7 ns as compared to the retained emission at 574 nm of 5.3 ns, as shown in Figures 2-4-9 and
Such thermally-induced structure conversion is tightly connected to the versatile dynamics of pseudohalide SeCN group, which may potentially enable energy-related applications.

![Figure 2-4-9. Static PL spectrum of (MA)$_2$Pb(SeCN)$_2$I$_2$ thermally treated at 100 °C for 10 minutes, where both 574-nm and 748-nm emissions are observed.](image)

On the contrary, decrease in temperature should supposedly shorten the interlayer distance, and eventually cause a phase transition to 3D perovskite. However, insightful temperature-dependent studies suggest that there was no phase transition on (MA)$_2$Pb(SeCN)$_2$I$_2$ upon cooling from room temperature to liquid nitrogen temperature (80 K), as based on the largely retained PL peak shapes.

![Figure 2-4-10. TRPL spectra of observed 574-nm emission (a) and 748-nm emission (b), where the lifetimes of 748-nm emission are significantly longer than the 574-nm emission.](image)
shown in Figure 2-4-11. The absence of such phase transition, simply indicates the stability of SeCN bonds during layer-to-layer approaching at low temperatures. The monotonic blueshift of PL peak intensities upon increased temperatures, on one hand, indicates the lengthened interatomic distances between Pb and Se/I atoms that consequently caused widened optical bandgaps, as typical for metal halide perovskites [38,145]. On the other hand, the shortened carrier lifetimes at higher temperatures, suggests the emphasized quantum confinement effects (Figure 2-4-12).

Figure 2-4-11. Static PL spectra of (MA)$_2$Pb(SeCN)$_2$I$_2$ thin film at different temperatures. A monotonic redshift in peak-intensity wavelength occurs upon decreased temperature.

Figure 2-4-12. Temperature-dependent charge carrier dynamics of (MA)$_2$Pb(SeCN)$_2$I$_2$ thin film. (a) TRPL spectra at 80 K (black), 200 K (red) and 300 K (green). (b) Extrapolated slow-component lifetimes at different temperatures.
3. DOPANT-INDUCED STABILITY IMPROVEMENTS IN HYBRID PEROVSKITE MATERIALS

3.1. Divalent Anion Doping in MAPbI₃ for Enhanced Chemical Stabilities¹

The poor moisture and thermal stabilities of perovskite MAPbI₃ have significantly hampered the large-scale and long-term photovoltaic applications. By scrutinizing the origin of the instability, one can find a common root cause—asymmetric MA⁺, that forms weak electrostatic attraction with PbI₃⁻ anionic framework due to the localized monocationic charge on its -NH₃⁺ group. [23] As such, it is urgently necessary to strengthen the electrostatic interaction between MA⁺ cation and inorganic lead iodide lattice, so as to enhance the stabilities of CH₃NH₃PbI₃ perovskite solar cells.

According to previous studies, the first step of moisture-induced structural degradation in CH₃NH₃PbI₃ involves the formation of MAPbI₃·2H₂O and MA₄Pb₆O·2H₂O intermediates. [146] To tackle this problem, modifications of chemical composition in the active perovskite layer has been practiced through additives of new chemical moieties. [32,147,148] Successful examples of enhancing moisture stability of perovskites were previously realized through partially replacing iodide with pseudohalide SCN⁻ or partially replacing the MA⁺ with BA⁺, converting the 3D perovskite structure to a Ruddlesden-Popper 2D layered structure, [32,34,149] as elaborated in Section 2.4. previously. However, the resulting 2D structure hinders charge transport through structurally confining carriers within the 2D inorganic layers. [33,149] As such, it is imperative to

¹ This section was previously published as Gong, J., Yang, M., Rebollar, D., Rucinski, J., Liveris, Z., Zhu, K., Xu, T. (2018). Divalent Anionic Doping in Perovskite Solar Cells for Enhanced Chemical Stability. Advanced Materials, 30(34), 1800973. It is reprinted by permission of John Wiley and Sons.
explore chemical pathways that can enhance structural stability while synergistically retaining the 3D perovskite structure for the desirable charge transport properties.

Coordination chemistry suggests that anions with less electronegative nature (e.g. I\(^-\) vs Br\(^-\), Cl\(^-\)) are capable of forming chemical bonds with Pb\(^{2+}\) in higher covalency, thus favoring charge generation and hole transport. [40] On the other hand, less electronegative anions lead to weak attractions and thereby deteriorating chemical stability. This is evident through Br\(^-\) (i.e. MAPbI\(_3\).\(_x\)Br\(_x\)), which aids the stability of the perovskite structure, but high doping levels of Br\(^-\) enlarges the band gap. MAPbI\(_2\)Br has an optical bandgap of ~1.8 eV, while MAPbIBr\(_2\) has an optical bandgap of ~2.0 eV. [6,150,151] Because the organic cations are pinned in the cuboctahedron void formed by inorganic framework via electrostatic interaction, [11,31,152-155] introducing a higher-valence anionic charge should greatly increase such electrostatic interaction so as to stabilize CH\(_3\)NH\(_3\)^+ from hydration. This inspires us to focus on multivalent ions such as S\(_2^-\) and Se\(_2^-\); both of which form chemical bonds with Pb\(^{2+}\) with high covalency. Plus, band gaps of PbS (0.37 eV) and PbSe (0.28 eV) are even smaller than MAPbI\(_3\). [156] As the difference in electronegativity (\(\Delta\chi\)) between Pb and Se is even slightly smaller than that for Pb and I (\(\Delta\chi\) for Pb-Se= 0.68, \(\Delta\chi\) for Pb-I= 0.79, on the Pauling Scale), doping PbSe is expected to have a minimum negative impact on the desired covalent nature of the inorganic framework in hybrid perovskite. Figure 3-1-1 shows a hypothesized lattice structure of PbSe doped MAPbI\(_3\) and illustrates the enhanced electrostatic interaction between CH\(_3\)NH\(_3\)^+ and the inorganic framework contributed by Se\(_2^-\). Moreover, we found that the addition of Se\(_2^-\) in the perovskite lattice mitigates the migration of iodine, thus suppressing the deterioration of silver electrode due to formation of AgI.
MAPbI$_3$ and 10% w/w PbSe doped MAPbI$_3$ thin films were then synthesized and prepared on TiO$_2$-coated FTO substrates. 10% w/w PbSe:MAPbI$_3$ was focused on due to its high stability as well as its relative better PV performance compared to other doped films.

Figure 3-1-1. Schematic illustration of hypothesized PbSe:MAPbI$_3$ lattice structure. Hypothesized lattice structure is oriented with 45˚ off a axis of a tetragonal unit cell with only one Se$^{2-}$ ion (yellow sphere) and one CH$_3$NH$_3^+$ (carbon: gray sphere, nitrogen: brown and hydrogen atoms: blue) shown for clarity. For PbI$_3^-$ framework, Pb$^{2+}$ is represented by green spheres, I$^-$ pink spheres. Divalent Se$^{2-}$ (dash circled) poses strong electrostatic interaction (dark red wedges) with partially cationic ammonium hydrogen. [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].

Specifically, 10% w/w PbSe:MAPbI$_3$ denotes a 10% mass content of PbSe with respect to the mass of PbI$_2$ in the PbSe+PbI$_2$+MAI precursor solution. The detailed methods of thin film synthesis are elaborated in Chapter 6. To rule out the physical effects of thin film surface morphology on their chemical stabilities, SEM was first performed on both MAPbI$_3$ and 10% w/w PbSe:MAPbI$_3$ thin films (Figure 3-1-2), where high surface coverages of perovskite grains were observed on both thin films. It can therefore attribute any difference in thin film properties to the intrinsic chemical natures of the samples. Also, energy-dispersive X-ray (EDX) analysis, as shown
in Figure 3-1-3, confirming the nearly stoichiometric existence of Se, Pb and I in 10% w/w PbSe:MAPbI₃ film sample. Table 3-1-1 lists the statistics of elemental analysis, which clearly demonstrates the existence of Se.

Figure 3-1-2. SEM images of pristine MAPbI₃ (a) and 10% w/w PbSe:MAPbI₃ (b) thin films. [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].

Figure 3-1-3. EDX elemental analysis of examined 10% w/w PbSe:MAPbI₃ thin film surface. [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].
Table 3-1-1
Statistics of elements on 10% w/w PbSe:MAPbI₃ thin film. Weight (%) indicates the mass content of element within the total mass of detected elements. Theoretical weight (%) refers to mass composition of elements in 0.04 g PbSe, 0.360 g PbI₂ and 0.149 g MAI precursor mixture. [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight (%) area 1</th>
<th>Weight (%) area 2</th>
<th>Weight (%) area 3</th>
<th>Average weight (%)</th>
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<td>0.92</td>
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</tr>
<tr>
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<td>62.30</td>
<td>60.69</td>
<td>57.78</td>
</tr>
<tr>
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<td>33.50</td>
<td>31.49</td>
<td>33.03</td>
<td>34.75</td>
</tr>
</tbody>
</table>

The evaluations of the moisture stabilities of MAPbI₃ and 10% w/w PbSe:MAPbI₃ thin films were then conducted by measuring respective time-dependent optical reflectance spectra, after corresponding accelerated aging time under 100% relative humidity (RH) at 40 °C in ambient illumination. The detailed method is given in Chapter 6, with schematic depiction of moisture aging chamber in Figure 3-1-4. Figure 3-1-5a shows the time-dependent reflectance spectra of MAPbI₃ thin film. Before aging, the as-fabricated MAPbI₃ film displays a reflectance profile (black graph) where the percentage of light reflected is low (< ~13%) between 400 and 780 nm. After aging in 100% RH at 40 °C for 30 min., reflectance of the perovskite film (red) largely upshifts with reflectance between 750 and 810 nm denoting reflectance onset, [54,157,158] vanishes. Insets are the images of tested film at 0 min. (left) and 30 min. (right) of accelerated aging time. Clearly, MAPbI₃ sample after being exposed to 30-min. accelerated aging shows a yellow-white film which should mainly consists of PbI₂ [146,159,160], an indication of full degradation of MAPbI₃ after only 30 min. of moisture aging. Figure 3-1-5b shows the evolution
of reflectance of 10% w/w PbSe:MAPbI₃ film, with inset being the photographs of tested film at corresponding aging times (0 hr, left; 72 hrs, right). Shockingly, no significant change in the reflectance profile was observed after 72 hrs of accelerated aging, and only slight blue shift of reflectance onset occurred after 120 hrs of aging (see Figure 3-1-6). The PbSe-doped film exhibited strengthened chemical stability over 140-fold with respect to pristine MAPbI₃ film (defined as the aging time for a detectable degradation of doped MAPbI₃ thin film/time for complete degradation of pristine MAPbI₃ thin film, thereby 72 hrs/0.5 hr=144). 5% w/w PbSe:MAPbI₃ was also tested to verify this trend in stability and to observe if there was a concentration dependence. As shown in Figure 3-1-7, 5% w/w PbSe:MAPbI₃ thin film still exhibits much better stability than the pristine MAPbI₃ thin film, although it is slightly overperformed by 10% w/w PbSe:MAPbI₃.

