Interface energetics and dynamics in organic-inorganic hybrid perovskites

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**INTERFACE ENERGETICS AND DYNAMICS
IN ORGANIC-INORGANIC HYBRID
PEROVSKITES**

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(B.Sc.(Hons.), NTU)

**A THESIS SUBMITTED
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
DEPARTMENT OF PHYSICS AND APPLIED PHYSICS
NANYANG TECHNOLOGICAL UNIVERSITY**

2018

To my family...

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Summary

Organic-inorganic lead halide perovskites have gained a lot of attention over the past six years as a desirable class of materials for various devices which has been shown to possess desirable properties such as long diffusion lengths, large carrier mobility, low trap states. At present, some important topics in this research have not been adequately addressed, like interface energetics, hot carrier dynamics and problems with UV degradation. This thesis is dedicated to address these issues. Firstly, the interface energetics of FAPbI₃-based perovskites with organic charge extraction layers showed apparent upward band bending, but its origin is unexpectedly due to presence of δ -FAPbI₃. This finding implicates solar cell operation as it causes inefficient extraction of photoexcited electrons to the PCBM. In the second part of the work, a successful homemade TR-2PPE system was set up, and preliminary studies on CsPbBr₃ single crystals found that hot carriers generated through carrier-carrier scattering ~ 1 eV above the conduction band edge possess long lifetimes ~ 3 ns under resonant excitation due to strong band-filling and long lifetimes of band edge carriers in single crystals which hinder hot carrier cooling. This observation in CsPbBr₃ may point towards using perovskite single crystals

to generate and extract hot carriers in solar cells. The last part of this work addresses the issue of UV instability of perovskites in MAPbI₃ through the addition of Hindered Amine Light Stabilisers (HALS) to suppress photodegradation by UV light through photo-oxidation and free radical formation of perovskite. A systematic study was performed by doping MAPbI₃ through antisolvent treatment with four representative HALS compounds with varying functional groups and molecular sizes to study their effects on film formation, morphology and resulting photostability enhancement under UV light. Surprisingly, doping with different HALS compounds provides varying photostability enhancements and may even result in more photodegradation in some cases due to the influence of functional group and size on surface morphology, crystallinity and surface coverage. Among the HALS compounds, the polymeric one gave the best photostability enhancement with reduction of photodegradation by 59.2%. This method would not only be potentially useful for solar cell applications, but also in optical spectroscopy that uses UV light like TR-2PPE.

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Introduction

In this chapter, an introduction to organic-inorganic lead halide perovskites and its importance in the search for sustainable energy shall be presented, followed by a brief outline of this thesis.

1.1 The need for sustainable energy

Modernisation has led to rapidly growing demands for energy consumption. At present, about 80% of global energy demands are provided by non-renewable sources, namely coal, oil and natural gas. It was estimated that oil and natural gas would be depleted by 2042, and the remaining coal would last until 2112[1]. In order to keep up with these energy demands, it is imperative that alternative, renewable sources of energy be established so that the sustainability of future generations is ensured. Amongst the sources of renewable energy sources, photovoltaic could be said to be the most efficient of all. It was estimated that present energy demands would be met covering a small 0.1% on the surface of Earth with photovoltaic devices which convert 10% of light into electricity[2]. This potential has led to the boom of solar cell research since sixty years back, which started out from

solar cells made of silicon. Along the way, solar cell research delved into other suitable materials[3] such as GaAs, CdTe, CIGS as well as alternative configurations like DSSC[2] and tandem cells[3].

Figure 1.1: NREL solar cell efficiency chart. Image adopted from [4], courtesy of the National Renewable Energy Laboratory, Golden, CO. downloaded on Apr 6, 2018.

1.2 Perovskite solar cells

Recently, organic-inorganic lead halide perovskites (hereafter termed perovskite) captured the attention of researchers for its potential to make efficient, economical photovoltaic devices. Research in this area started with the works of Kojima *et al.*[5] using methylammonium lead iodide (MAPbI_3) and methylammonium lead bromide (MAPbBr_3) to fabricate solar cells with the dye-sensitized solar cell configuration with PCE of 3.8%. Various improvements have been made over the years to the solar cell configuration. These included replacing the liquid electrolyte with spiro-OMeTAD [6], meso-super structured solar cell structure[7], dual-source evaporation of the perovskite layer [8], multi-cation and/or halide mixing of the perovskite[9–12], solvent engineering[13], and interface engineering[14], and deep defect control[15]. The most efficient cell is currently at 22.7% PCE[16] which is also shown in Figure 1.1. Other possibilities for perovskite solar cells include tandem[17] and potentially hot carrier solar cells[18]. The keen research interest in this material shows its potential to be a viable route towards clean energy using photovoltaics.

The following sections shall highlight some key material properties of perovskites contributing to good device performance.

1.3 The Perovskite Material

1.3.1 Crystal Structure

Figure 1.2: A generic perovskite crystal structure (Adapted from Ref. [19] with permission from *Springer Nature*).

Perovskite, originally termed to describe a structural class of compounds with same crystal structure as CaTiO_3 , was discovered by Gustav Rose in Russia and named after the mineralogist Lev Perovski in the 18th century. This class of compounds has the general chemical formula ABX_3 , where the monovalent A^+ cation sits within the cuboctahedra cage formed by B^{2+} and X^- ions $[\text{BX}_6]^{4-}$ corner-sharing octahedra network, as illustrated in Figure 1.2. Despite them being discovered as far back in 1980's, methylammonium lead iodide ($\text{A}=\text{MA}^+$ (chemical formula: CH_3NH_3^+), $\text{B}=\text{Pb}^{2+}$, $\text{X}=\text{I}^-$) is the first of such organic-inorganic hybrid perovskite to gain recent interest as a prospective solar cell material. An advantage in this class of compound lies in its versatility, as seen from substitution of the A-site cation ($\text{A}=\text{MA}^+$, FA^+ (chemical formula: $\text{CH}(\text{NH}_2)_2^+$) or GA^+ (chemical formula: $\text{C}(\text{NH}_2)_3^+$)), B-site cation ($\text{B}=\text{Pb}^{2+}$, Sn^{2+} , Ge^{2+}), or halide ($\text{X}=\text{I}^-$, Br^- or Cl^-). However, not all combinations of ions give structurally stable compounds, and

structural distortions can cause the compound to form different crystal structures. The stability and distortion for a compound is determined by Goldschmidt tolerance factor[20], which is a dimensionless ratio between the ionic radii in perovskite:

$$t = \frac{r_A + r_0}{\sqrt{2}(r_B + r_0)}, \quad (1.1)$$

where r_A , r_B and r_0 denote the ionic radii of the A^+ , B^{2+} and X^- respectively.

The relative ionic sizes of the ions in perovskite determines the perovskite crystal structure. An ideal perovskite has a cubic structure when all ions have the same ionic radii. If the A-site cation is either too large or too small, the surrounding octahedra network will tend to tilt or rotate to compensate for the size difference[21]. This distortion from the cubic structure due to octahedra tilting and rotation are also described as different structural phases of the perovskite[22]. Perovskites can also undergo various phase transitions with temperature[23] and pressure[24]. For the case of hybrid perovskites, there is an interplay between the cation orientational movement and the structural phase due to hydrogen bonding interaction between the organic cation and surrounding iodide[25]. Such phase transitions, which affect the Pb—I—Pb bond angles[26, 27] have strong influences on their optical[26] and electronic properties[28], which should be taken into consideration for device specifications.

1.3.2 Summary of Physical Properties

Since recent interest in the perovskite material, researchers sought to uncover the properties which attributed to its success as a solar cell material. Some of the remarkable properties in solution-processed films include long-range balanced electron and hole diffusion lengths[29, 30] in orders of 100 nm, large carrier mobilities[31] of at least $8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and low bulk trap densities[32] of $5 \times 10^{-16} \text{ cm}^{-3}$. These are superior, or at least comparable to values of $<20 \text{ nm}$ [33], $\sim 5 \text{ cm}^2$

Table 1.1. Key physical properties of MAPbI₃.

Physical Property	Values
Phase transition temperatures	333 K (cubic to tetragonal)[23], ~150 K (tetragonal to orthorhombic)[23]
Band gap (E_g)	1.55 eV[23]
Absorption coefficient (α)	$>3 \times 10^4 \text{ cm}^{-1}$ [40]
Carrier diffusion length (L_D)	$>100 \text{ nm}$ [29, 30]
Exciton binding energy (E_b)	$\sim 75 \text{ meV}$ [41]
Trap density	$\sim 5 \times 10^{16}$ (bulk), $\sim 1.6 \times 10^{17}$ (surface)[32]

$\text{V}^{-1} \text{ s}^{-1}$ [34], and $10^{-15} - 10^{-18} \text{ cm}^{-3}$ [35] in organic materials for carrier diffusion lengths, mobilities and trap densities respectively. These remarkable properties were unprecedented at the time, especially for solution-processed materials where it would be expected that large amounts of defects present in these amorphous films should not give rise to the good carrier properties in perovskite. Over time, other novel properties are being unveiled such as slow hot carrier cooling[18], strong optical nonlinearity[36], spin-polarised transport[37], white light generation[38] and ferroelectricity[39] have been reported for this class of compounds. Even though much has been uncovered in recent years, there is still a need for deep, insightful studies to reconcile material, structural and optoelectronic properties to further research into this material. Despite the massive developments happening in this field, methylammonium lead iodide (MAPbI₃) being the first of the compounds perovskite solar cells are made from, is known to be the archetypal compound in the research community. Hence, novel scientific discoveries would often use it either as a starting point or as a basis of comparison to which some of the key physical properties of MAPbI₃ are summarised in Table 1.1.

1.3.3 Material Versatility

Using MAPbI₃ as a solar cell absorber has a few shortcomings, such as material instability[42] and slightly large band gap[43] for sunlight absorption. The phase transition temperature between tetragonal and cubic phase is also near room temperature[23] which could pose a problem for use in hot places where sunlight is abundant. Although the alternative FAPbI₃ can overcome these issues, it is also highly susceptible to degradation to form the yellow δ -phase[44] which is not suitable for solar light absorption. It was found that by mixing the compositions of the ions in perovskite, the stability of the devices was improved[9–12]. The mixing of composition can be at either the A, B or X sites of the crystal structure was shown to be a great advantage for perovskites in terms of tuning its optical and electronic properties.