Figure 3-1-4. Schematic depiction of the moisture chamber utilized to perform accelerated degradation tests. [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].
Figure 3-1-5. Reflectance spectra of MAPbI\textsubscript{3} (a) and 10\% w/w PbSe:MAPbI\textsubscript{3} (b) thin films at different aging times. [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].

Figure 3-1-6. Reflectance spectra of 10\% w/w PbSe:MAPbI\textsubscript{3} at various aging time under 100\% RH at 40 °C. [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].
Due to greater electronegativity, divalent $S^{2-}$ in the form of PbS, was also considered to compare with PbSe. Figure 3-1-8 displays the evolution of reflectance spectra of 10% w/w PbS:MAPbI$_3$ thin film after aging in 100% RH for various time. Within expectation, time-dependent reflectance spectra are highly overlapped across 196 hrs of accelerated aging, and onset area between 800 and 850 nm is still preserved after 196 hrs of aging, thereby indicating the fact that 10% w/w PbS:MAPbI$_3$ thin film also had enhanced chemical stability.
Tauc plots (Figure 3-1-9) display the evolutions of bandgaps of MAPbI$_3$ thin film and 10% w/w PbSe:MAPbI$_3$ thin film at various aging time. Over a longer aging period, (0 hr to 120 hrs) as compared to MAPbI$_3$ film (0 min. to 30 min.), 10% w/w PbSe:MAPbI$_3$ film demonstrates a small widening of bandgap from 1.54 eV to 1.56 eV, while bandgap in pristine MAPbI$_3$ film was widened from 1.54 eV to 2.31 eV. Both 5% w/w PbSe:MAPbI$_3$ and 10% w/w PbS:MAPbI$_3$ films also exhibited negligible change in bandgaps after long-time aging (Figure 3-1-10).

Figure 3-1-9. Tauc plots of pristine MAPbI$_3$ (a) and 10% w/w PbSe:MAPbI$_3$ (b) thin films at different moisture aging time. [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].

Figure 3-1-10. Tauc plots of 5% w/w PbSe:MAPbI$_3$ (a) and 10% w/w PbS:MAPbI$_3$ (b) thin films at different aging time. [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].
X-ray diffraction (XRD) studies on PbSe, MAPbI₃, 5% w/w PbSe:MAPbI₃ and 10% w/w PbSe:MAPbI₃ samples were collected in Figure 3-1-11. PbSe (red) exhibited three strong diffraction peaks found at 25°, 30° and 42° of 2θ; [161] these peaks are absent in 5% w/w PbSe:MAPbI₃ (blue) as well as 10% w/w PbSe:MAPbI₃ (purple), thus proving that single PbSe phases did not exist in either PbSe:MAPbI₃ samples. By closely examining MAPbI₃ diffraction pattern (black), it has distinctive (110), (220), (310), (224), (314) structures at 14.9°, 29.2°, 32.6°, 41.3° and 43.9° of 2θ angles, agreeing well with the patterns reported elsewhere, [3,12,47] while both 5% w/w and 10% w/w PbSe:MAPbI₃ samples exhibit similar patterns to those of MAPbI₃, with change in the relative intensities of diffraction peaks. This fact demonstrates that the perovskite natures of PbSe:MAPbI₃ materials were not structurally altered due to the PbSe dopant, but detailed preferred orientation of crystallographic planes was indeed influenced by dopant. In fact, as PbSe dopant increased in concentration, FWHMs of (110) and (112) planes (with large lattice spacings) monotonically decreased and therefore indicated improved crystallinities of the long-range structures. However, at small lattice spacings, high-concentration 10% w/w PbSe dopant resulted in reduced crystallinities of (220) and (310) planes, thereby signifying disordered short-range structures, as shown in Figure 3-1-12. Visually guided by dashed lines in Figure 3-1-11, diffraction peaks of 10% w/w PbSe:MAPbI₃ shift towards smaller 2θ angles for (110), (112), (220) and (310) planes in comparison with MAPbI₃, and therefore signifies enlarged lattice constants as caused by intercalation of dopant atoms into the perovskite lattice. Such observation is in accordance with previous reports, [6,162] where increased content of I⁻ in MAPbI₃₋ₓBrₓ and insertion of water molecules in MAPbBr₃ systems result in diffraction peaks shifted to smaller 2θ angles. Although Se²⁻ (r=198 pm) has an ionic radius slightly smaller than I⁻ (r=220 pm), [118,163-
it is still perfectly reasonable to result in an expanded perovskite lattice due to interstitial intercalation (instead of X-site lattice points), and interstitial intercalation should lead to inefficient atomic packing, as in the cases of small alkali metal ion (Rb\(^+\), Li\(^+\), etc.) doped perovskite structures. [166,167] These facts justify the illustration of Se\(^2-\) intercalataion scenario shown in Figure 3-1-1. It can herein be inferred that the origin of enhanced chemical stability of 10% w/w PbSe:MAPbI\(_3\) should lie in lattice-incorporated Se\(^2-\). Supportively, such shifts toward smaller 2\(\theta\) also occurs in 10% w/w PbS:MAPbI\(_3\), as shown in Figure 3-1-13. Electrically, the incorporated Se\(^2-\) and S\(^2-\) ions lead to notably enhanced conductivities of thin films in comparison with pristine MAPbI\(_3\) (Figure 3-1-14), which is in good agreement with previous observations of increased conductivities due to ion intercalations. [166,168,169]

Figure 3-1-11. XRD patterns of MAPbI\(_3\) (black), PbSe (red), 5% w/w PbSe:MAPbI\(_3\) (blue) and 10% w/w PbSe:MAPbI\(_3\) (purple). [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].
Figure 3-1-12. Column charts summarizing the FWHMs of perovskites MAPbI$_3$, 5% w/w PbSe:MAPbI$_3$ and 10% w/w PbSe:MAPbI$_3$. [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].

Figure 3-1-13. XRD patterns of 10% w/w PbS:MAPbI$_3$ (violet) and MAPbI$_3$ (black). [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].
To fundamentally probe electrostatic interactions between $\text{Se}^{2-}$ and cationic $\text{CH}_3\text{NH}_3^+$, MAPbI$_3$ and 10% w/w PbSe:MAPbI$_3$, thin films were characterized by FTIR. Figure 3-1-15 illustrates normalized FTIR spectra of MAPbI$_3$ (black) and 10% w/w PbSe:MAPbI$_3$ (red) thin films, with peak around 3201 cm$^{-1}$ for MAPbI$_3$ corresponding to N-H stretch. [44,86,170] N-H stretching modes at 3201 cm$^{-1}$ in MAPbI$_3$ redshifts to 3114 cm$^{-1}$ in 10% w/w PbSe:CH$_3$NH$_3$PbI$_3$ films due to the electrostatic attraction between $\text{Se}^{2-}$ and cationic CH$_3$NH$_3^+$. Our IR study follows the observation that Se interacts with H in N-H and retard stretching modes of N-H. [171] Also, significant band broadening is witnessed on N-H stretch in 10% w/w PbSe:MAPbI$_3$, relative to the peak of N-H stretch in MAPbI$_3$, matching the pattern of strong electrostatic interaction. [172] Apart from the redshift of N-H stretching frequency, no obvious change of N-H bending frequency was observed, likely due to the poor alignment of 2-D N-H symmetric bending (scissor mode) [44,86] with the vector of H--Se$^{2-}$ interaction.
Figure 3-1-15a shows the photocurrent density-voltage (J-V) study of 10% w/w PbSe:MAPbI$_3$ solar cell. Power conversion efficiency (PCE) of the champion cell through reverse scan was 10.44% and corresponding short-circuit current density, open-circuit voltage and fill factor were 16.7 mA/cm$^2$, 0.94 V and 0.66, respectively. Forward scan exhibited an 8.59% PCE with corresponding short-circuit current density, open-circuit voltage and fill factor as 16.8 mA/cm$^2$, 0.91 V and 0.56, respectively. As shown in Figure 3-1-15b, stabilized output of 9.93% PCE and 13.8 mA/cm$^2$ current density were achieved. By comparison, a reference MAPbI$_3$ cell demonstrated 15.08% and 10.64% PCEs through reverse and forward scans, respectively, as shown in Figure 3-1-16. The PCEs of MAPbI$_3$ cell were characteristic of short-circuit current density, open-circuit voltage and fill factor that are correspondingly greater than the 10% w/w PbSe:MAPbI$_3$ counterpart, as shown in Table 3-1-2. Nevertheless, the control MAPbI$_3$ device has a PV efficiency below average reported value (>18%), [173,174] as all the cells adopted mesoporous structure and fabricated in ambient atmosphere via one-step antisolvent approach [175] (method detailed in Chapter 6). We believe switching to planar architecture and inert atmosphere for device processing should help further improve PV performance. [173,174,176] Although the efficiency gap between 10% w/w PbSe:MAPbI$_3$ cell and control device is phenomenal at this point, we do not consider such gap as a fundamental limitation since it can be reduced through further optimizing the PbSe dopant concentration, thin film fabrication methods (e.g. one-step or two-step deposition), annealing conditions and device architectures in more detailed research.
Figure 3-1-15. Photovoltaic performance of 10% w/w PbSe:MAPbI₃ solar cell device. (a) J-V curves of the 10% w/w PbSe:MAPbI₃ solar cell. (b) Stabilized power conversion efficiency (red) and current density (black). [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].