1.4 Overview of Thesis

Despite the attractiveness of using perovskites for photovoltaic applications, there are still major issues hindering its commercialisation, namely general instability with light, oxygen, heat and/or moisture[45, 46], and the J - V hysteresis[47, 48] effect during cell characterisation, a lot of which can stem from the surface and interfaces of perovskites which has not been thoroughly studied. There are research gaps in surface and interface studies of perovskite as well which shall be discussed further in the next chapter. Despite the stellar performance of solar cells obtained in laboratories, practical realisation of highly efficient devices still has some way to go with these obstacles against commercialisation. This thesis is outlined as follows:

- Chapter 2: Background knowledge of surface and interface phenomena, research developments in hybrid lead perovskites

- Chapter 3: Experimental methods to interrogate said surfaces and interfaces in hybrid lead perovskites
- Chapter 4: Band bending in formamidinium lead iodide and its derivatives at organic charge extraction interfaces
- Chapter 5: Implementation of TR-2PPE setup and preliminary results on APbBr_3 ($\text{A}=\text{Cs}^+$, MA^+ or MA^+) single crystals
- Chapter 6: Improvements in UV stability of MAPbI_3 thin films using Hindered Amine Light Stabilisers (HALS) additives
- Chapter 7: Conclusions of works performed in this thesis
- Chapter 8: Future works arising from this thesis

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Surface and Interface Properties of Perovskites

With the development of perovskite solar cells, increasing attention is placed on the study of surfaces and interfaces of perovskite with its charge extraction layers, as they are fundamentally crucial towards making more efficient devices. Predictions of device performance, such as charge extraction efficiency in solar cells are determined by the energy level alignment at the interfaces of perovskite which is influenced by phenomena such as band bending and interface dipole formation. In this chapter, background knowledge about these interface phenomena will be covered, followed by a review in the research of electronic structure and interface energetics of perovskite.

2.1 Common Phenomena in Surfaces and Interfaces

Surfaces are created as a result of termination of the bulk crystal[1]. Since this termination results in fewer neighbours for the surface atoms in comparison with

those at the bulk, some chemical bonds which constitute the bulk crystal structure are broken. This results in marked differences in the surface electronic structure compared to the bulk, when the crystal surface commonly undergoes relaxation and reconstruction in order to minimise surface potential. Even if the positions of surface atoms remain at its bulk-like position, new electronic levels in its electronic structure still emerges due to changes in chemical bonding. This makes comprehensive study of surfaces and interfaces crucial as these newly formed surface states can have strong influence on the functioning of actual devices.

Broadly speaking, there are two types of surface states, classified between intrinsic and extrinsic surface states:

Intrinsic surface states come from clean, ideal surfaces which create dangling bonds and back bond states having planar symmetry. These states deviate from the bulk bands as the splitting and shifts of their atomic levels are smaller for such surface atoms. Typically, electronic levels created from dangling bonds experience greater perturbations from the bulk, compared to those that originate from back bond states. Since these are deviations from the bulk electronic bands, surface states derived from conduction (valence) bands are electronically neutral when they are empty (occupied), and becomes negatively (positively) charged when they are charged (ionised). Therefore surface states derived from conductor (valence) bands are also called acceptor (donor) type surface states.

Extrinsic surface states, on the other hand, are the result of defects and imperfections at the crystal surface. Atomic and ionic vacancies on the surface are some types of surfaces which possess extrinsic defects. Ionic vacancies like O^{2-} ions on the atomic surface of ZnO creates a positively charged surface with Zn^{2+} ions which acts as electron traps[2], thus creating extrinsic surface states with acceptor-like behaviour. In the case of GaAs surface, the extrinsic surface states caused by As atomic vacancies also exhibit acceptor-like behaviour. Other perturbations to the

ideal surface, such as line defects and adsorbates also create extrinsic surface states, the former due to differences in dangling bond characteristics of step atoms while the latter due to changes in chemical bonds of surface atoms with the adsorbate atoms.

The formation of a semiconductor interface can result in the formation of band bending and interface dipoles as described below:

2.1.1 Band Bending

The presence of charged surface or interface states results in screening from bulk carriers to maintain a charge neutral state. The screening depth at which this occurs depends on the carrier concentration of the material. Typically, charged surfaces of metals are screened within regions of atomic length due to high electron densities ($n_e \sim 10^{22}\text{cm}^{-3}$). In semiconductors however, surface charges are screened in orders of $100\text{\AA}$ due to lower carrier concentrations available ($n_e \sim 10^{17}\text{cm}^{-3}$). This long screening length results in bending of electronic bands in the space charge region to neutralise charged surface states.

Assuming an infinite metal/n-type semiconductor interface with Schottky approximation, the amount of band bending $V_{\text{BB}}(z)$ can be obtained based on the material dielectric constant ϵ_r , density of bulk donors N_d , and the depletion layer thickness D as follows:

$$V_{\text{BB}}(z) = -\frac{eN_d}{2\epsilon_r\epsilon_0}(z - D)^2, \quad (2.1)$$

for $0 \leq z \leq D$.

Band bending of electronic levels plays an important role in practical devices, as it affects device functionality such as charge extraction in photovoltaics, and charge recombination in light emitting diodes. It can significantly affect the charge dynamical processes occurring at the interface despite having appropriate band

offset between the conduction and valence levels across the heterojunction. Therefore, band bending has to be taken into account especially when the direction of bending does not favour the intended process across the heterojunction. Surface sensitive techniques like photoelectron spectroscopy (Section 3.1) are often used to elucidate the presence of band bending while complementary techniques like time-resolved photoluminescence or transient absorption spectroscopy (TAS) are used to assess its carrier dynamics.

2.1.2 Interface Dipole

The formation of interfaces typically entails one or more of the following processes: (a) interface charge transfer, (b) chemical reactions, or (c) electronic charge re-distributions which give rise to interface dipoles. Essentially, the formation of interface dipoles results in abrupt shift of vacuum level across the interface with its magnitude proportional to the dipole strength.

2.1.3 Interface States

Similar to the formation of surface states as elaborated in 2.1, a distinguishing class of interface states can also occur when additional chemical interactions occur at the interface between both constituents of the heterojunction during its formation, resulting in extraneous features of DOS in the UPS spectrum, which typically happens when the two materials forming the interface are reactive in nature.

2.2 Electronic Structure and Interface Energetics in Perovskites

The first paper elucidating the electronic structures of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$ perovskites using UPS was back in 2003 by Umebayashi *et al.*[3] and with a combination of density-functional theory found that the valence band maximum (VBM) was contributed by the σ -antibonding states of Pb 6s and I 5p, while that of conduction band minimum by σ -antibonding states of Pb 6p and I 5s. Since then, it has been commonly understood that the molecular orbitals of the organic cations which lie in deeper levels do not contribute much towards the frontier bands of the perovskite material. The effective masses of electrons and holes in $\text{CH}_3\text{NH}_3\text{PbI}_3$ were calculated to be much lighter than electron mass, of $0.23 m_0$ and $0.29 m_0$ respectively[4]. Therefore, due to this wide dispersion of the frontier bands, determining VBM and CBM positions of perovskites has been refined to take the onset from logarithmic intensity scale[5, 6]. This shall also be elaborated further in section 3.1.2.

A unique feature of perovskite is its tunability of optoelectronic properties by substitution or mixing either A, B or X ions in the perovskite composition[7–10]. Of all, the effect of varying the composition of B^{2+} or X^- cation has significant effect due to their contributions to the VBM and CBM described in the preceding section. These changes are reflected in UPS as well and several studies to investigate the effect of ionic substitution has been reported. Replacing the iodide with either bromide or chloride was shown to increase its work function (ϕ) and ionisation potential (IP), from $\phi = 4.67$ eV, IP=5.96 eV to $\phi = 5.12$ eV, IP=6.62 eV and $\phi = 4.93$ eV, IP=7.04 eV for MAPbBr_3 and MAPbCl_3 respectively[11]. Although halide substitution causes a band gap increase from $\text{I} \rightarrow \text{Br} \rightarrow \text{Cl}$ measured using optical measurements, changes in band positions from this series could be determined

using a combination of UPS and IPES to determine the effect on the frontier bands. This same study found that varying the halide substitution predominantly shifts the VBM to deeper level for the I $\rightarrow$ Br substitution up to mixed Br-Cl composition. This was correlated with calculations which predicted similar trends arising from changes in np valence orbitals of the halides[12].

Substitution of the B-cation from Pb^{2+} has some practical advantages such as reducing the toxicity from Pb. Some of these candidates which can replace Pb^{2+} include Sn^{2+} and Ge^{2+} . At present, the effect of Pb $\rightarrow$ Sn substitution has been the most established. The substitution of B-cation causes a shift in the CBM as observed in a study which found smaller optical band gap from 1.55 eV to 1.30 eV and largely unchanged IP from 5.45 eV to 5.47 eV with substitution from a pure Pb to pure Sn of MABl_3 [13]. However, anomalous band gap bowing occurs when there is a mixture of Pb^{2+} and Sn^{2+} , where the band gap of the perovskite is the lowest at 1.17 eV in $\text{MASn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ and $\text{MASn}_{0.75}\text{Pb}_{0.25}\text{I}_3$ [13]. For the mixture, both VBM and CBM changes due to the the competition between spin-orbit coupling and lattice distortion[14]. This anomalous band gap behaviour also occurs even if the A-cation is different, as reported in the case of $\text{FA}_{1-x}\text{Cs}_x\text{Sn}_y\text{Pb}_{1-y}\text{I}_3$ in various x [10].

An interesting phenomenon regarding the electronic properties of MAPbI_3 is that the band positions of MAPbI_3 could be tuned to either n-type or p-type depending on the underlying substrate the perovskite was deposited[15]. The Fermi level of MAPbI_3 fabricated onto a p-type substrate shifts closer to the VBM, while the Fermi level of MAPbI_3 fabricated on a n-type substrate causes it to shift away from VBM as shown in Figure 2.1. This is possible due to the relatively low intrinsic carrier density in MAPbI_3 [16], resulting in depletion region in orders of μm . The consequence of a long depletion region shall also be discussed in the results of Chapter 4. Thus, the electronic properties of MAPbI_3 can be tailored

for device specific applications.

Figure 2.1: Energy level diagrams showing the variation of electronic levels of MAPbI₃ deposited on various substrates as measured by UPS (Ref. [15] - Adapted by permission of the *PCCP Owner Societies*).

The energy level alignment of perovskite interfaces is an important indication of device performance, as efficient charge transport processes is achieved with proper energetic alignment. Proper tuning of interface energetics is desirable to reduce unwanted back transfer processes, or unnecessary V_{oc} losses in solar cells. These are commonly done by measuring the electronic structure as the interface is being build up through the sequential evaporation of an overlayer. The first of such studies investigated the effects of halide substitution of the perovskites, namely MAPbI₃, MAPbI_{3-x}Cl_x and MAPbBr₃ towards their interfaces with the organic hole transporting layer (HTL) spiro-OMeTAD[5]. The band alignment of these

interfaces shown in Figure 2.2 showed no hole extraction barrier across the interface due to the HOMO level of spiro-OMeTAD being closer to the Fermi level compared to that of the perovskites. However, large offsets between the perovskites' VBM and HOMO of spiro-OMeTAD were observed, the greatest being with the interface of MAPbBr₃ of 0.8 eV resulting in greatest V_{oc} loss in the corresponding device. The 0.4 eV and 0.3 eV offsets for MAPbI₃ and MAPbI_{3-x}Cl_x respectively results in less severe losses in V_{oc} in their devices. The downward level bending of spiro-OMeTAD away from interfaces of 0.1 eV to 0.3 eV also create hole traps which can prevent hinder hole extraction across spiro-OMeTAD.

Figure 2.2: Energy level alignment between spiro-OMeTAD and MAPbX (X=I₃, I_{3-x}Cl_x, Br₃) films deposited on TiO₂. (Adapted from Ref. [5] with permission from Royal Society of Chemistry).

Another systematic study was conducted[17] by Wang *et al.* to investigate how energy level alignment is affected from various types of organic HTL, namely NPB, spiro-OMeTAD, F₁₆CuPc, HAT-CN and MoO₃ with MAPbIBr₂ which is also shown in Figure 2.3. The various types of interface formation mechanisms were

demonstrated with these interfaces. Both MAPbIBr₂/NPB and MAPbIBr₂/spiro-OMcTAD interfaces are nearly vacuum aligned, and form staggered-gap heterojunctions, which is favourable for hole extraction from the perovskite, however large valence offsets are also observed here which has to be reduced using HTL with deeper HOMO levels in order to realise good V_{oc} in solar cells. The MAPbIBr₂/F₁₆CuPc interface demonstrates one which is not vacuum aligned due to 0.7 eV difference in work function, and forms a straddling-gap heterojunction. Despite smaller valence offset of 0.4 eV, there is no electron barrier hence this interface is not suitable for hole transport. In the case of MAPbIBr₂/HAT-CN interface, there is interface dipole formation from an abrupt shift of vacuum level with no shift in either HOMO or XPS core levels. The resulting energy level alignment creates a hole barrier which does not serve as a hole transport layer. Lastly the MAPbIBr₂/MoO₃ interface creates a reverse straddling-gap heterojunction in which the band gap of MoO₃ completely covers that of MAPbIBr₂. This creates a recombination region at the MAPbIBr₂ side as neither electron nor holes could be extracted across the interface. However there are interface states present that are caused by chemical reactions due to reduction of Mo⁶⁺ to Mo⁵⁺ from oxygen vacancies. These interface states could provide an alternative route for hole extraction. This comprehensive study details the possible forms of heterojunctions at perovskite interfaces for hole transfer.

Figure 2.3: Interface energy level alignment of a) MAPbI₃/Spiro-OMeTAD, b) MAPbI₃/NPB, c) MAPbI₃/F₁₆CuPc, d) MAPbI₃/HAT-CN, and e) MAPbI₃/MoO₃ (Adapted from Ref. [17] with permission from *John Wiley & Sons, Inc.*).

Other studies were also conducted to investigate various perovskite interfaces with HTL. Chen *et al.* studied the MAPbI₃/CuPc interface[18] which demonstrated its suitability for hole transfer with staggered-gap energetic alignment. However, the presence of a 0.3 eV downward level bending away from the interface form hole traps which can affect the subsequent transport of holes across CuPc. Therefore, it is desirable to look for matching HTL which has an upward level bending away from the interface to facilitate hole extraction. Currently, studies

done on MAPbI₃/pentacene[19] and MAPbI₃/single-walled carbon nanotube (SW-CNT)[20] interfaces fulfil this criterion. For the former, the presence of ~ 0.2 eV upward level bending away from the interface and 0.1 eV interface dipole would be good for hole extraction away from the interface. However, the large valence offset of ~ 0.7 eV would result in great energetic losses for the perovskite solar cell using pentacene as HTL. In the case of MAPbI₃/SWCNT interface, an interface dipole is formed due to electron donation from MA compound which induces upward energy level bending of over 0.5 eV in SWCNT away from the interface as the interface SWCNT region is now n-type. Detailed analysis of the VBM and HOMO onsets gives an inferred value of valence offset of ~ 0.1 eV which gives small losses of V_{OC} in devices.

Figure 2.4: Energy level diagram of sNiO_x/perovskite interfaced with C₆₀ ETL. (Adapted from Ref. [21] with permission from John Wiley & Sons, Inc.).

The interface between the perovskite and the electron transport layer (ETL) is also an important area of study to optimise the extraction of photoexcited electrons. Independent studies have been performed on various organic and inorganic

ETL. For organic ETL, a few studies had been done for the MAPbI₃/C₆₀ interface. Schulz *et al.* found a small interface dipole of ~ 0.1 eV as shown in Figure 2.4, and that the LUMO of C₆₀ was aligned closely to the VBM of MAPbI₃, which does not create an electron barrier and at the same time has a small loss in potential of 0.1 eV which is good for the V_{OC} of the solar cell[21]. Similar interface study conducted by Wang *et al.* however showed a larger interface dipole of 0.5 eV and significant level bending in the C₆₀ layer[22]. The differences in the observations is likely due to variations in sample preparation of MAPbI₃ which provides significantly different values of work functions and VBM positions. Lo *et al.* performed a study on evaporated MAPbI_{3-x}Cl_x/C₆₀ and solution-processed MAPbI₃/PCBM interfaces and found that both form nested $n-n$ junctions with the band gap of perovskites within that of the fullerenes[23]. The wide disparity of observations compels the need for more well-controlled, systematic studies in order to conclusively decipher the characteristics of perovskite-fullerene interfaces. One such recent study was performed by Shin *et al.*[24] to look at the effect of various MAI concentration in two-step solution-processed films on its energy level alignment with C₆₀ to address the issue of hysteresis in perovskite solar cells. Three MAI concentration at 10 mg ml⁻¹, 25 mg ml⁻¹ and 35 mg ml⁻¹ were tested, whereby devices using 25 mg ml⁻¹ gave the best solar cell performance. In all the three cases, the energy level alignment shows that the CBM of the perovskites are above the LUMO level of C₆₀, by 0.25 eV and 0.20 eV in the 10 mg ml⁻¹ and 35 mg ml⁻¹ case respectively. There is no conduction band offset for the case of 25 mg ml⁻¹, which may result in hysteresis-free devices.

Research on the energy level alignment of perovskite with inorganic ETL has also been sporadic. Lindblad *et al.* used hard X-rays to interrogate the valence band states of the buried mesoporous TiO₂ below the MAPbI₃ layer. The energy level alignment was found to facilitate electron transfer due to the staggered-gap

alignment but with conduction offset of 0.4 eV, and showed no difference between one-step and two-step solution processing methods. Another work conducted with MAPbI₃/ZnO revealed similar staggered-gap alignment[25] showed that the interface facilitates electron extraction from MAPbI₃. Still, the presence of significant conduction offsets compels the search for suitable inorganic ETL to minimise potential losses in solar cells. A study then found that energy level alignment of perovskite with SnO₂ is more favourable than TiO₂ for solar cells due to the deeper conduction band of SnO₂ for both MAPbI₃ and the double cation perovskite (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}, in which the solar cells produced over 18%, high V_{OC} and good hysteresis characteristics[26]. The FAPbI₃/ZnO interface has also been reported, which is not favourable for electron extraction as the band gap of FAPbI₃ is nested within that of ZnO[27].

Despite the relatively long period of time of perovskite solar cell research, studies on its surfaces and interfaces is still quite lacking. This is mainly due to typical solution-processing nature of perovskite films, whose surfaces are sensitive to variations in stoichiometry, morphologies, sample history, amongst others. The surfaces of these solution-processed films are typically passivated with the exposed gaseous environments which also obscures studying its fundamental properties. It would be beneficial to the community to standardise certain guidelines, like eliminating exposure to ambient, on the treatment of solution-processed samples for interface studies. More studies should be performed using thermally evaporated samples for controllable, stringent studies of its fundamental surface and interface properties to advance this field of study.

2.3 Summary

Research over the recent years has provided an appreciable level of understanding of the material properties which makes perovskite so useful in photovoltaics. However,

existing knowledge gap on the surface and interface properties of this material has to be answered in order to drive the field forward. Interface phenomena, such as band bending and interface dipoles have important implications on subsequent carrier dynamics in devices, like charge extraction in the case of solar cells.

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Experimental Methods

The experimental methods used for the work in this thesis are outlined in this chapter, namedly photoelectron spectroscopy and time-resolved two-photon photoemission. These techniques shall be described in detail throughout the following sections.

3.1 Photoelectron Spectroscopy

Photoelectron spectroscopy is used to characterize the electronic energy levels of a material using the photoelectric effect. This effect was discovered by Hertz in 1887 and subsequently described by Einstein in 1905. This process happens when incident photons having energy larger than sample work function liberate photoelectrons with specific kinetic energy based on energy conservation, and is represented by the following equation

$$h\nu + A \rightarrow A^+ + e^-, \quad (3.1)$$

where $h\nu$ is the energy of the excitation photon. The above equation implies that the photon energy required should be sufficient to free the bound electrons.

The generated photoelectrons depend on the electronic binding energy and photon energy described quantitatively for solid samples as follows

$$E_k = h\nu - (\phi_s + E_b), \quad (3.2)$$

where E_k denotes the kinetic energy of the photoelectrons, ϕ_s the sample work function and E_b the binding energy referenced to Fermi level E_F . The convention adopted here E_b is positive for bound electronic states below E_F , which is the convention used in XPS.

Figure 3.1: Schematic showing the ejection of photoelectron from core or valence level and its corresponding spectrum. (Adapted from Ref. [1])

From equation 3.2, we see that E_k varies with the energetic position of the bound electron E_b for constant photon energy, hence an atomic level in the system corresponds to a photoelectron signature detected by the electron analyser. In photoelectron spectroscopic measurement, an energy distribution curve (EDC) of electron count with a distribution of various E_k under monochromatic incident light excitation provides information on the electronic binding energy within the

material, the process depicted in Figure 3.1. This is the definition of photoelectron spectroscopy and was formally developed by the group of Kai Siegbahn in the 1960's. Since electrons are detected in this measurement, the experiment is done in ultra high vacuum to avoid electron collision with atmospheric particles. An attractive feature of photoelectron spectroscopy is that the photoelectron counts against energy interval gives a replica of the density of states of the material, providing important insights into the electronic structure of material surfaces.

Figure 3.2: A typical XPS wide scan spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$.

Figure 3.2 shows a sample photoelectron spectrum of photoelectron counts against binding energy. For samples with multiple elements, the spectrum features roughly summed photoelectron contributions from each elements. Quantitative analysis, like atomic ratios between elements or chemical state, is done with peak area while chemical state is performed with binding energy peak position. Core level analysis is usually performed with X-ray excitation, referred to as XPS. The valence electrons for a semiconductor participate in chemical bonding, and hence can be delocalised among several atoms to determine the frontier energy levels important for optoelectronic applications. Specifically, they provide information on bonding, surface states and density of states. However, the complexity posed

by contributions from various elements and atoms may make the frontier states harder to interpret. UPS is used to characterise valence bands and energy levels, due to better energy and momentum resolution of ultraviolet light.

Binding energies are commonly referenced to the Fermi level for solid films, and vacuum level for liquids and gases. In other words, the zero binding energy for solid films for our case is the Fermi level. The zero binding energy can be calibrated directly by measuring the Fermi level of metals.

3.1.1 X-ray Photoelectron Spectroscopy

XPS, also known as electron spectroscopy for chemical analysis (ESCA), is commonly used to analyse surface chemical properties. As its name implies, soft X-ray emission sources such as Al K_α (1486.6 eV) or Mg K_α (1253.6 eV) line are commonly used as excitation sources for the core level electrons. Phenomenon occurring in XPS experiments are elaborated in the following sections.