Figure 3-1-16. J-V curves of pristine MAPbI₃ solar cell with reverse voltage scan (red) and forward scan (black). [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].
Table 3-1-2
PV parameters of the solar cell device based on pristine MAPbI3. [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].

<table>
<thead>
<tr>
<th>Scan</th>
<th>J_{sc} (mA/cm^2)</th>
<th>V_{oc} (V)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forward</td>
<td>21.3</td>
<td>1.04</td>
<td>0.48</td>
<td>10.64</td>
</tr>
<tr>
<td>Reverse</td>
<td>21.2</td>
<td>1.06</td>
<td>0.67</td>
<td>15.08</td>
</tr>
</tbody>
</table>

For comparison, Figure 3-1-17 shows the J-V curve of 10% w/w PbS:MAPbI3 with corresponding PV parameters summarized in Table 3-1-3. However, only 1.7% PCEs was achieved. This inferior PV performance suggests that S\(^2\)- profoundly hinders charge transport in PbS-doped MAPbI3 perovskite, likely due to its greater electronegativity. Indeed, TRPL studies (Figure 3-1-18) show that 10% w/w PbSe:MAPbI3 thin film has a surprisingly long carrier lifetime (544.5 ns), in contrast to the 10% w/w PbS:MAPbI3 thin film that has much shorter carrier lifetime (60.2 ns) as compared to the carrier lifetime of pristine MAPbI3 thin film (111 ns), and thus signifying more recombination centers as introduced by the PbS dopant. Worth mentioning, charge carrier lifetimes up to this point were extrapolated based on equation [13,44]:

\[
I_{PL}(t) = I_{peak}[\alpha e^{-t/\tau_1} + \beta e^{-t/\tau_2} + I_0]
\]

in which \(I_{PL}(t)\), \(I_{peak}\), \(\tau_1\) and \(\tau_2\) refer to time-dependent PL intensity, PL peak intensity, slow component (free carrier recombination process) and fast component (surface trap-assisted carrier recombination), respectively.[13,44] The order in carrier lifetime magnitude closely correlates with the electronegativity order of S>I>Se. Noticeably, as shown from the static PL spectra in Figures 3-1-18 a, c & e, we can see both PbSe and PbS dopants result in electronic states within the bandgaps of doped MAPbI3 perovskites while pristine MAPbI3 does not show any radiative intragap states. Meanwhile, the IPCE spectrum of 10% w/w PbSe:MAPbI3 solar cell device (Figure
3-1-19) displays high external quantum efficiencies that are ~60% in average between 375 nm and 750 nm, agreeing with the IPCE spectrum reported for MAPbI$_3$.\cite{31,175} Figure 3-1-20 shows that unencapsulated 10% w/w PbSe:MAPbI$_3$ solar cells retained 85% of original PCE after 624 hrs aging in open air, in contrast with 16% retained original PCE of MAPbI$_3$ cell after 432 hrs. These results clearly indicate much enhanced chemical stability of 10% w/w PbSe:MAPbI$_3$. Most importantly, we have also observed that unencapsulated 10% w/w PbSe:MAPbI$_3$-based solar cell shows a highly reflective silver cathode after aging in ambient atmosphere for two weeks, while regular MAPbI$_3$ solar cell exhibits purple-brown electrodes under the same aging conditions, as shown in Figure 3-1-21. This can be explained by the diffusion of iodine in regular MAPbI$_3$ cells, \cite{177,178} that eventually halogenated silver into silver iodide (AgI). AgI consequently creates large resistivity at the charge collection electrode and accounts for the drop of PV performance on regular MAPbI$_3$ cell. Atomically, Se$^{2-}$ poses strong electrostatic interaction with MA$^+$ in perovskite materials, supressing librational motions of MA$^+$, reducing iodine migration. \cite{79,80} As such, PbSe dopant effectively aid in suppressing iodine diffusion and contributes to stable solar cell performance. X-ray photoelectron spectroscopy (XPS) studies show the absence of iodine on the Ag electrode for 10% w/w PbSe:MAPbI$_3$-based sample in contrast to the presence of I on the Ag electrode for MAPbI$_3$-based sample (Figure 3-1-22). By examining the areas other than Ag electrode, XPS results further reveal a decrease in binding energies of Pb 4f electrons under higher doping concentrations of PbSe or at lower concentrations of PbS in MAPbI$_3$ (Figure 3-1-23a and Table 3-1-4), with binding energies of I 3d electrons displaying a similar trend (Figure 3-1-23b and Table 3-1-4). These results clearly demonstrate a difference in electronegativities of structurally incorporated Se$^{2-}$ and S$^{2-}$ dopant ions.
Figure 3-1-17. J-V curves of the 10% w/w PbS:MAPbI\textsubscript{3} solar cell. [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].

Table 3-1-3
PV parameters extrapolated from the J-V curve of photovoltaic device based on 10% w/w PbS:MAPbI\textsubscript{3}. [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].

<table>
<thead>
<tr>
<th>J\textsubscript{sc} (mA/cm\textsuperscript{2})</th>
<th>V\textsubscript{oc} (V)</th>
<th>FF</th>
<th>η (%)</th>
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</thead>
<tbody>
<tr>
<td>5.5</td>
<td>0.78</td>
<td>0.34</td>
<td>1.7</td>
</tr>
</tbody>
</table>

(Continued on following page)
Figure 3-1-18. Optoelectronic properties of pristine and doped perovskite thin films. (a), (c) and (e) Static PL spectra of MAPbI$_3$, 10% PbSe:MAPbI$_3$ and 10% PbS:MAPbI$_3$ thin films, respectively. (b), (d) and (f) TRPL spectra of MAPbI$_3$, 10% PbSe:MAPbI$_3$ and 10% PbS:MAPbI$_3$ thin films, respectively. [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].

Figure 3-1-19. IPCE spectrum of 10% w/w PbSe:MAPbI$_3$ solar cell device. [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].
Figure 3-1-20. Stability tests of unencapsulated 10% w/w PbSe:MAPbI$_3$ (red) and pristine MAPbI$_3$ (black) solar cells. [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].

Figure 3-1-21. Photographs of undoped MAPbI$_3$ (a) and 10% w/w PbSe:MAPbI$_3$ (b) solar cell devices, where tarnished edges of silver electrodes can be seen on undoped MAPbI$_3$ device. [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].
Figure 3-1-22. XPS spectra of Ag 3d electrons (a) and I 3d electrons (b) on Ag electrode areas of pristine and PbSe doped MAPbI₃ solar cells. [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].

Figure 3-1-23. XPS spectra of Pb 4f electrons (a) and I 3d electrons (b) on perovskite areas of pristine and doped MAPbI₃ devices. [37] © 2018, John Wiley and Sons. Reprint with permission of John Wiley and Sons from ref. [37].

<table>
<thead>
<tr>
<th></th>
<th>Pb 4f₃/2 (eV)</th>
<th>Pb 4f₇/₂ (eV)</th>
<th>I 3d₃/₂ (eV)</th>
<th>I 3d₅/₂ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI₃</td>
<td>142.1</td>
<td>137.2</td>
<td>629.7</td>
<td>618.2</td>
</tr>
<tr>
<td>5% w/w PbSe:MAPbI₃</td>
<td>142.0</td>
<td>137.1</td>
<td>629.6</td>
<td>618.1</td>
</tr>
<tr>
<td>10% w/w PbSe:MAPbI₃</td>
<td>141.9</td>
<td>137.0</td>
<td>629.6</td>
<td>618.1</td>
</tr>
<tr>
<td>5% w/w PbS:MAPbI₃</td>
<td>142.1</td>
<td>137.2</td>
<td>630.2</td>
<td>618.6</td>
</tr>
<tr>
<td>10% w/w PbS:MAPbI₃</td>
<td>142.2</td>
<td>137.3</td>
<td>630.2</td>
<td>618.7</td>
</tr>
</tbody>
</table>

Since divalent chalcogenide Se²⁻ as in the form of PbSe mitigated low moisture stability of MAPbI₃ thin films, phenomenal PV performance with long-term stability was achieved on 10% w/w PbSe:MAPbI₃-based solar cell device. In the meantime, the Ag cathode of 10% w/w PbSe:MAPbI₃ solar cell was chemically preserved due to suppressed I diffusion in device after aging over a long period of time. Our work has opened a workable route to improve the chemical...
stability of the components in perovskite solar cells, while simultaneously achieving workable PV performance. Continuous efforts will be made to realize the divalent anion doping methods in much more efficient devices through optimizing the processing conditions, doping concentrations and material compositions of perovskite absorbers in future studies.