The Photoemission Process

Figure 3.3: Photoelectron spectroscopy as a three-step model.

In photoelectron spectroscopy, the three-step model[2] is commonly adopted to describe the photoemission process. Photoionisation takes place in the first step to generate photoelectrons, followed by its travel to the surface and finally escaping into the vacuum. A schematic of the steps is shown in Figure 3.3. It can be seen that during propagation to the crystal surface, the photoelectron can undergo inelastic scattering which loses information on its original binding energy state providing a background intensity. Despite the less rigorous approach to the photoemission process than considering all three steps into one, the simplicity and decent approximation derived from the three-step model justifies its use in common understanding of the photoemission process.

The photoemission lines described above originate from the core or valence levels from which the photoelectrons are excited from, giving an ionised atom at

the ground state. However, other processes can be present which contribute to the spectra. One of which happens when the original photoelectron loses energy during the propagation stage by exciting a valence electron, known as the shake-up process. The resulting ion is in an excited state giving an additional photoelectric line at higher binding energies with the main line. In the shake-off process, the photoelectron loses energy to a valence electron by removing it from the atom. Likewise, it shows up as an additional peak at the higher binding energy side of the main photoelectric line.

Figure 3.4: The various secondary process involving an ionised photohole state: (a) original photohole state; (b) the generation of an Auger electron; (c) generation of an Auger photon. (Adapted from Ref. [1])

Auger electrons or photons can be emitted when electrons from upper energy state relax to fill original core photoholes created from the photoemission process. Since the kinetic energy of the Auger electron is the difference between the initial photohole state and the doubly ionised ionic state, it is independent of the excitation photon energy. These Auger processes are depicted in Figure 3.4.

The ionised core photohole has a finite lifetime as it eventually relaxes by combining with another electron. Hence the associated energy uncertainty shows up as a linewidth in the photoemission peak. This intrinsic linewidth takes on a

Lorentzian lineshape. However, due to instrumental contributions giving rise to a Gaussian broadening, experimentally measured photoelectron lines often takes on a Voigt lineshape.

Final States in Photoelectron Spectroscopy

The photoemission process produces a final state that is one electron short compared to that of the initial state. Hence, photoelectron spectroscopy experiments measure energies of the final state. The initial state energies can only be calculated theoretically. The final state energies are also known as hole state energies, which also encompass many-body effects. Measurements of final-state energies agrees well with the single-electron band structure calculations where there is virtually perfect screening of the photo-hole, like in the case of valence states in metals.

Considering final-state effects in photoelectron spectroscopy, an exact definition of binding energy can be restated as the following:

$$E_b = E_f^{N-1} - E_i^N \quad (3.3)$$

where E_f^{N-1} is total energies of state with $(N - 1)$ electrons, while E_i^N is that having N electrons. However, since total energies are difficult to calculate, they are estimated through approximations such as Koopmans' approximation. Koopmans' approximation neglects relaxation energies by assuming that other orbitals remain unperturbed in the final photohole state. Another useful approximation to approximate core-level binding energies models the removal of a core electron by adding a proton to the nucleus is known as the equivalent-core, or $(Z + 1)$ approximation.

Spin-orbit Coupling

If the originating photoelectron comes from an orbital with non-zero angular momentum, the unpaired spin from the photoemission process can couple with these

Table 3.1. Spin orbit coupling j -states and corresponding ratios for the orbitals with non-zero angular momentum.

orbital	j -values	Intensity ratio
p	1/2, 3/2	1:2
d	3/2, 5/2	2:3
f	5/2, 7/2	3:4

orbitals to give total angular momentum $j = l \pm s$ having different energies at the different j states. This is known as the spin-orbit interaction. Therefore, the photoemission spectra shows splitting of the p , d and f peaks, with intensity ratios proportional to the degeneracy of the particular j -state, which is summarized in Table 3.1. Because the amount of spin orbit splitting of core electrons for a single element is unique and independent of chemical environment, the spin orbit splitting is useful to identify and differentiate the different elements in the material.

Chemical Shift

Electronic levels in the system are affected when atoms come together to form the bulk which mainly occur at frontier orbitals through the formation of either valence/conduction band for inorganic semiconductors or HOMO/LUMO levels for organic materials. The core electronic levels remain much less perturbed but are still affected by surrounding atoms. Depending on the nature of surrounding atoms, different species of the same element have slightly different binding energies. For example, the C 1s elemental spectra in a triple cation perovskite in Figure 3.5 shows three distinct peaks at 285.8, 289.0 and 287.3 eV which correspond to carbon atoms of CH_3NH_3^+ , $\text{CH}(\text{NH}_2)_2^+$ and surface contaminants respectively. These chemical shifts are useful for the analysis of various species present in the

material.

Figure 3.5: XPS elemental spectra of the C 1s peaks in triple cation perovskite.

3.1.2 Ultraviolet Photoelectron Spectroscopy

Ultraviolet photoelectron spectroscopy (UPS) is commonly used to probe electronic density of states at the valence levels of a material which provides the position of the VBM. It works on the same principle with XPS, and complements XPS to probe the valence levels of the material system. It is typically performed using He-I emission line having 21.2 eV photon energy.

Valence Band Maximum

UPS provides direct information on valence electronic structure and work function referenced at Fermi level. Determination of valence band maximum (VBM) or highest occupied molecular orbitals (HOMO) is usually done via linear extrapolation of the slope at the feature closest to the Fermi level which is illustrated in Figure 3.6. However, some care should be taken in its data interpretation, in cases like the VBM of perovskite. A clear difference is observed from a single set of data when extrapolation is performed between linear (1.61 eV) and logarithmic (1.42 eV) intensity axis shown in Figure 3.7. This is likely due to the fact that highly dispersive valence states^[3] of perovskite provide small contributions to the density of states which can be only be observed significantly with the logarithmic intensity scale.

Figure 3.6: VBM of FAPbI₃ determined from linear intensity scale.

Figure 3.7: VBM of FAPbI₃ determined extrapolated from exponential intensity scale.

Work Function

The work function can be determined using the secondary electron cutoff (SECO) feature at the high binding energy side of the spectrum under a negative sample bias with respect to the analyser. This applied bias increases the kinetic energy of

the photoelectrons which makes the SECO visible when the sample work function is smaller than that of the analyser. The work function can then be determined using the following equations:

$$\phi_s = h\nu - BE_{SECO} \quad (3.4)$$

$$\phi_s = \phi_a + KE_{onset} + U \quad (3.5)$$

in binding energy scale and kinetic energy scale respectively, where BE_{SECO} denotes the binding energy position of SECO and KE_{onset} denotes the kinetic energy position of SECO under applied bias U with respect to analyser, which is negative.

3.1.3 Ultra-high Vacuum System

Photoelectron spectroscopic measurements are conducted under ultra high vacuum (UHV) conditions of 1×10^{-9} torr which ensures that photoelectrons propagate to the electron analyser unimpeded. The UHV pressure is maintained using turbomolecular and ion pumps. Standard features of the UHV system include sample bias, resistive heating and Ar^+ sputtering. Adjacent evaporation chambers were installed for evaporation of either organic molecules or perovskite in-situ to perform interface studies. A schematic of the UHV system is shown in Figure 3.8.

Figure 3.8: Schematic of UHV system used for this work.

Photoelectrons are collected at a hemispherical electron analyser (*Omicron EA-125*), consisting of electrostatic lens and two concentric hemispheres. The electrostatic lens adjusts the focus and retarding potential R of the electrons before they reach the space between the concentric hemispheres. After passing through the lens, photoelectrons enter the concentric hemispheres which only allow electrons with the appropriate pass energy E_p through to the channeltron. Sweeping mode of the analyser can be set at either constant analyser energy (CAE) or constant retard ratio (CRR) mode. The former varies R while keeping E_p constant, and conversely for the latter. CAE mode is used throughout the experiments in this thesis. A set of pulse counting electronics converts the photoelectrons at the detector to be read at the computer software.

3.2 Time-Resolved Two-Photon Photoemission

TR-2PPE being a pump-probe photoemission technique, is used to probe and study electron dynamics in image potential states (IPS), charge transfer excitons, or other excited states at a material's surface. As its name implies, the photoemission process occurs from the action of two photons, with intensity dependence $\propto I_{pu}I_{pr}$. A pump photon excites the electron from an occupied ground state to an unoccupied or quasiparticle state and then is ejected into a vacuum state by the probe photon before it relaxes. This two-quantum process, as an incoherent sequential process, directly probes unoccupied state and the kinetic energy of the resulting photoelectron is directly proportional to the probe photon energy $h\nu_{pr}$. A coherent interference process also occurs simultaneously, where the two photons directly eject an electron from an occupied ground state to a vacuum state without transitions to any real intermediate state. This provides information about the occupied energy states in the system and the kinetic energy of ejected photoelectrons is proportional to the sum of pump and probe energies ($h\nu_{pu} + h\nu_{pr}$). A schematic of these two processes occurring in TR-2PPE experiments is shown in Figure 3.9. Temporal information of unoccupied or quasiparticle states is achieved by varying the time delay between the pump and probe pulses using a motorised micro delay stage similar to those used in conventional pump-probe techniques. Typical pump-probe techniques like TAS measure the pump-induced change of probe transmittance, therefore shows the presence of a transition from a reference state. The transition selective nature of pump-probe spectroscopy is illustrated in Figure 3.10. The state selective nature of this technique is complementary to optical pump-probe spectroscopy as it can definitively confirm the position of the state origin of electronic transitions. An overview of the principles and experimental details shall be elaborated in Section 3.2.2.

Figure 3.9: The two processes in TR-2PPE: (a) two-photon process which directly excites the occupied electronic state electron into the vacuum without transitions into any real intermediate state and (b) two-quantum process where the first photon excites the occupied electronic state electron into an available real intermediate state and the second photon ejects it into the vacuum before it relaxes back into its ground state (Adapted from Ref [4]) with permission from *Elsevier*).

Figure 3.10: Optical pump-probe spectroscopy showing: (a) the experimental setup, and (b) energy level diagram showing one possible transition detected by the delayed probe pulse.

3.2.1 Background

The 2PPE process can be modelled through density matrix formulation[4, 5] of a three level system with eigenstates $|g\rangle$, $|e\rangle$, and $|p\rangle$ which correspond to the initial ground state, intermediate excited state and final photoelectron state respectively. The whole process involves a $|g\rangle \rightarrow |e\rangle$ transition through the action of a pump photon which couples the initial and intermediate states, followed by a $|e\rangle \rightarrow |p\rangle$ through the probe photon which liberates the electron from $|e\rangle$ to the final photoelectron state $|p\rangle$. The Hamiltonian of the system is as follows:

$$H = \sum_{i=g,e,p} \epsilon_i |i\rangle \langle i| - \mu \cdot E(t), \quad (3.6)$$

where the ϵ_i is the energy of eigenstate $|i\rangle$, and the dipole moment operator and time dependent photon field are represented respectively as follows:

$$\mu = \mu_{eg} |e\rangle \langle g| + \mu_{pe} |p\rangle \langle e|, \quad (3.7)$$

$$E(t) = E_{pu}(t) \exp(-i\omega_{pu}t) + E_{pr}(t) \exp(-i\omega_{pr}t) + h.c, \quad (3.8)$$

with $E_{pu}(t)$ and $E_{pr}(t)$ denote the pulse envelopes of pump and probe respectively. The dipole moment operator only considers the excitation transitions, namely $|g\rangle \rightarrow |e\rangle$ and $|e\rangle \rightarrow |p\rangle$ for pump and probe photons respectively.

The dynamics of the system due to excitation from pump and probe photons are described using the equation of motion for the density matrix ρ :

$$\frac{d}{dt}\rho_{ij} = \frac{1}{i\hbar} \langle i| [H, \rho] |j\rangle + \frac{d}{dt}\rho_{ij}^{\text{diss}}, \quad (3.9)$$

where the diagonal terms ρ_{ii} represent state population while off-diagonal ones ρ_{ij} ($i \neq j$) represent optically induced coherence between states. The diagonal dissipative terms ρ_{ii}^{diss} only applies to ρ_{ee}^{diss} ($d\rho_{ee}^{\text{diss}}/dt = (-1/T_1^{ee})\rho_{ee}$) which denotes

the population decay of the intermediate state $|e\rangle$ to $|g\rangle$ from inelastic scattering. The off-diagonal terms ρ_{ij}^{diss} ($d\rho_{ij}^{\text{diss}}/dt = (-1/T_2^{ij})\rho_{ij}$) represent the total dephasing between $|i\rangle$ and $|j\rangle$ during excitation, where $1/T_2^{ij} = 1/2(1/T_1^i + 1/T_1^j) + \Sigma_{ij}^*$ and $\Sigma_{ij}^* = \Sigma_i^* + \Sigma_j^*$ represents the 'pure' dephasing rate between $|i\rangle$ and $|j\rangle$ resulting from a decay of coherence due to elastic scattering.

The solutions $\rho(t)$ are solved by perturbation expansion with respect to $E(t)$ as follows

$$\rho(t) = \begin{bmatrix} \rho_{gg}^{(0)} & \rho_{eg}^{(1)} & \rho_{pg}^{(2)} \\ \rho_{ge}^{(1)} & \rho_{ee}^{(2)} & \rho_{pe}^{(3)} \\ \rho_{gp}^{(2)} & \rho_{ep}^{(3)} & \rho_{pp}^{(4)} \end{bmatrix}$$

to yield the excited state population to second order $\rho_{ee}^{(2)}(t)$ and final state up to fourth order $\rho_{ee}^{(4)}(t)$.

3.2.2 Femtosecond Laser System

The experimental setup for TR-2PPE requires two parts, the UHV system and laser system, for electron analysis and initiating the photo-physical process respectively. The UHV system was described previously in Section 3.1.3. In this section, the laser system used in this work is described in detail.

The laser system comprises of a CW pump (*Coherent Verdi G12*) and 80 MHz oscillator laser (*Coherent Vitara-T*) seeding a repetition rate tunable (50 - 300 KHz output) regenerative amplifier (*Coherent RegA 9050*) generating 65 fs, 800 nm pulses at 6 μJ pulse energy with 250 KHz repetition rate. This output was split into 65:35 ratio, where the former pumps a visible OPA (*Coherent OPA 9050*) while the latter was used to generate UV light (~ 270 nm) through a home-built third harmonic generation (THG) setup. The OPA output was designated as pump while the UV light as probe for the study of perovskites in Section 5.2.1, in which

the path length was varied through a motorized delay stage (*Micos LS-180*). A schematic of the beamlines is shown in Figure 3.11. The beams were p-polarised when incident on the sample surface.

The output pulses from OPA and THG setup were individually compressed using prism pairs which introduces negative dispersion to compensate for pulse broadening from group velocity dispersion (GVD) after passing through lens and nonlinear optical crystals. The pump and probe beams were focused individually with 50 cm lenses outside the chamber and enter the UHV chamber through a UV fused silica viewport. A CCD camera was used to align the beams visually to the same spot on the sample. Beam alignment and stability were determined by aligning the beams through a 50 μm pinhole outside the UHV chamber which was reflected from a flipper mirror at the viewport entrance. Figure 3.11 shows the details of the beamline setup described earlier. The TR-2PPE setup requires an interface which is able to extract photoelectron counts from the electron analyser at various delay positions. Technically, the interface requires communication between the electron analyser and the motorised delay, which was set up and implemented during the course of this work. The interface system, and details on calibrating the set up for measurements are described in Section 3.2.3.

Figure 3.11: Schematics of beam lines assembled for the TR-2PPE setup.

3.2.3 Data Acquisition Interface

Building the TR-2PPE requires both UHV system and a femtosecond laser system, which were elaborated in Sections 3.1.3 and 3.2.2 respectively. However, the complete TR-2PPE setup requires an interface to bridge between the two systems to extract photoelectron counts from the UHV system at various delay positions at the laser system. The lack of such ready-made interfaces, together with the fact

that different electron analysers companies have propriety electronics to process the collected photoelectrons present requires this work to program a self-assembled interface. The lack of commercially available software development kits (SDKs) for the proprietary software of the analyser increases this challenge. It is not straightforward to couple the electron analyser output with the delay stage, unlike the universality of equipment in usual optical pump-probe setups. Despite these challenges, such an interface was successfully created and implemented for this work. A description of the requirements, details on implementing the interface system and calibrating the TR-2PPE system are elaborated in this section.

The electron analyser used in this work uses a set of units to convert photoelectron signal to computer TTL signals through a pulse counting pre-amplifier, HV supplies, and multichannel receiver to perform electronic-to-optical signal conversion, multiplication, and optical-to-electronic conversion processes respectively. Fortunately, there exists seven analog outputs (one for each individual channel) at the back of the multichannel receiver which acts as ratemeters and could be tapped to measure the photoelectron counts with voltage. These voltage signals are proportional to channeltron count rate (1V to 100kcps). These seven channels were extracted to a *BNC-2110* connector block where the signals were summed in a NI-DAQmx acquisition software in the acquisition computer. A *LabView* program was modified to produce the photoelectron counts at various delay positions, shown in Figure 3.12 for the block diagram. The real-time mode dialog box in the *Omicron EIS* interface was used to continuously monitor the photoelectron counts shown in Figure 3.13. The kinetic energy being probed and the characteristics of energy resolution (CAE/CRR mode and pass energy) can be adjusted to a certain extent to obtain sufficient photoelectron counts.

Figure 3.12: *LabView* block diagram for TR-2PPE interface. Figure 3.13: Real-time mode in *EIS* software interface.

3.2.4 System Initialisation and Calibration

The next procedure was to obtain time-zero and calibration of the system. This was done using Cu(111) single crystal. The surface was prepared through a series

of Ar^+ ion sputtering having 1.5 keV energy and annealing at 420 °C to obtain a clean surface. Surface cleanliness was confirmed with XPS, UPS in Figure 3.14.

Figure 3.14: XPS spectra of Cu(111) single crystal: (a) XPS wide scan, (b) Cu 2p, (c) O 1s and (d) C 1s. UPS spectra of Cu(111): (e) SECO and (f) VBM region.

The probe delay was swept slowly past the time-zero while tracking the photoelectron counts of $n = 1$ IPS of Cu(111) in *EIS* real-time mode. The position of the probing kinetic energy depends on the pump and probe energies, and the kinetic energy position of the pump-probe signal can be quickly determined to be $\Delta h\nu$ smaller than the IPS signal from the probe background signal as shown in the energy diagram of Figure 3.15. Probing at this energy, an appreciable rise of photoelectron count occurs when the delay is at time-zero due to temporal overlap of the pump and probe pulses on the Cu(111) sample, and falls to its background level beyond that. By tracking the historical high using "Maximum Values" in the real-time mode, it can be determined if the delay has past the position of time-zero.

Figure 3.15: 2PPE schematic showing the excitation and ionisation process of Cu(111) single crystal IPS.

In TR-2PPE work on perovskites[6–8], the visible light acts as the pump while UV light as probe for the measurements. The existing setup is also set up in similar fashion - OPA: pump, THG output: probe. Hence, from here on the beams will be assigned as such even though technically it is the other way round for Cu(111), where UV light excites the electron from either an occupied d-band or $n=0$ surface state to the IPS with the visible/IR light acting as the probe to ionise the photoelectron.

Once time-zero was obtained, a series of steady-state measurements were taken to discern the additional pump-probe signal from the IPS of Cu(111). The pump-probe signal depends on the action of both pulses on the material, hence the probing kinetic energy depends on various situations the intermediate state was reached. Details on this, especially pertaining to perovskites, shall be elaborated further in Section 5.2.1. For clean Cu(111) surface, the result of steady-state 2PPE measurements is shown in Figure 3.16 for pump energy of 2.38 eV (520 nm) and probe energy of 4.59 eV (270 nm). The Cu(111) single crystal surface was excited with fluence $10.5 \mu\text{J}/\text{cm}^2$ and $0.5 \mu\text{J}/\text{cm}^2$ from the pump and probe respectively.

Figure 3.16: (a): 2PPE spectra of Cu(111) single crystal for different beam configurations: pump only (black), probe only (blue), pump-probe at time-zero (red). Inset: background 2PPE signal for SS and the $n=1$ IPS state of Cu(111) single crystal. (b): TR-2PPE spectra probed at $E-E_F \sim 1.7$ eV.

The background signal of the single colour 2PPE of the probe has two features corresponding to the occupied SS and $n=1$ IPS state of Cu(111) which reside in the 3.6 - 4.4 eV of $E-E_F$ region, shown in the inset of Figure 3.16(a). The energy level diagram of this excitation process is also shown on the left side of Figure 3.15. When the pump and probe beams meet at time-zero, an extra replica of these features appear in the 1.0 - 2.0 eV of $E-E_F$ region shown in the red curve of Figure 3.16(a). The difference between the two set of peaks correspond to the difference of pump and probe energies represented as $\Delta h\nu$ in Figure 3.15. The appearance of this signal is an indication of the temporal overlap of the two beams, as these features disappear at other time delays. The best cross-correlation between pump and probe beams was found to be 230 fs, as shown in Figure 3.16(b). This was optimised through fine-tuning the positions of the prism compressors and ensuring good spatial overlap between the beams.

3.3 Sample Preparation

One of the crucial aspects in experimental perovskite research is in sample preparation, as the fabrication of perovskite compounds is highly versatile from the variety of solution-processing methods discovered over the years to improve film quality. Thin film fabrication of perovskite solar cells has undergone major advancements since initial reports by Kojima *et al.*[9] and Kim *et al.*[10] using single step deposition of the perovskite layer. Interests garnered by the efficiency jump from $\sim 3.8\%$ to $>9\%$ led to variations like the two-step spincoating process[11] to enhance pore filling of the perovskite in TiO_2 , and the toluene antisolvent treatment[12] to smooth the surface thus enhancing its morphology and crystallinity.

This antisolvent treatment involves dripping a solvent at a particular point in time while the substrate is spinning during the spincoating step. The choice of solvent is chosen which has low solubility for perovskite so as not to wash it away after the treatment. Toluene or diethyl-ether are commonly used for this treatment. The films fabricated for this work are made using antisolvent washing to enhance the film quality for the spectroscopic measurements. Specific details would be covered in the relevant 'Results and Discussion' section of Chapters 4 and 6.