3.2. MA⁺/Cs⁺ Mixed-Cation Lead Iodide for Thermally Stable Perovskites

Due to the high decomposition temperatures of Cs⁺-based inorganic perovskites, such as CsPbI₃ and CsPbBr₃ [179-182], Cs⁺ has the potential to enhance the thermal stabilities of alloyed hybrid perovskites. As such, MAPbI₃ and MA₀.₉₅Cs₀.₀₅PbI₃ thin films were first synthesized, in which they exhibited comparable crystal structures but with the crystallinity of MA₀.₉₅Cs₀.₀₅PbI₃ outperformed by pristine MAPbI₃ (Figure 3-2-1). Then, these two perovskite films were thermally treated at various temperatures with 10 minutes of equilibration time, before being measured on optical reflectance. The thermal stabilities of perovskite thin films were subsequently evidenced from the evolutions of temperature-dependent reflectance spectra. As shown in Figure 3-2-2a, regular MAPbI₃ thin film experienced phenomenal degradation after being thermally treated at 190 °C for 10 minutes, as indicated by the significant upshift of reflectance from 500 nm to 750 nm and considerably decreased slope of onset area between 750 nm and 800 nm, when compared with the reflectance profiles measured after treatments at lower temperatures; while at 200 °C treatment for 10 min, MAPbI₃ thin film exhibited further degradation, as illustrated by the largely elevated reflectance from 500 nm to 750 nm along with an apparently diminished onset area, and thus signifying a massive loss of light-harvesting activity of perovskite. Nevertheless, as displayed

---

in Figure 3-2-2b, no obvious change in reflectance spectra was observed on MA$_{0.95}$Cs$_{0.05}$PbI$_3$ thin film after thermally treated at set temperatures up to 200 °C, where the slope of reflectance onset between 750 nm and 800 nm was largely unaffected. To quantify the change in optical absorption ability of thermally treated thin films, optical bandgaps were extrapolated from Tauc plots of corresponding reflectance spectra. As shown in Figure 3-2-3a, after 200 °C treatment for 10 min. (red), degraded thin film had a 2.35 eV bandgap, in contrast with original 1.54 eV bandgap on as-prepared MAPbI$_3$ thin film (black); whereas for MA$_{0.95}$Cs$_{0.05}$PbI$_3$ thin film, as shown in Figure 3-2-3b, 1.52 eV bandgap was observed after 200 °C treatment (red), which was only 0.01 eV widened relative to 1.51 eV on as-prepared thin film (black). The retained reflectance profiles of MA$_{0.95}$Cs$_{0.05}$PbI$_3$ thin film illustrated its significantly enhanced thermal stability, in comparison with the pristine MAPbI$_3$.

Figure 3-2-1. Structural properties of perovskite thin films. (a) XRD patterns of MAPbI$_3$ (blue) and mixed-cation MA$_{0.95}$Cs$_{0.05}$PbI$_3$ (red) thin films. (b) Comparison of diffraction peak FWHMs of MAPbI$_3$ (blue) and MA$_{0.95}$Cs$_{0.05}$PbI$_3$ (red) thin films.
Figure 3-2-2. Optical reflectance spectra of MAPbI$_3$ (a) and MA$_{0.95}$Cs$_{0.05}$PbI$_3$ (b) thin films. [23] © 2017 Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Reprint with permission of Elsevier from ref. [23].

Figure 3-2-3. Tauc plots of MAPbI$_3$ (a) and MA$_{0.95}$Cs$_{0.05}$PbI$_3$ (b) thin films before and after thermal treatments. [23] © 2017 Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Reprint with permission of Elsevier from ref. [23].

3.3. Reductive Small Organic Molecules for Extended Photoactive Longevity of Tin(II)-Based Perovskites

Being a health concern to human body and environment, toxic lead element in regular lead-based perovskite solar cells has hampered their large-scale commercial application. [183-185] Many alternatives have been attempted to replace lead with low-toxicity metal ions in halide perovskites, where the most promising route was to utilize tin(II) as the metal ion composition.
Nonetheless, tin(II)-based cells exhibit photovoltaic performance that is far from being comparable with the lead(II)-based counterparts. [186-193] By scrutinizing the chemical origin of tin(II) perovskites, one can attribute the oxidation of Sn$^{2+}$ to Sn$^{4+}$ to be a crucial factor responsible for their inferior optoelectronic properties, which is caused by the energetic Sn 5$s^2$ electrons [194] that are easily engaged in chemical reactions with oxidizing agents. As such, it is critically important to prevent the oxidation of Sn$^{2+}$, so as to extend the photoactive longevity of tin(II) perovskites for stable photovoltaic performance. In this study, reductive organic molecules—hydroquinone [195,196] and poly(4-vinylphenol) [197,198] were introduced into the methylammonium tin(II) iodide (MASnI$_3$) precursor solutions, before perovskite MASnI$_3$ thin films were deposited for stability tests, with the detailed experimental methods given in Chapter 6. As shown in Figure 3-3-1a, the pristine MASnI$_3$ thin film experienced large upshift of its optical reflectance from 800 to 1600 nm as well as a significantly blueshifted onset area from original 1300-1600 nm to 800-1000 nm region across 7 days of oxidation in dry air, which was closely corroborated by the film colors shown in inset, thereby indicating the largely lost light absorption of the perovskite material. The RH content of the dry air was controlled below 10% in order to minimize the moisture degradation effects that could concurrently happen to MASnI$_3$. By contrast, 3 wt.% hydroquinone in MASnI$_3$ precursor solution resulted in highly overlapped reflectance profiles across 7 days of aging under the same condition, as shown in Figure 3-3-1b, which signified the largely preserved light absorption of the doped MASnI$_3$ thin film.
Figure 3-3-1. Time-dependent optical reflectance evolutions of \( \text{MASnI}_3 \) (a) and 3% w/w hydroquinone:MASnI3 (b) thin films in dry air (<10% RH), with corresponding schematic illustration of oxygen reactions with perovskite and/or hydroquinone molecule shown above corresponding reflectance spectra.

By recording static PL on \( \text{MASnI}_3 \) perovskite thin films as a function of exposure time in the air, it is clear to observe a minute-kinetics decay of the PL intensity on pristine \( \text{MASnI}_3 \) thin film, as demonstrated in Figure 3-3-2a, which echoes the oxidation-induced degradation of light-absorbing function, as imparted by reflectance spectra in Figure 3-3-1a. Notably, with the presence of hydroquinone in \( \text{MASnI}_3 \) precursor solution, the fabricated \( \text{MASnI}_3 \) thin film displayed a distinctively retarded decay of its PL peak intensity (Figure 3-3-2b), thereby signifying the sacrificial effects of the organic reductant that was reductively preserving the photoactivity of perovskite \( \text{MASnI}_3 \). However, \( \text{MASnI}_3 \) thin film doped with poly(4-vinylphenol) surprisingly revealed an accelerated decay of its PL peak intensity, which may arise from the enlarged interface between perovskite grains and oxygen molecules due to the incorporated large-size polymer.
molecules. By summarizing the time-dependent PL peak intensities of the studied thin film samples, it is explicit to view the much slower decay of PL peak intensity on 3% w/w hydroquinone.

(Continued on following page)
Figure 3-3-2. Evolutions of static PL spectra of pristine (a), 3% w/w hydroquinone doped (b) and 5% v/v poly(4-vinylphenol) doped (c) MASnI$_3$ thin films with respect to time exposure in air. Measurement time with respect to the initial exposure to air shown to the right.

Doped MASnI$_3$ thin film in comparison to pristine MASnI$_3$ and 5% v/v poly(4-vinylphenol) counterparts, as shown in Figure 3-3-3. Furthermore, it is clear to note that the PL intensity decay of poly(4-vinylphenol) doped MASnI$_3$ followed a biexponential kinetics, as different from the exponential decay kinetics observed on pristine and hydroquinone-doped MASnI$_3$ counterparts, which again confirms the much different doping effects of poly(4-vinylphenol).

Figure 3-3-3. Summary of the normalized peak intensities of three tin(II)-based perovskite thin films as a function of exposure time in air.
4. CRYSTALLINITY IMPROVEMENT IN PEROVSKITE FORMAMIDINIUM LEAD CHLORIDE FOR ENHANCED UV PHOTORESONSE WITH ENERGY AND LIGHT-INTENSITY OSCILLATION DISTINGUISHABILITY

Due to the suitable bandgaps (~2.9 – 3.1 eV) and superior charge transport properties, chloride (Cl⁻)-based perovskite materials (e.g. MAPbCl₃, CsPbCl₃) have demonstrated high-performance visible-blind UV detection. [198-201] Nonetheless, these photodetectors were never able to differentiate UV photons at different wavelengths; plus, they were not sufficiently sensitive to detect UV radiations with temporally varying intensities. Developing a photodetector with such distinguishing abilities is thus highly desirable to accurately identify energy and intensity information of the UV photons. Here, through small amount of lithium chloride (LiCl, 1 mg/mL) mixed in the formamidinium chloride (FACl, 10 mg/mL)/2-propanol solution, synthesized formamidinium lead chloride (FAPbCl₃) nanowires (detailed methods elaborated in Chapter 6) exhibited greatly increased crystallinity as compared to the FAPbCl₃ nanowires grown without LiCl additive, and consequently led to significantly enhanced photoresponse upon UV illumination. As shown in Figure 4-1, solution-grown LiCl:FAPbCl₃ nanostructured thin film displays much more intensive diffraction peaks of (100), (110) and (200) planes (red trace), as compared with FAPbCl₃ counterpart (blue trace). The XRD patterns on both perovskite FAPbCl₃ thin films closely match the reported pattern (black), [202] and indicate a complete reaction of PbCl₂ precursor (green) and free of LiCl additive (magenta).
Figure 4-1. XRD patterns of FAPbCl₃ nanostructures grown with LiCl additive (red), without LiCl additive (blue), reported FAPbCl₃ (black) by Govinda et al. [202], LiCl powder (magenta) and PbCl₂ precursor (green).

As displayed in Figure 4-2a, detailed analysis of the diffraction peaks reveals notably smaller FWHMs on LiCl:FAPbCl₃ thin film, thereby signifying the much greater crystallinity of FAPbCl₃ nanostructures grown with the presence of LiCl additive than the pristine FAPbCl₃ counterpart. Substantially, LiCl:FAPbCl₃ also exhibits greater average crystalline sizes of all (200), (110) and (100) orientations (Figure 4-2b), as calculated through Scherrer’s equation: [203-206]

\[
D = \frac{k\lambda}{b\cos\theta}
\]

in which \(D\), \(k\), \(\lambda\), \(b\) and \(\theta\) respectively stand for crystallite size, shape factor (0.9), wavelength of X-ray photons (1.54 Å) and diffraction angle. In fact, the increased crystallinity on LiCl:FAPbCl₃ can be explicitly viewed through its microscopic images, as shown in Figures 4-3b and 4-3d, where LiCl:FAPbCl₃ nanowires display highly ordered morphology as featured with sharp edges and flat end facets on micrometer-size crystals, in contrast with pristine FAPbCl₃ nanostructures that are much more disordered in shapes (Figures 4-3a and 4-3c).
Figure 4-2. Crystallinity analysis of FWHMs (a) and average crystalline sizes (b) of FAPbCl$_3$ thin films grown with (red) or without (blue) LiCl additive.