3.4 Summary

This chapter describes the principles of photoelectron spectroscopy as well as the TR-2PPE spectroscopy technique, which was also successfully assembled during the course of this work. The system was calibrated using the image potential state of Cu(111) single crystal and has a time resolution of 230 ± 10 fs. Development in fabrication processes of solution-processed perovskite films is described.

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Energetic Bending and Charge Extraction at Perovskite Interfaces

In this chapter, energy level alignment of representative interfaces in perovskite solar cells was determined using thickness dependent photoelectron spectroscopy with evaporated organic charge extraction layers, either PCBM or spiro-OMeTAD on FAPbI₃ and repeated with MAPbI₃ as control. The presence of upward band bending in FAPbI₃, in contrast to MAPbI₃ which has none, was investigated to determine its origin, and the detrimental effect of this band bending on electron extraction was demonstrated using TR-PL. The physical origin of its formation was investigated while possible mechanism of this formation was proposed. The pervasive influence of this band bending even in stabilised mixed-cation perovskite is demonstrated, suggesting that cation mixing has its limitations in making the surface stable to remove the band bending. Possible solution to circumvent the problem of electron extraction caused by band bending is suggested.

4.1 Introduction

Initial rapid progress in perovskite solar cell performance has led to increasing challenges in further efficiency advancements. So far, much of the progress has been attributed to the replacement using solid state spiro-OMeTAD hole transport layer and the use of what is known as the triple and quadruple cation perovskites to stabilise FAPbI₃, the main constituent in the absorber layer. Although some effort was dedicated to the interface engineering of devices[1–5], not enough is done to study the systematic energy level alignment to understand charge extraction between perovskite and its adjacent charge extraction layers. The unbalanced diffusion lengths between that of electrons and holes in FAPbI₃[6] is also not well addressed. Previously in Chapter 2, surface and interface studies of perovskites and their influence towards charge extraction and solar cell efficiency were discussed in detail. Such knowledge is useful in addressing these open questions, which shall be discussed in this chapter. Differences in using a triple cation mixture on its energy level alignment and charge extraction shall also be discussed.

4.2 Results and Discussion

4.2.1 Film Preparation and Quality

The perovskite thin films were fabricated through single step antisolvent solution-processing using stoichiometric amounts of organic precursors as detailed in 3.3, either FAI (*Greatcell*) or MAI (*Greatcell*), and PbI₂ (*TCI Japan*, purity 99.99%) in anhydrous dimethylformamide (*Sigma-Aldrich*, purity 99.8%). The concentration used to make the films for PES and PL experiments were 1.2 M and 10 wt% respectively to vary the film thickness of either ~ 300 nm and ~ 40 nm respectively. Antisolvent treatment with diethyl-ether was performed during the spincoating

process to improve film coverage and morphology. The fresh films were annealed at 100 °C and 160 °C for the same duration of 10 minutes for MAPbI₃ and FAPbI₃ respectively. Samples for PES experiments were transferred to UHV chamber through an airtight enclosure without exposure, while those for TR-PL experiments remain sealed in an airtight enclosure under glovebox environment.

It can be seen from Figures 4.1, 4.2 and 4.3 that the films provide good crystallinity and coverage, having optical properties consistent with those reported in existing literature which are suitable for the spectroscopic measurements described in the following sections.

Figure 4.1: XRD spectra for FAPbI₃ (red) and MAPbI₃ (black).

Figure 4.2: Absorption spectra of FAPbI₃ (red) and MAPbI₃ (black).

(a) SEM image of FAPbI₃ surface.

(b) SEM image of MAPbI₃ surface.

Figure 4.3: Morphological characteristics of FAPbI₃ and MAPbI₃ surfaces.

Chemical Composition

The surface chemical composition of perovskite surfaces was determined through XPS in a backscattering geometry of detection angle $\sim 54.7^\circ$ from the source. The monochromatic soft X-ray excitation used was Al K_α emission line of 1486.6 eV. Experiments were conducted under UHV conditions at pressure $< 1 \times 10^{-9}$ torr. The results of XPS are presented in Figures 4.4 and 4.5 for FAPbI₃ and MAPbI₃ respectively.

Figure 4.4: XPS spectra of FAPbI₃: (a) wide scan, (b) N 1s, (c) I 3d, (d) Pb 4f, (e) C 1s.

Figure 4.5: XPS spectra of MAPbI₃: (a) wide scan, (b) C 1s, (c) N 1s, (d) Pb 4f, (e) I 3d.

The binding energy values summarised in Table 4.1 shows that the similar Pb 4f and I 3d binding energies between the two perovskites is consistent with the fact that the corner sharing $[\text{PbI}_6]^{4-}$ octahedral network remains largely unchanged except for a minute size increase under $\text{MA}^+ \rightarrow \text{FA}^+$ cation substitution. On the

Table 4.1. Summary of binding energy positions for elemental peaks in FAPbI₃ and MAPbI₃.

Elements	Binding Energy (eV)	
	FAPbI ₃	MAPbI ₃
Pb 4f ^{7/2}	139.0	139.0
I 3d ^{5/2}	619.8	619.8
N 1s	401.2	402.8

other hand, electrochemical differences between MA⁺ and FA⁺ cations result in significant binding energy differences in N 1s and C 1s peaks. These results are also consistent with reported literature.

Valence Electronic Structure

The WF and valence electronic structure of FAPbI₃ surface are shown in Figures 4.6a and 4.6b respectively. Experimental conditions were identical to those in XPS except for the excitation source used, which was the He-I emission at 21.2 eV in energy. The VBM of perovskites were determined using logarithmic intensity scale previously described in Section 3.1.2. The UPS spectra for MAPbI₃ is also shown in Figure 4.7 for reference.

(a) SECO of FAPbI₃ surface.

(b) Valence electronic spectra of FAPbI₃ surface.

Figure 4.6: Representative UPS spectra of FAPbI₃ surface.

(a) SECO of MAPbI₃ surface.

(b) Valence electronic spectra of MAPbI₃ surface.

Figure 4.7: Representative UPS spectra of MAPbI₃ surface.

The following section describes the energy level alignment of FAPbI₃ interfaces with PCBM and spiro-OMeTAD to compare them with those of MAPbI₃ to elucidate the effects of cation substitution from FA⁺ to MA⁺.

4.2.2 Energetics of FAPbI₃ and MAPbI₃ Interfaces

Photoelectron Spectroscopy Results

Organic charge extraction layers (either PCBM or spiro-OMeTAD) were evaporated in-situ in an adjacent UHV evaporation chamber described in Section 3.1.3 at $\sim 1.0 \times 10^{-8}$ torr. The growth rate was calibrated using a quartz crystal microbalance (QCM) before the experiment. The growth temperature for PCBM was $\sim 200^\circ\text{C}$, and about $\sim 160^\circ\text{C}$ for spiro-OMeTAD. XPS and UPS spectra were taken at incremental thickness of the evaporated overlayer until the accumulated film thickness reached about 20 nm for PCBM and 30 nm for spiro-OMeTAD.

Thickness dependent XPS spectra are shown in Figure 4.8 for the evaporation of PCBM on FAPbI₃. The shift in binding energy positions of N 1s, I 3d and Pb 4f in Figures 4.8 (b), (c) and (d) respectively were used to determine the energetic changes at the perovskite side of the FAPbI₃/PCBM interface. Since these elements are exclusive to the perovskites, this set of selection is reliable for analysis. Binding energy positions for each spectrum was obtained by fitting a Voigt profile over a Shirley background. The variation in binding energy positions of N 1s, I 3d and Pb 4f are summarised in Figure 4.8(f), which shows a concomitant binding energy shift of 0.14 ± 0.03 eV towards low binding energies. Likewise, the same analysis applied for FAPbI₃/spiro-OMeTAD interface in Figure 4.9 also shows a slight 0.06 ± 0.03 eV shift of the perovskite peaks towards lower binding energies.

Figure 4.8: XPS spectra of FAPbI₃/PCBM interface: (a) wide scan, (b) N 1s, (c) I 3d, (d) Pb 4f, (e) C 1s and (f) binding energy shifts of the N 1s, Pb 4f and I 3d over various PCBM thickness in nm.

Figure 4.9: XPS spectra of FAPbI₃/spiro-OMeTAD interface: (a) wide scan, (b) N 1s, (c) I 3d, (d) Pb 4f, (e) C 1s and (f) binding energy shifts of the N 1s, Pb 4f and I 3d over various spiro-OMeTAD thickness in nm.

SECO and VBM regions from thickness dependent UPS measurements in Figure 4.10(a) and (b) describe the WF and valence band maximum variations of the evaporated PCBM overlayer respectively. A decrease in WF shown in Figure 4.10(a) by 0.13 ± 0.03 eV for FAPbI₃/PCBM interface shows electron transfer from the PCBM to FAPbI₃ during interface formation. The HOMO onset of PCBM in Figure 4.10(b) shifts by a similar magnitude by 0.11 ± 0.03 eV towards higher binding energies, which is expected as the material's vacuum and electronic levels shift concomitantly during interface formation. The same analysis applied to FAPbI₃/spiro-OMeTAD interface in Figure 4.11 shows both WF reduction and HOMO level shift towards large binding energy by 0.44 ± 0.03 eV.

Figure 4.10: UPS spectra of FAPbI₃/PCBM interface: (a) WF onsets, and (b) valence states at various PCBM thicknesses.

Table 4.2. Summary of values with FAPbI₃ interfaces. *positive values denote shifts to smaller BE toward the interface.

Interface	*BE shift in FAPbI ₃ (eV)	*HOMO shift in organic layer (eV)
FAPbI ₃ /PCBM	+0.14 ± 0.03	+0.12 ± 0.03
FAPbI ₃ /spiro-OMeTAD	+0.06 ± 0.03	+0.44 ± 0.03

Figure 4.11: UPS spectra of FAPbI₃/spiro-OMeTAD interface: (a) WF onsets, and (b) valence states at various spiro-OMeTAD thicknesses.

A summary of obtained values is shown in Table 4.2.

Interpretation of Results to Interface Energetics

The results in Section 4.2.2 are used to map the energetics at FAPbI₃ interfaces. Since the determined BE and VBM positions are referenced to Fermi level, shifts in these values represent actual variations in energetics and electronic structure of both constituents during interface formation.

In such interface studies, BE shifts of elemental peaks in XPS are used to determine the energetic variations of the perovskite underlayer as the organic layer is evaporated on top of it. The amount of BE shift represents the bending of electronic band of the underlayer material if it remains chemically unchanged during the interface formation process. Shifts of elemental peaks toward lower BE during the growth process denote upward bending towards the interface, whereas shifts toward larger BE denotes downward bending towards the interface.

On the other hand, VBM shifts observed in UPS are used to determine the electronic structure of the evaporated organic overlayer. The WF and VBM values of the clean perovskite surface represent that of the bulk perovskite. The much shorter probing depths of photoelectrons within one monolayer in UPS easily obscure the valence DOS of the underlayer. Therefore, the change in valence DOS features from UPS measurements follows the electronic structure variation of the organic overlayer side during the evaporation process. At sufficiently thick organic extraction layer, the values of WF and VBM should represent bulk values of the organic layer.

The determination of conduction levels for electron extraction cannot be directly measured using photoelectron spectroscopy. Therefore, band gaps determined from Tauc plots of linear absorption measurements were used to estimate the conduction levels to construct complete energy level diagrams of the interfaces. The band gaps of perovskites, PCBM and spiro-OMeTAD are extrapolated from the Tauc plots of Figure 4.12.

Figure 4.12: Tauc plots of (a) FAPbI₃, (b) MAPbI₃, (c) spiro-OMeTAD and (d) PCBM to obtain their respective direct band gap values.

The energy level diagrams for FAPbI₃ interfaces are shown in Figure 4.13(a) and (b) for FAPbI₃/PCBM and FAPbI₃/spiro-OMeTAD interfaces respectively. There is upward bending of the electronic bands/levels toward the interface from both sides for both interfaces.

Figure 4.13: Energy level alignment for: (a) FAPbI₃/PCBM and (b) FAPbI₃/spiro-OMeTAD interfaces.

In order to determine if this upward bending of the electronic bands/levels toward the interface from both sides for both interfaces in FAPbI₃ arises from interactions between FAPbI₃ and the organic extraction layer, energy level alignments are compared between interfaces with FAPbI₃ and MAPbI₃. The results from XPS in Figures 4.14 and 4.15 for both MAPbI₃/PCBM and MAPbI₃/spiro-OMeTAD interfaces respectively show the absence of band bending on the MAPbI₃ side of both interfaces due to lack or inconsistent binding energy shifts in Figures 4.14(f) and 4.15(f) for MAPbI₃/PCBM and MAPbI₃/spiro-OMeTAD respectively.

Figure 4.14: XPS spectra of MAPbI₃/PCBM interface: (a) wide scan, (b) N 1s, (c) I 3d, (d) Pb 4f, (e) C 1s and (f) binding energy shifts of the N 1s, Pb 4f and I 3d peaks with PCBM growth.

Figure 4.15: XPS spectra of MAPbI₃/spiro-OMeTAD interface: (a) wide scan, (b) N 1s, (c) I 3d, (d) Pb 4f, (e) C 1s and (f) binding energy shifts of the N 1s, Pb 4f and I 3d peaks with spiro-OMeTAD growth.

Figure 4.16: UPS spectra of MAPbI₃/PCBM interface: (a) WF onsets, and (b) valence states at various PCBM thicknesses.

Figure 4.17: UPS spectra of MAPbI₃/spiro-OMeTAD interface: (a) WF onsets, and (b) valence states at various spiro-OMeTAD thicknesses.

Using the same analysis previously with FAPbI₃, the resulting energy level diagrams are shown in Figures 4.18.

Figure 4.18: Energy level alignment for: (a) MAPbI₃/PCBM and (b) MAPbI₃/spiro-OMeTAD interfaces.

Comparing between the perovskites' interfaces with PCBM, upward band bending in the perovskite of 0.14 ± 0.03 eV towards the interface is observed at FAPbI₃/PCBM interface, but not in MAPbI₃/PCBM. Likewise for the interfaces with spiro-OMeTAD, a slight upward band bending for FAPbI₃/spiro-OMeTAD of 0.06 ± 0.03 eV is also observed with no consistent band bending in the perovskite for MAPbI₃/spiro-OMeTAD. This shows the upward bending towards the interface from both sides in FAPbI₃ interfaces is independent of the organic charge extraction layer, therefore the origins of band bending in FAPbI₃ shall be the main focus for the remaining of this work.

4.2.3 Influence of Energy Level Alignment on Charge Extraction

The presence of this upward band bending for FAPbI₃ in its interfaces upon formation have implications on charge extraction of photoexcited carriers from FAPbI₃, as it can act as a barrier to hinder photogenerated electrons from getting extracted efficiently across the interface. Likewise, this upward band bending can facilitate hole extraction from FAPbI₃. To investigate this, time-resolved photoluminescence (TR-PL) measurements of these four interfaces relative to their bare films were taken but using thinner films. The lifetime quenching from a bare film by the extraction layer would be used as a measure of extraction efficiency. The TR-PL spectra collected using a streak camera are shown in Figures 4.19 and 4.20 for 2.07 eV (600 nm) and 2.48 eV (500 nm) excitation energies respectively. The fluence was kept constant at 0.8 $\mu\text{J}/\text{cm}^2$ for both excitation energies.

Figure 4.19: TR-PL spectra for: (a) FAPbI₃ interfaces (bare (black squares), with PCBM (red circles) and with spiro-OMeTAD (green triangles)) and (b) MAPbI₃ interfaces (bare (black squares), with PCBM (red circles) and with spiro-OMeTAD (green triangles)). The samples were excited at 2.07 eV energy, with fluence 0.8 $\mu\text{J}/\text{cm}^2$.

Figure 4.20: TR-PL spectra for: (a) FAPbI₃ interfaces (bare (black squares), with PCBM (red circles) and with spiro-OMeTAD (green triangles)) and (b) MAPbI₃ interfaces (bare (black squares), with PCBM (red circles) and with spiro-OMeTAD (green triangles)). The samples were excited at 2.48 eV energy, with fluence 0.8 $\mu\text{J}/\text{cm}^2$.

Under 2.07 eV excitation, we see from Figure 4.19(a) that the lifetime of FAPbI₃

films decreases from 44.8 ± 0.1 ns to 10.1 ± 0.2 ns with the PCBM layer, compared to 1.68 ± 0.02 ns with the spiro-OMeTAD layer which is correlated with the prediction of inefficient electron extraction as a result of the band bending. In Figure 4.19(b), the difference in carrier lifetime quenching in MAPbI₃ is not so significant as compared to that of FAPbI₃, where the lifetime was quenched from 42.2 ± 0.3 ns to 2.54 ± 0.06 ns with PCBM and 2.52 ± 0.08 ns with spiro-OMeTAD.

Interestingly, exciting the samples at 2.48 eV results in more balanced electron and hole quenching dynamics of the FAPbI₃ film as shown in Figure 4.20. The lifetime of FAPbI₃ decreases from 9.6 ± 0.4 ns to 2.00 ± 0.03 ns with PCBM and 2.9 ± 0.4 ns with spiro-OMeTAD. A summary of values for this discussion is tabulated in Table 4.3.

In addition, electron and hole diffusion lengths for each film under both excitation energies can be obtained by solving the one dimensional drift-diffusion model:

$$\frac{\partial n(x, t)}{\partial t} = D \frac{\partial^2 n(x, t)}{\partial x^2} - kn(x, t), \quad (4.1)$$

where $n(x, t)$ denotes the carrier concentration at coordinate x and at time t , D denotes the diffusion constant and k represents the radiative recombination rate. The derived values for electron and hole diffusion lengths are summarised in Table 4.3.

The ratio L_D^h/L_D^e was used to examine the balanced charge extraction between the electrons and holes of the perovskites in Table 4.3 and it can be seen that varying the excitation energy from 2.07 eV to 2.48 eV causes slight decrease from 1.0 ± 0.1 to 0.6 ± 0.2 for MAPbI₃. However, significant difference in the charge extraction balance was observed for FAPbI₃, from unbalanced hole-to-electron diffusion length of 2.9 ± 0.1 with 2.07 eV excitation to 0.7 ± 0.5 using 2.48 eV excitation. This observation is quite consistent with the energy level alignment suggesting

Table 4.3. Values of TR-PL lifetimes, film thickness, electron and hole diffusion lengths for FAPbI₃ and MAPbI₃ at 2.07 eV and 2.48 eV excitation.

	$h\nu$ (eV)	L (nm)	L_D^e (nm)	L_D^h (nm)	L_D^h/L_D^e	τ_0 (ns)	τ_{PCBM} (ns)	$\tau_{\text{spiro-OMeTAD}}$ (ns)
MAPbI ₃	2.07	34±0.6	79±5	80±5	1.0±0.1	42.2±0.3	2.54±0.06	2.52±0.08
FAPbI ₃	2.07	41±0.6	39±2	112±5	2.9±0.1	44.8±0.1	10.1±0.2	1.68±0.02
MAPbI ₃	2.48	34±0.6	65±8	39±2	0.6±0.2	14.0±0.6	2.25±0.05	0.95±0.01
FAPbI ₃	2.48	41±0.6	36±6	26±9	0.7±0.5	9.6±0.4	2.00±0.03	2.9±0.4

hot electrons with sufficient energy in the conduction band can get extracted to PCBM effectively which also might uncover interesting hot carrier extraction dynamics which is not part of this discussion.

4.2.4 Origins of Band Bending in FAPbI₃

The origin of this band bending is crucial to understand what is happening at FAPbI₃ perovskite's surface, which may provide solutions to mitigate the problem. Background on the phenomenon of band bending at semiconductor surfaces and interfaces is described in Section 2.1.1. Here, we investigate the various factors that could cause band bending in FAPbI₃.

One possibility could be due to the presence of additional defect states on the surface by cation substitution. Surface stoichiometric defects caused by atomic vacancies can be determined through the relative atomic ratio of the elemental composition using XPS. The change in atomic ratios for evaporated PCBM were compared between two perovskites in Figure 4.21. The trends in the atomic ratio change were similar for both perovskites. In Figure 4.21, a gradual decrease in the I/Pb ratio is observed over PCBM growth thickness, while A/Pb ratio remains relatively unchanged for both FAPbI₃ and MAPbI₃. This suggests that switching between MA⁺ and FA⁺ cations do little to influence the surface vacancy defects

of the perovskites.

Figure 4.21: Changes in A/Pb and I/Pb ratios for (a): FAPbI₃ and (b) MAPbI₃ over evaporated PCBM thickness.

In fact, the observation of significant band bending in FAPbI₃ in the orders of ~ 10 nm is unlikely, which can be calculated from known values of bulk carriers and dielectric constant. Assuming the band bending of 0.1 eV arising from ionised donor to neutralise a negatively charged surface, and using the reported values of $N_D = 3.9 \times 10^9 \text{cm}^{-3}$ [7] and $\epsilon_r = 6.6$ [8] into Equation 2.1, a long depletion region of $\sim 1.3 \times 10^5$ nm was found, which is much larger than the experimental range of ~ 10 nm. Thus, there should be no observable appearance of band bending in this work.

This leaves the remaining possible factor for the appearance of this band bending in FAPbI₃. FAPbI₃ is known to have an alternate δ -phase which is not desirable for photovoltaic applications due to its wider band gap of ~ 2.43 eV[8]. There could be a possibility of surface δ -FAPbI₃ even though the bulk perovskite is stabilised. To determine if this is the case, a comparison of the XPS peaks were performed on δ -FAPbI₃ and the spectra shown in Figure 4.22 and tabulated in Table 4.4. From Table 4.4, the binding energies of Pb 4f and I 3d is at lower binding energies compared to that of FAPbI₃ itself which coincide with the peak shift towards lower binding energies during the formation of the interfaces of FAPbI₃. This supports the apparent band bending observed is actually the presence of surface δ -FAPbI₃.