Optoelectronically, by comparing with the pristine FAPbCl$_3$, LiCl:FAPbCl$_3$ clearly exhibits a PL spectrum with redshifted peak intensity (Figure 4-4), and therefore indicates a distinctively narrowed optical bandgap and again corroborates the observed increased material crystallinity. [59,120,207] To validate the feasibility for UV photodetector, optical reflectometry was subsequently performed on pristine FAPbCl$_3$ nanostructured thin film, where the amount of light reflected quickly approaches 0% as photon wavelength goes below 400 nm (Figure 4-5), thereby indicating the large absorption of UV photons and the consequently favored generation/collection of photoelectrons. Indeed, as shown in Figure 4-6, upon a 365-nm UV illumination, both pristine FAPbCl$_3$ and LiCl:FAPbCl$_3$ nanostructured thin films show functional photocurrent response. Nevertheless, LiCl:FAPbCl$_3$ thin film exhibits much larger photocurrent densities at around 9 $\mu$A/cm$^2$, in contrast with 1.6 $\mu$A/cm$^2$ on pristine FAPbCl$_3$, which therefore indicates the much enhanced optoelectronic properties as due to LiCl-induced crystallinity improvement.
Figure 4-3. SEM images of pristine FAPbCl$_3$ (a, c) and LiCl:FAPbCl$_3$ (b, d) nanostructures, where (a) and (b) were 2.46-kx magnification images, while (c) and (d) were taken under 5.21-kx magnification.
Figure 4-4. PL spectra of FAPbCl$_3$ nanostructured thin films grown with (red) and without (blue) LiCl additive.

Figure 4-5. Optical reflectance spectrum of FAPbCl$_3$ nanostructured thin film.

Figure 4-6. On-off photocurrents of LiCl:FAPbCl$_3$-based (red) and FAPbCl$_3$-based (blue) photodetectors under 365-nm UV illumination.
Additionally, the improved crystallinity on LiCl:FAPbCl$_3$ was also manifested in its outstandingly enhanced photostability, in which LiCl:FAPbCl$_3$ retained ~80% of its original photocurrent density after 15 minutes of continuous UV illumination while pristine FAPbCl$_3$ exhibited <60% retention of its initial current density, as shown in Figure 4-7. Accordingly, what accounts for the enhanced photoelectronic performance of LiCl:FAPbCl$_3$ nanostructured thin film are its remarkable electronic properties. As shown in Figure 4-8, it is unambiguous to see that LiCl:FAPbCl$_3$ had exceptionally increased electrical conductivity (Figure 4-8a) and much smaller electrochemical impedance (Figure 4-8b) as compared to pristine FAPbCl$_3$ counterpart. By adopting a common resistance//capacitance (R//C) circuit model for metal/perovskite/metal constructions [208,209] as shown in Figure 4-8c, the charge recombination resistances ($R_{rec}$), chemical capacitances (constant phase element, CPE) as well as the electron transit times ($R_{rec}$*CPE) were calculated and summarized in Table 4-1. The fact that LiCl:FAPbCl$_3$ exhibited shorter electron lifetime (0.000150 s) than pristine FAPbCl$_3$ (0.00144 s) implies its exceptionally greater carrier mobility [210]. As shown in Figure 4-8d, Mott-Schottky plots further suggest that LiCl:FAPbCl$_3$ had remarkably greater free charge carrier density ($1.977*10^{17}$/cm$^3$) in contrast to pristine FAPbCl$_3$ ($1.028*10^{16}$/cm$^3$), as evidenced by its much smaller voltage-dependent curve slope [211] through the following equation:[211,212]

\[
N_c = \frac{2}{e_0 \varepsilon \varepsilon_0} \left[ \frac{\partial \left( \frac{1}{C^2} \right)}{\partial V} \right]^{-1}
\]
where $N_c$, $e_0$, $\varepsilon$, $\varepsilon_0$ and $\frac{\partial (\frac{1}{\varepsilon})}{\partial V}$ represent carrier concentration, electron charge ($1.602 \times 10^{-19}$ C), dielectric constant ($\approx 30$ for pristine FAPbCl$_3$ at room temperature [202]), vacuum permittivity ($8.854 \times 10^{-12}$ F/m) and slope of Mott-Schottky plot, respectively.

Figure 4-7. Photostability plots of pristine FAPbCl$_3$ (blue) and LiCl:FAPbCl$_3$ (red) nanostructured thin films under the 365-nm UV light.

(Continued on following page)
Figure 4-8. Electrical characterizations of LiCl:FAPbCl₃ (red) and pristine FAPbCl₃ (blue) nanostructured thin films. (a) Linear sweep voltammogram of perovskite thin films measured in dark condition. (b) Nyquist plots of perovskite thin films under 365-nm UV illumination. (c) Equivalent circuit applied in fitting the impedance curves shown in (b). (d) Mott-Schottky plots of perovskite thin films measured under 365-nm UV illumination.

Table 4-1
Summary of $R_{\text{rec}}$, CPE chemical capacitances and time constants obtained from the electrochemical impedance fittings in Figure 4-8b.

<table>
<thead>
<tr>
<th>Thin film</th>
<th>$R_{\text{rec}}$ (Ω)</th>
<th>CPE (F)</th>
<th>Lifetime (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAPbCl₃</td>
<td>729.6</td>
<td>1.97*10⁻⁶</td>
<td>0.00144</td>
</tr>
<tr>
<td>LiCl:FAPbCl₃</td>
<td>276.9</td>
<td>5.41*10⁻⁷</td>
<td>0.000150</td>
</tr>
</tbody>
</table>

Importantly, abovementioned photoresponse was achieved with UV light source powered by batteries (UVL-4F UV lamp, picture shown in Figure 4-9a inset), which therefore operates on constant current and UV light intensity. This is verified by the frequency-domain Fourier-transform coefficient plots, where no frequency components are found, thus signifying the absence of periodically occurring photocurrents (Figure 4-9). However, in the presence of a 365-nm UV light (UVGL-25, Figure 4-11f) as powered by AC, LiCl:FAPbCl₃ exhibited photocurrents with
temporally varying magnitudes (Figure 4-10), which is on par with the varying intensity of UV light and implies the highly sensitive photoelectronic response of LiCl:FAPbCl\textsubscript{3}-based detector. Moreover, by performing Fourier transform (FT) of the observed chronoamperogram, distinctive frequency components (60-Hz, 120-Hz, 180-Hz and 240-Hz) are witnessed, as shown in Figure 4-11, which thus indicates that photocurrents were periodically oscillating. Astonishingly, under 254-nm AC-powered UV illumination, LiCl:FAPbCl\textsubscript{3} detector unexpectedly shows current signals both above and below the dark current, and hence reveals that the UV-induced photoelectron injection was temporally switching directions, as shown in Figure 4-12. The periodically damping nature of photocurrents is once again confirmed by FT coefficient plot of the observed chronoamperogram. Similarly, frequency-domain coefficient plots clearly show the existence of 60-Hz frequency component, which is characteristic of 120-Hz, 180-Hz and 240-Hz harmonic current frequencies (Figures 4-13) and closely corroborates the AC-powered UV lamp with 60-Hz current oscillation frequency (Figure 4-11f). Visually, the periodically damping and direction-switching of photoelectron injection on LiCl:FAPbCl\textsubscript{3} photodetector under 365/254 nm UV illuminations are also explicitly viewable from video clips, which were taken on the photocurrent responses during chronoamperometry experiments, as displayed in Supplemental Files. Substantially, the temporal electron injection direction switching is further validated through chronopotentiometry studies, where LiCl:FAPbCl\textsubscript{3} demonstrates bipolar photovoltage signals with respect to the background $V_{oc}$ under the 254-nm AC-powered UV illumination; meanwhile, 365-nm AC-powered UV photons led to on-off photovoltage signals that are unipolar to the $V_{oc}$, as shown in Figure 4-14.
Figure 4-9. FT of the chronoamperogram of LiCl:FAPbCl₃ nanostructured thin film shown in Figure 4-6. (a) FT coefficient plot, with inset being the photograph of the battery-powered 365-nm UV lamp. (b) FT coefficient plot with real part. (c) FT coefficient plot with imaginary part.

Figure 4-10. On-off photocurrents of LiCl:FAPbCl₃-based photodetector under 365-nm AC-powered UV illumination. (a) Chronoamperogram showing on-off photocurrents. (b) Zoomed-in view of the photocurrent signal between 25th and 32nd seconds.
Figure 4-11. FT of the chronoamperogram of LiCl:FAPbCl$_3$ nanostructured thin film shown in Figure 4-10a. (a) FT coefficient plot. (b) Zoomed-in view of the coefficient plot in the range of 56 to 64 Hz. (c) Logarithmic scale of coefficient plot. (d) and (e) Real-part and imaginary-part coefficient plots, respectively. (f) Picture of the AC-powered UV lamp.
Figure 4-12. On-off photocurrents of LiCl:FAPbCl$_3$-based photodetector under 254-nm AC-powered UV illumination. (a) Chronoamperogram showing on-off photocurrents across 60 seconds. (b) Zoomed-in view of the photocurrent signal between 22nd and 29th seconds.

(Continued on following page)
Figure 4-13. FT of the 254-nm chronoamperogram of LiCl:FAPbCl₃ nanostructured thin film shown in Figure 4-12a. (a) FT coefficient plot. (b) Zoomed-in view of the coefficient plot in the range of 57 to 64 Hz. (c) Logarithmic scale of coefficient plot. (d) and (e) Real-part and imaginary-part coefficient plots, respectively.

Figure 4-14. On-off photovoltages of LiCl:FAPbCl₃-based photodetector under 254-nm (a) and 365-nm (b) AC-powered UV irradiations.

Vitally, by quantitatively analyzing the FT coefficient plots of 365-nm and 254-nm photocurrents (Figures 4-11 a-e & 4-13), one can find that the magnitudes of coefficients under 254-nm UV are much greater than the 365-nm counterparts. Moreover, 365-nm-induced photocurrents have a frequency distribution between 100 and 150 Hz that is prominently comparable with the frequency distributions within 50-75 Hz, and 175-200 Hz. This frequency
profile, however, is evidently different from 254-nm FT coefficients, which have very small frequency composition in the range of 100-150 Hz (Figures 4-13 c, d & e). Such perturbed frequency components, can be valuably exploited in future optical communications, as information can be effectively ciphered and decoded through modulating amplitude, frequency and also the phase of current. Furthermore, the temporal direction switching of photoelectron injection under 60-Hz 254-nm UV is unique to the demonstrated LiCl:FAPbCl₃ photodetector. Through chronoamperometry studies on a commercial Si photodiode, it is discovered that 60-Hz 254-nm UV photons did not give rise to any bipolar photoelectron injections, as manifested by the photocurrent signals that are one-sided to the background dark currents, although the benchmark Si photodiode is also capable of sensitively detecting the AC-powered 254-nm and 365-nm UV photons via periodically oscillating currents (Figures 4-15 and 4-16). The indifferent photoresponse of Si photodiode under 254-nm and 365-nm irradianes implies the absence of distinguishability toward UV photons with different energies in regular device architecture.

Figure 4-15. On-off photocurrents of Si photodiode under 254-nm (a) and 365-nm (b) AC-powered UV illuminations with sampling period of 0.01 s.
To account for the photophysical origin of bipolar photoresponses under 60-Hz 254-nm UV photons, UV-Vis absorbance was subsequently performed on LiCl:FAPbCl₃ nanostructured pellet. As shown in Figure 4-17a, absorbance at 254 nm (1.878) and 365 nm (0.179) leads to a ratio of corresponding light attenuation coefficients (absorption coefficients) of ~10.5 according to Beer-Lambert’s equation:

\[ A = \alpha cl \]

in which \( \alpha \), \( c \) and \( l \) stand for absorption coefficient, density and thickness of material, respectively. Since density and thickness of LiCl:FAPbCl₃ sample are invariant, ratio of absorbances at 254 nm and 365 nm is simply equal to the ratio of corresponding absorption coefficients. Under average optical power densities of 60-Hz 254-nm (0.007532 mW/cm²) and 365-nm (0.008517 mW/cm²), the difference in absorption coefficients therefore results in 254-nm photoelectrons that are six times in number to the 365-nm photoelectrons. Explicitly, the large number of 254-nm photoelectrons is manifested in the large responsivity (~1.54 A/W) and photocurrent magnitude that is nearly 4 times to the photocurrent achieved under 365-nm AC-powered UV, as shown in
Figure 4-17b. It is noteworthy that the photocurrent densities summarized in Figure 4-17b are average magnitudes, so as to be on par with the average optical power densities measured by light meter (LI-250A), through the following equation due to their sinusoidally oscillating nature:

\[ J_{\text{avg}} = \frac{2J_p}{\pi} \]

where \( J_p \) and \( J_{\text{avg}} \) respectively represent peak and average photocurrent densities. Fundamentally, it is the large concentration of 254-nm-induced photocarriers in the conduction band of LiCl:FAPbCl\(_3\) that enables bidirectional electron transfers, where electrons selectively flow toward FTO side at the beginning of 254-nm UV illumination due to the much scarcer density of states in FTO, which can be clearly perceived from the smaller work function of FTO [213,214] with respect to gold. After FTO is fully saturated with charge, migration of photoelectrons will switch to gold side, with the whole charge transfer process repeating reciprocally between the two electrodes, as illustrated in Figure 4-18. To further elucidate the 4-time photocurrent magnitudes achieved under 254-nm with respect to 365-nm illumination, electrochemical impedance spectroscopy was subsequently performed on LiCl:FAPbCl\(_3\) photodetector under continuous 60-Hz 254-nm and 60-Hz 365-nm illuminations. As shown in Figure 4-19, the Nyquist plot shows a notably smaller half circle for LiCl:FAPbCl\(_3\) photodetector under 60-Hz 254-nm illumination. The extracted charge carrier lifetime, as displayed in Table 4-2, is much smaller under 254-nm illumination (~70 μs) when compared with 365-nm illumination (~94 μs), which thus suggests a much greater carrier mobility under 254-nm UV condition. In the meantime, higher carrier mobility directly results in larger charge transport efficiency, [215] and therefore rationalizes the witnessed large photocurrent under 254-nm UV.
Figure 4-17. UV-Vis absorbance spectrum (a) and summary of photocurrent densities (left y-axis) with corresponding responsivities (right y-axis) of LiCl:FAPbCl$_3$ (b).

Figure 4-18. Energy level diagram and charge transfer processes of FTO/LiCl:FAPbCl$_3$/gold photodetector device, in which energy level of VBM (~5.8 eV) is approximated based on the fact that FAPbCl$_3$ has slightly smaller optical bandgap than the previously studied MAPbCl$_3$ analogue. [198,216]
Figure 4-19. Nyquist plots under continuous illuminations of 60-Hz 365-nm (magenta) and 60-Hz 254-nm (violet) UV.

Table 4-2
Summary of $R_{\text{rec}}$, chemical capacitances and time constants obtained from the electrochemical impedance fittings in Figure 4-16.

<table>
<thead>
<tr>
<th>UV</th>
<th>$R_{\text{rec}}$ (Ω)</th>
<th>CPE (F)</th>
<th>Lifetime (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60-Hz 365-nm</td>
<td>301.8</td>
<td>$3.134\times10^{-7}$</td>
<td>0.00009458</td>
</tr>
<tr>
<td>60-Hz 254-nm</td>
<td>282.1</td>
<td>$2.484\times10^{-7}$</td>
<td>0.00007007</td>
</tr>
</tbody>
</table>
5. CONCLUSION

This dissertation reveals that organic cations play a pivotal role in determining the optoelectronic properties of perovskite materials; in solid-state MAPbI₃, it is manifested as the electron-rotor interaction, where charge carrier lifetimes, through coupling between cationic side of organic MA⁺ rotors and photoexcited free electrons in PbI³⁻ framework, are effectively dependent on the rotational frequencies of MA⁺ rotors as in the form of polarons. [31] This is greatly different from conventional solid-state condensed matters where materials’ electronic structures are mainly influenced by the interplay between electrons and lattice vibration. The importance of rotational A-site cations was further illustrated via the TRPL studies of MAPbBr₃, FAPbBr₃ and CsPbBr₃ single crystals, in which the carrier lifetimes exhibit a clear trend as MAPbBr₃ ≈ FAPbBr₃ > CsPbBr₃. However, prolonged carrier lifetimes observed on mixed-cation MA₀.₉₅ Cs₀.₀₅ PbI₃ perovskite in comparison to MAPbI₃ counterpart indicate the existence of fluctuating lattice disorders, which may stem from the band inversion process through the synergistic effects of different types of cations as reported by previous studies [107,217]. Other than the distinctively improved optoelectronic properties, isotropic Cs⁺ also led to notably enhanced thermal stability of perovskite MA₀.₉₅ Cs₀.₀₅ PbI₃ by comparing with pristine MAPbI₃, owing to its strong and more homogenous attraction with PbI³⁻ framework than the asymmetric MA⁺. Likewise, due to strengthened attraction between MA⁺ cation and inorganic PbI³⁻ framework in the presence of divalent Se²⁻ anion, moisture stabilities of PbSe-doped MAPbI₃ perovskites were greatly enhanced. As a result, fabricated PbSe-doped solar cell device exhibited long-term stability while maintaining phenomenal power conversion efficiency of 10.4%. Because of the suppressed
reorientational motions of MA$^+$ cations, iodine diffusion in PbSe-doped perovskite solar cells is significantly suppressed and thus resulted in chemical stability of silver electrodes. Since hydroquinone reduced the decay kinetics of PL intensity on MASnI$_3$, small organic reductive molecules can be deemed as useful chemical dopants to effectively extend the photoactive longevity of tin(II)-based perovskites. Finally, small ion additive as in the form of LiCl, notably increased the crystallinity of solution-grown FAPbCl$_3$ perovskite nanostructures and consequently realized enhanced photocurrent under UV illumination. Since over-exposure in UV radiation results in skin cancers [218,219], the high-performance UV detection based on LiCl:FAPbCl$_3$ will greatly benefit the health and safety of human body. Most importantly, as UV radiation gives rise to high-speed, wide-coverage and non-line-of-sight optical communications due to its small susceptibility to solar background interference and flexibility of transmitter/receiver orientations such as pointing, acquisition and tracking, [220-223] the sensitive distinguishability of UV photon energy and intensity oscillation via periodically damping photocurrents/photovoltages with temporal phase switching, as well as perturbed frequency distributions, will effectively realize acquisition, ciphering and decoding of optical information carried in UV photons, and thus lead to further development and application of this emerging communication technology. This dissertation addresses the major aspects of hybrid perovskites—carrier processes and stabilities, through emphasizing the underlying fundamental structure-property relationships and chemical doping methods applicable for continuous improvements in both material and optoelectronic settings.
6. MATERIALS AND METHODS

6.1. Chemicals

\( \gamma \)-Butyrolactone, methylamine solution (CH$_3$NH$_2$, 40 wt.% in H$_2$O), isotopic CD$_3$NH$_2$ gas (99.9 atom%), deuterium oxide (D$_2$O, 99.9 atom % D), formamidine acetate salt (HC(NH$_2$)NH·HCOOCH$_3$, 99%), cesium hydroxide hydrate (CsOH·xH$_2$O, ≥90%), N-methyl-2-pyrrolidinone (NMP), sodium sulfide nonahydrate (Na$_2$S·9H$_2$O), lead(II) chloride (PbCl$_2$, 99.999%) and 2-propanol (anhydrous, 99.5%) were purchased from Aldrich. Hydriodic acid (HI, 57 wt.% in H$_2$O), lead iodide (PbI$_2$, 99.9985% metal basis), N, N-Dimethylformamide (DMF, anhydrous, 99.8%) and sodium bromide (NaBr, 99.0% min.) were purchased from Alfa Aesar. Hydrobromic acid Standard Solution (HBr, 1.997 mol/L) was purchased from Fluka. Lead nitrate (Pb(NO$_3$)$_2$) and lead acetate (Pb(C$_2$H$_3$O$_2$)$_2$·3H$_2$O) were purchased from Mallinckrodt. Ethyl ether (anhydrous), hydrochloric acid (HCl, 37.0%) and lithium chloride (LiCl, 96.1%) were obtained from Fischer Chemical. All chemicals were used as received without further purification.

6.2. Synthesis of Perovskite Precursors

CH$_3$NH$_3$I was synthesized through reacting 1:1 ratio of CH$_3$NH$_2$ and HI by following method reported in literature [224]. In detail, equimolar of HI was dropwise introduced into ice-temperature CH$_3$NH$_2$ in a 100-mL round bottom flask with stirring, as followed by rotary evaporation at 60 °C to dry off the water. Next, yellow solid was obtained and washed with copious amount of ethyl ether on filter paper, as accompanied by vacuum filtration. Washed CH$_3$NH$_3$I powder was then dried in a vacuum oven at 80 °C overnight to yield the pure product. In the case of isotopic CH$_3$ND$_3$I, it was synthesized by dissolving as-obtained CH$_3$NH$_3$I in excessive D$_2$O at
a 1:40 molar ratio, as followed by rotary evaporation at 60 °C to dry off the solvent. This process was repeated four times to ensure complete substitution of ammonium hydrogen by deuterium.

[31] As for CD$_3$NH$_3$I, it was synthesized via reacting 1:1 ratio of CD$_3$NH$_2$ gas and HI, and by dissolving in excessive D$_2$O and subsequent rotary evaporation, fully deuterated CD$_3$ND$_3$I was prepared. CH$_3$NH$_3$Br (MABr) was synthesized with the same procedure except HBr was used instead of HI. In terms of HC(NH$_2$)$_2$Br (FABr), HC(NH$_2$)$_2$Cl (FACl) and CsBr, they were synthesized through reacting 1:1.1 molar ratio of HC(NH$_2$)NH·HCOOCH$_3$/HBr, HC(NH$_2$)NH·HCOOCH$_3$/HCl and CsOH·xH$_2$O/HBr, respectively. PbBr$_2$ was synthesized by mixing 2:1 molar ratio of NaBr and Pb(NO$_3$)$_2$. Precipitated solid was filtered out and purified with copious amount of deionized water, vacuum filtration and vacuum drying at 80 °C overnight. PbSe was synthesized by first adjusting an aqueous solution of SeO$_2$ to a pH of 2 using HCl, then equimolar amount of Pb(C$_2$H$_3$O$_2$)$_2$·3H$_2$O was added into the solution followed by formation of gray precipitate. Mixture solution was then stirred for 12 hrs at 80 °C. Subsequently, precipitate solid was filtered out, washed with excess deionized water for 5 times accompanied by vacuum filtration for each time, then dried in an oven at 120 °C overnight. [225] PbS was synthesized by reacting equimolar amounts of Pb(C$_2$H$_3$O$_2$)$_2$·3H$_2$O and Na$_2$S·9H$_2$O in deionized water, under continuous stirring for 1 hr. The resulted black precipitate was filtered, then washed thoroughly with deionized water for 5 times, followed by drying at 100 °C in an oven overnight. SnI$_2$ was synthesized according to method reported in [47].
6.3. Growth of Perovskite Single Crystals

6.3.1. MAPbI$_3$ Single Crystals for Section 2.1.$^1$

The preparation of MAPbI$_3$ single crystals followed the method reported in literatures [85,107]. CH$_3$NH$_3$PbI$_3$, CH$_3$ND$_3$PbI$_3$, CD$_3$NH$_3$PbI$_3$, and CD$_3$ND$_3$PbI$_3$ single crystals were synthesized, respectively, by first mixing 1:1 molar ratio of CH$_3$NH$_3$I, CH$_3$ND$_3$I, CD$_3$NH$_3$I, and CD$_3$ND$_3$I with PbI$_2$ in γ-Butyrolactone, in a glove box to avoid possible exchange of deuterium on nitrogen with moisture in air and material oxidation. The concentration of all the resulting solutions is 1 M in terms of (CH$_3$NH$_3$/PbI$_2$), (CH$_3$ND$_3$/PbI$_2$), (CD$_3$NH$_3$/PbI$_2$), or (CD$_3$ND$_3$/PbI$_2$). Consequently, the solutions were heated at 110 °C for 3 hrs to produce small perovskite seed crystals of CH$_3$NH$_3$PbI$_3$, CH$_3$ND$_3$PbI$_3$, CD$_3$NH$_3$PbI$_3$, and CD$_3$ND$_3$PbI$_3$, respectively. These seed crystals were then transferred to corresponding fresh 1 M CH$_3$NH$_3$PbI$_3$, CH$_3$ND$_3$PbI$_3$, CD$_3$NH$_3$PbI$_3$, and CD$_3$ND$_3$PbI$_3$ solutions, respectively, for continuous growth for 48 hrs at 70 °C in darkness in argon without disturbance. The as-grown single crystals were all stored in argon atmosphere before experimental studies.

6.3.2. Mixed-Cation MA$_{0.95}$Cs$_{0.05}$PbI$_3$ Single Crystals

Stoichiometric MAI, CsI and PbI$_2$ were dissolved in γ-Butyrolactone to form 1 M solution, the precursor solution was then heated at 110 °C for 3 hrs to precipitate sizable crystals as shown in Figure 2-2-1.

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6.3.3. Bromides Perovskite Single Crystals for Section 2.3.

The crystallization and growth of MAPbBr\(_3\) perovskite crystals were performed according to methods [85,107,132] reported previously. For MAPbBr\(_3\) single crystal, 1:1 molar ratio of CH\(_3\)NH\(_3\)Br/PbBr\(_2\) were first dissolved in DMF to form 1 M solution at room temperature. Next, 3 mL of precursor solution was heated at 80 °C on a hotplate for 6 hrs. Finally, large (3-4 mm) MAPbBr\(_3\) crystals were formed, harvested out of solution and blown dry with N\(_2\) flow. In terms of FAPbBr\(_3\), equimolar of FABr and PbBr\(_2\) were dissolved in 1:1 v/v γ-Butyrolactone/DMF to first make 1 M solution, which was heated at 80 °C to precipitate small cubic-shape crystals (1 mm * 1 mm), which were subsequently transferred to fresh 1 M solution at 60 °C for continuous growth for another 3 hrs. Finally, crystals with ~3 mm size were taken out of solution and dried under N\(_2\) flow. Experimental procedures reported in literatures [125,133] were adopted to synthesize CsPbBr\(_3\) single crystals.

6.4. Preparation of Perovskite Thin Films and Solar Cell Fabrication

6.4.1. Perovskite Thin Films and Solar Cells for Section 2.1.

FTO substrate (TEC 15, Hartford Glass Co) was patterned using wet-etching method with zinc powder and HCl solution. Pre-patterned FTO was cleaned and then deposited with a thin compact TiO\(_2\) layer by spray pyrolysis using 0.2 M titanium diisopropoxide bis(acetylacetonate) in 1-butanol solution at 450 °C. The TiO\(_2\) layer was annealed at 450 °C for 1 h. Perovskite films were prepared via non-stoichiometric precursor method as reported before. [226] Briefly, organic salt

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(CH$_3$NH$_3$I or CH$_3$ND$_3$I):PbI$_2$ = 1.2:1 were dissolved into 1-methyl-2-pyrrolidinone/$\gamma$-butyrolactone (7/3, weight ratio) solution to form 50 wt.% precursor. Precursor was coated on top of the substrate by spin-coating at 4500 rpm for 25 s, and wet film was immediately transferred into diethyl ether (DEE, Fisher Chemical) bath for 90s. A thermal annealing was processed at 150 °C for 20 min with a petri dish covered on top under low-humidity atmosphere. 2,2′,7,7′-tetrakis(N,N-dip-methoxyphenylamine)-9,9′-spirobifluorene (Spiro-MeOTAD; Merck, Germany) was used as a hole transport layer (HTL) by spin-coating a HTL solution, which consists of 80 mg Spiro-MeOTAD, 30 μL bis(trifluoromethane) sulfonimide lithium salt stock solution (500 mg Li-TFSI in 1 mL acetonitrile), and 30 μL 4-tert-butylpyridine (TBP), and 1 mL chlorobenzene solvent, at 4000 rpm for 30 s. Finally, a 150-nm Ag layer was deposited on the HTL layer by thermal evaporation. The J–V characteristics of the cells, which have 0.12-cm$^2$ masked area, were measured using a 2400 SourceMeter (Keithley) under simulated one-sun AM 1.5G illumination (100 mW cm$^{-2}$) (Oriel Sol3A Class AAA Solar Simulator, Newport Corporation). IPCE was measured using a solar cell quantum efficiency measurement system (QEX10, PV Measurements). Stabilized power output was recorded by a potentiostat (VersaSTAT MC, Princeton Applied Research) near a maximum power output point. Thin-film surface morphology images were taken by using a Quanta 600 scanning electron microscope.

6.4.2. Solar Cell Fabrication for Section 3.1.3

To prepare PbX (X=Se$^{2-}$, S$^{2-}$) doped perovskite precursor solutions, 0.04 g PbSe, 0.360 g PbI$_2$ and 0.149 g CH$_3$NH$_3$I were dissolved in 0.7 mL of GBL to form a 10% w/w PbSe:MAPbI$_3$ precursor

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solution. In terms of the 5% w/w PbSe:MAPbI₃ precursor, 0.019 g PbSe, 0.360 g PbI₂ and 0.149 g CH₃NH₃I were dissolved in 0.7 mL of GBL to form a mixture solution. Similarly, 10% w/w PbS:MAPbI₃ precursor solution was prepared by dissolving 0.04 g PbS, 0.360 g PbI₂ and 0.149 g CH₃NH₃I in 0.9 mL DMF. Precursor solutions with lead chalcogenide dopants were then stirred at 80 °C for 15 hrs. FTO substrates were then patterned by Zn powder and HCl etching. After overnight base bath cleaning, substrate was coated by a compact TiO₂ (c-TiO₂) using spray pyrolysis. A layer of mesoporous TiO₂ was spin-coated at 6000 rpm for 35 s using 5.4% TiO₂ nanoparticles and 1.6% ethyl cellulose in terpineol/ethanol (3/7 wt ratio) solution, followed by 450 °C air annealing for 30 min. Aforementioned PbSe doped precursor was dispensed on mesoporous substrate, and spun at 4000 rpm for 5 s. In the case of pristine MAPbI₃ based device, 1:1 molar ratio of PbI₂/CH₃NH₃I NMP precursor solution was spun on mesoporous substrate instead, by following method reported previously. [175] Substrates were immediately transferred into rigorously stirred ether bath. After the crystallization in ether bath, perovskite films were further treated with CH₃NH₂ gas. Substrates were further annealed at 100 °C for 10 min. The pervoskite films were then covered by hole transport layer (HTL) via spin-coating a HTL solution, which consisted of 80 mg 2,2’,7,7’-tetrakis(N,N-dip-methoxyphenylamine)-9,9’-spirobiﬂuorene (spiroOMeTAD), 30 μl bis(trifluoromethane) sulfinamide lithium salt stock solution (500 mg Li-TFSI in 1 ml acetonitrile), and 30 μl 4-tert-butylpyridine (TBP), and 1 ml chlorobenzene solvent. Finally, a 150 nm Ag layer was deposited using thermal evaporator and a shadow mask.

6.5. Theoretical Modelling

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6.5.1. DFT calculations

The DFT calculations are conducted using the Vienna ab initio Simulation Package code.[227]

The ionic potentials are described by the projector augmented wave (PAW) method within the generalized gradient approximation (GGA),[228] the long-range van der Waal’s interactions are also taken into account by the empirical Grimme’s method.[229] The plane-wave cutoff energy is 500 eV. For the entire MAPbI₃ unit cell, both the lattice vector and atomic positions are fully relaxed until the residual Hellmann-Feynman forces become smaller than 0.02 eV/Å. The dielectric constants are obtained by density functional perturbation theory using the linear response method.

6.5.2. Calculation on Ratio of Rotational Frequencies of MA⁺

The estimation of the ratio of the in-plane rotation frequency along the C-N axis of the four isotope MA⁺ ν(CH₃NH₃⁺):ν(CH₃ND₃⁺):ν(CD₃NH₃⁺):ν(CD₃ND₃⁺) is depicted as follows. If we treat MA⁺ as a rigid rotor about its center of mass with the methyl group as an entity, ammonium as another, the moment of inertia of this bi-unit cationic molecule can be modeled through equation,[230]

\[ I = m_1 \cdot R_1^2 + m_2 \cdot R_2^2 \]

where \(m_1\) is mass of methyl group and \(m_2\) is mass of ammonium group; \(R_1\) is distance from the center of mass of MA⁺ to the center of mass of methyl group, and \(R_2\) is distance from the center of mass of MA⁺ to the center of mass of ammonium group. Likewise, it can be rewritten as the following equation,[230]

\[ I = \mu \cdot R_e^2 \]

where \(R_e\) is the distance between the center of mass of methyl group and center of mass of ammonium group, so \(R_e = R_1 + R_2\); \(\mu\) is the reduced mass of methyl and ammonium groups and \(\mu\)
Therefore, the ratio for $\mu(\text{CH}_3\text{NH}_3^+) : \mu(\text{CH}_3\text{ND}_3^+) : \mu(\text{CD}_3\text{NH}_3^+) : \mu(\text{CD}_3\text{ND}_3^+) \approx 1 : 1.1 : 1.1 : 1.2$. Knowing the bond angles and bond lengths in MA$^+$ (note that isotopes do not change bond length and angle), we estimate the ratio for $Re(\text{CH}_3\text{NH}_3^+) : Re(\text{CH}_3\text{ND}_3^+) : Re(\text{CD}_3\text{NH}_3^+) : Re(\text{CD}_3\text{ND}_3^+) \approx 1 : 1.03 : 1.03 : 1.05$; consequently, the ratio for $I(\text{CH}_3\text{NH}_3^+) : I(\text{CH}_3\text{ND}_3^+) : I(\text{CD}_3\text{NH}_3^+) : I(\text{CD}_3\text{ND}_3^+) \approx 1 : 1.17 : 1.17 : 1.32$. Furthermore, the molecular rotational constant $B$ can be expressed as equation, [230]

$$B = \frac{h}{8\pi^2 I}$$

where $h$ is Planck’s constant and $I$ is moment of inertia. Thus, the rotational frequency $\nu$ can be determined by equation, [230]

$$\nu = \frac{h(J+1)}{4\pi^2 I}$$

where $J$ is the rotational quantum number and $J=0, 1, 2$ and so on. Thus, the ratio of their rotational frequencies is $\nu(\text{CH}_3\text{NH}_3^+) : \nu(\text{CH}_3\text{ND}_3^+) : \nu(\text{CD}_3\text{NH}_3^+) : \nu(\text{CD}_3\text{ND}_3^+) \approx 1 : 0.85 : 0.85 : 0.76$ with the assumption that they take on the same rotational quantum state.

### 6.6. Accelerated Moisture Aging Experiment Setup

The accelerated moisture aging experiment was carried out in a constructed two-beaker chamber system. A beaker was first reversely suspended in water, as contained inside a larger beaker. Large container beaker was enclosed by a glass cover with a piece of filter paper spaced between for avoiding condensation of moisture; container beaker was then placed on a hot plate with temperature set at 40 °C. After water inside the large beaker reached 40 °C, moisture content rose to 100%. At this point, thin film samples were placed into the chamber, on top of inverted beaker

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to initiate accelerated aging. The detailed schematic illustration of the moisture aging chamber is given in Figure 3-1-4.

6.7. Deposition of MASnI₃ Thin Films for Stability Measurements

Equimolar of SnI₂ and MAI were first dissolved in DMF under stirring to make 1 M solution. Maintained at 60 °C, the precursor solution was then spun-coated on cut, pre-cleaned microscope slides (1.5 cm * 1.5 cm) at 1000 rpm for 30 s. Wet films were then annealed on a hotplate at 100 °C for 10 min.

6.8. Static PL and TRPL

Lead-based perovskite thin films and single crystals were photoexcited at 405 nm or 450 nm with 40 nJ/cm² intensity via a 35-ps pulse width laser diode. In the case of tin(II)-based perovskite thin films, 705 nm excitation was utilized. PL photons were then collected with a lens and directed to a 300 mm focal length grating spectrograph outfitted with a thermoelectrically cooled charge coupled diode and avalanche photodiode with time-correlated single-photon counting electronics.

6.9. Preparation of FAPbCl₃ Nanostructures

PbCl₂ was first spun-coated on FTO substrates at 1000 rpm for 10 s, coated substrate was then quickly placed in 20-mL ethyl ether bath. After 5 min., PbCl₂ films were then placed into 10 mg/mL FACl or 10 mg/mL FACl & 1 mg/mL LiCl in 2-propanol solutions for growth of 24 hours to synthesize pristine FAPbCl₃ or LiCl:FAPbCl₃ nanorods, respectively. It is worth noting that such solution method can also lead to high-quality MAPbI₃ and MAPbBr₃ nanowires, nanocubes and nanoplates that were synthesized previously, as shown in Figures 6-9-1 and 6-9-2. The highly crystalline morphology of synthesized nanostructures indicated the robustness of applied solution method.
Figure 6-9-1. MAPbI$_3$ nanostructures grown with lead precursor in MAI/2-propanol solution.

(Continued on following page)
6.10. Fabrication and testing of LiCl:FAPbCl$_3$ and FAPbCl$_3$ UV photodetectors

As-formed LiCl:FAPbCl$_3$ perovskite nanostructures were deposited with a 60-nm gold layer with a thermal evaporator (Edward 306 A) to finish construction of the UV photodetector (schematic illustration shown in Figure 6-10-1). 365-nm UVL-4F UV lamp was utilized to generate photocurrents without magnitude oscillation, while UVGL-25 Multiband UV lamp with 254/365 nm wavelengths was used to generate photocurrents with damping magnitudes. Photocurrents were collected under chronoamperometry on a Gamry Reference 600 potentiostat under sample period of 0.001 s, with equilibration time of 5 s and no voltage bias. Potentiostatic electrochemical impedance spectroscopy was performed to acquire Nyquist plots on LiCl:FAPbCl$_3$ photodetector, with 10-s initial delay, 100000-Hz initial frequency, 0.001-Hz final frequency, 10 points/decade, 5-mV·rms AC voltage, zero DC voltage vs. open-circuit voltage.
Figure 6-10-1. Schematic illustration of LiCl:FAPbCl$_3$ nanorod photodetector device structure.
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APPENDIX A

REPRINT PERMISSION FOR PUBLISHED MATERIALS: J. GONG ET AL. (2018),
JOURNAL OF ENERGY CHEMISTRY, 27(4), 1017-1039, DOI:
Title: Cation engineering on lead iodide perovskites for stable and high-performance photovoltaic applications

Author: Yue Gong, Peijun Guo, Savannah E. Benjamin, P. Gregory Van Ratten, Richard D. Schaller, Tao Yu

Publication: Journal of Energy Chemistry
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APPENDIX B

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JOURNAL OF PHYSICAL CHEMISTRY LETTERS, 7(15), 2879-2887, DOI: 
10.1021/ACS.JPCLET.6B01199.
Electron–Rotor Interaction in Organic–Inorganic Lead Iodide Perovskites Discovered by Isotope Effects

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Date: Aug 1, 2016

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