Figure 4.22: XPS spectra of δ -FAPbI₃ showing: (a) wide scan, (b) C 1s, (c) N 1s, (d) I 3d and (e) Pb 4f peaks.

Table 4.4. Binding energy positions for elemental peaks in δ -FAPbI₃ and FAPbI₃.

Elements	Binding Energy (eV)	
	δ -FAPbI ₃	FAPbI ₃
Pb 4f ^{7/2}	138.8	139.0
I 3d ^{5/2}	619.5	619.8
N 1s (FA ⁺)	401.1	401.2

4.2.5 Triple Cation Perovskite

The previous section showed that surface δ -FAPbI₃ gives an appearance of this apparent bend bending at its interface, thus it would be useful to determine if the triple cation mixture (FA_{0.83}MA_{0.17})_{0.95}Cs_{0.05}Pb(I_{0.83}Br_{0.17})₃ (TCP), being one of the top candidate for perovskite solar cell performance, eliminates the surface δ -FAPbI₃. The same thickness dependent studies were also performed on the triple cation perovskite with PCBM and spiro-OMeTAD, and the results are shown in Figures 4.23 and 4.24 respectively.

Figure 4.23: Thickness dependent XPS spectra of $(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Cs}_{0.05}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3/\text{PCBM}$ interface, showing: (a) wide scan, (b) N 1s, (c) Pb 4f, (d) I 3d, (e) Br 3d, (f) Cs $3d^{5/2}$, (g) C 1s and (h) binding energy shifts.

Figure 4.24: Thickness dependent XPS spectra of $(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Cs}_{0.05}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3/\text{spiro-OMeTAD}$ interface, showing: (a) wide scan, (b) N 1s, (c) Pb 4f, (d) I 3d, (e) Br 3d, (f) Cs 3d $^{5/2}$, (g) C 1s and (h) binding energy shifts.

Table 4.5. Binding energy positions for elemental peaks in the triple cation perovskite $(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Cs}_{0.05}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$. Two different values of N 1s (MA^+) is possibly due to light sample differences.

$(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Cs}_{0.05}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$			
Elements	BE (eV)	Elements	BE (eV)
Pb 4f ^{7/2}	139.1	N 1s (MA^+)	402.8/403.1
I 3d ^{5/2}	619.9	Br 3d	69.2
N 1s (FA^+)	401.3		

XPS elemental spectra show the presence of N 1s, Pb 4f, I 3d, Br 3d, Cs 3d^{5/2}, C 1s of the perovskite. However Cs 3d^{5/2} appears in trace amounts $\sim 1\%$ which suggests that some of the Cs^+ ions had escaped during the fabrication process. For the TCP/PCBM interface, the elemental peaks of the perovskite shift towards lower binding energy by ~ 0.2 eV over PCBM growth thickness, whereas those of the TCP/spiro-OMeTAD also shift towards lower binding energy by ~ 0.1 eV. The binding energy shifts for the peaks in both interfaces are shown in Figure 4.23 and 4.24 for TCP/PCBM and TCP/spiro-OMeTAD respectively. The similarity of peak shifts between TCP and FAPbI_3 perovskites at their interfaces suggests that using the triple cation mixture does not completely eliminate surface δ - FAPbI_3 .

4.2.6 FAPbI_3 based Perovskites as an Absorber Layer

Much of recent progress in perovskite solar cells has been attributed to the use of FAPbI_3 and its derivatives. The main reason for this is due to its smaller optical band gap, however its instability converting from α -phase to the undesirable δ -phase raises some concern and drove the community to enhance the stability of the α -phase.

In this work, it was found that existence of surface δ -FAPbI₃ acts as an electron barrier which hinders extraction of low lying electrons which has not been understood at present. This would raise some concerns in using FAPbI₃-based materials for light harvesting, as being not able to extract low lying electrons reduces the effective potential of the device, even though low energy photons is captured, likely due to recombination of these low lying electrons with available holes. The effect of this is also shown in the observation of unbalanced diffusion lengths between the electron and holes, which has not been explained so far. The formation of δ -FAPbI₃ has been reported to arise from the thermodynamic instability of α -FAPbI₃, hence this transformation occurs spontaneously, and it has been shown that this process is also aggravated by the presence of moisture. It is possible that this thermodynamic instability of α -FAPbI₃ is exacerbated due to additional instability posed by the termination of FAPbI₃ surface, which the cation engineering is unable to stabilise. Therefore, it is imperative that this issue is addressed in future to fully demonstrate the advantage of this material.

4.3 Summary

In this work, extensive energy alignment studies were done to the FAPbI₃ perovskite with organic charge extraction layers, PCBM and spiro-OMeTAD. Unexpectedly, upward band bending towards the interface was observed in FAPbI₃ for its interfaces. This upward band bending creates a potential barrier for electrons which can hinder its extraction across the FAPbI₃/PCBM interface. TR-PL quenching experiments were performed to confirm this effect of energy alignment on its charge extraction and diffusion length. The lifetime of FAPbI₃ was quenched from 44.8 ± 0.1 ns to 10.1 ± 0.2 ns and 1.68 ± 0.02 ns for FAPbI₃/PCBM and FAPbI₃/spiro-OMeTAD respectively. The electron and hole diffusion lengths are 39 ± 2 nm and 112 ± 5 nm respectively, which is 2.9 ± 0.1 times in comparison. The

TR-PL results support the effect of electron extraction as predicted by the energy level alignment. The origin of this apparent band bending is not supported by the conventional notion of additional surface vacancy defects, while the known carrier concentration and dielectric constant of the material gives a large depletion width in the order of $\sim 10^5$ nm, which is much beyond the range during the experiment. This apparent band bending is actually due to the presence of surface δ -FAPbI₃. Using a triple cation does not alleviate this surface δ -FAPbI₃ as XPS elemental peaks shift towards lower binding energies as well, similar to that of FAPbI₃. This raises some concern with using FAPbI₃-based perovskites for solar cells as the surface δ -FAPbI₃ acts as a tunnelling barrier for electron extraction in n-i-p solar cell configuration, thus appropriate interface engineering would be useful for further improvement in its performance.

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Surface Dynamics of Evaporated MAPbI₃ and Lead Bromide Perovskite Single Crystals

In this chapter, preliminary TR-2PPE measurements were performed using the experiment setup assembled in the course of this work as described in Section 3.2 to investigate electron dynamics in some perovskite systems under resonant pump excitation to complement optical pump probe studies done in this field. The unaddressed issue of perovskite photostability was inadvertently uncovered during an initial experiment to replicate a published work on evaporated MAPbI₃ perovskite which will be discussed in detail at Chapter 6. Thereafter, APbBr₃ (A=Cs⁺, MA⁺ or FA⁺) single crystals were studied using TR-2PPE instead since they would be expected to be more stable against irradiation of the laser beams. UV stability of these single crystals were determined to ensure experimental accuracy before performing the actual TR-2PPE experiment. Electron dynamics from the preliminary TR-2PPE data are discussed in detail.

5.1 Introduction

The surfaces and interfaces of perovskites can greatly influence photophysical processes happening in the material which determine their device performance. This interplay was demonstrated in the previous chapter through the influence of energy level alignment on the charge extraction properties of FAPbI₃ interfaces through the combination of complementary techniques of photoelectron spectroscopy and photoluminescence.

Such use of complementary techniques has its merits in leveraging on their respective niches. The state selective nature of photoelectron spectroscopy has the advantage of mapping the energy levels/bands in the material, whereas the transition sensitive nature of optical spectroscopy obscures this information. However, the nature of optical transitions in coupling two states of the system has its advantage, as the presence of particular intermediate states in the system can be deduced despite its energetic positions cannot be confirmed. Using pulsed lasers, the dynamics of these intermediate states can also be determined in a pump-probe configuration. With this respect, photoelectron spectroscopy is unable to reveal information on any intermediate states in the system, only ground state levels/bands can be determined.

However, due to the different probes used in these experiments, the use of complementary techniques has limitations in trying to reconcile the analysis obtained from each technique. The probing profile of photoelectron spectroscopy is limited by the inelastic mean free path (IMFP) of electrons in solids while escaping the material. Although the penetration depth of X-rays in solids is in μm range, the electrons which retains information about its original electronic state comes from within few Å up to ~ 10 nm of the surface. This makes photoelectron spectroscopy a surface sensitive technique. On the other hand, the probing profile of optical spectroscopies varies, but is much longer than that of photoelectron spectroscopy.

The probing depth depends on factors like absorption coefficient, particle density, film thickness amongst others, which can be altered to some extent by changing various experimental parameters. This makes optical spectroscopy versatile in this aspect, but lacks surface sensitivity.

Therefore experimental setups like TR-2PPE, which combines state selectivity and transition selectivity, is useful in identifying and determining the dynamics of photoexcited intermediate energetic states. Despite the advantages of this technique, limited studies performed using this technique have not provided a complete picture of electron dynamics in perovskite, which this chapter attempts to address. The numerous studies performed with TAS and TR-PL do not directly distinguish between possibly different dynamics of the electrons and holes during hot carrier cooling process. This chapter addresses these concerns by first highlighting some preliminary TR-2PPE results using the setup which was self-assembled in the course of this work. However, the issue of sample instability under irradiation was inadvertently uncovered which will be addressed further in Chapter 6. Thereafter, APbBr₃ (A=Cs⁺, MA⁺ or FA⁺) single crystals were selected for TR-2PPE measurements as they were expected to be more stable against irradiation. Photostability studies to ensure experimental accuracy were carried out before the TR-2PPE experiments. The TR-2PPE measurements were performed on stable samples. The electron dynamics obtained from the preliminary study complement the widely reported optical studies, which are mostly performed using TAS or TR-PL, by looking at the electron side of the picture. This helps in proper tuning of respective hot carrier charge extraction interfaces for optimum device efficiency.

5.2 Results and Discussion

In this section, preliminary results using the self-assembled TR-2PPE setup in Section 3.2 on some perovskite samples are presented and discussed. It was inadvertently found that evaporated MAPbI₃ films were unstable under irradiation during an attempt to replicate an existing work in literature, which shall be addressed in subsequent chapter of this thesis. Subsequently, TR-2PPE was performed on APbBr₃ (A=Cs⁺, MA⁺ or FA⁺) perovskite single crystals which afforded greater UV stability using resonance pump excitation. UV stability tests were conducted prior to the actual experiment. The findings and their importance in answering questions on hot carrier dynamics in perovskites were discussed.

5.2.1 Evaporated MAPbI₃ on Cu(111)

In this section, we discuss some preliminary results of evaporated perovskites and single crystals performed with the home-made TR-2PPE setup assembled during the course of this work. The main concern encountered during the experiments was the issue of photodegradation of the perovskites using the UV probe which shall be discussed and possible methods to mitigate this problem.

Sample Characterisation

It is desirable to evaporate MAPbI₃ in UHV as the freshly grown surface is free of any surface contaminants. For this work, the perovskite was grown in-situ in the UHV chamber by evaporating MAI and PbCl₂ precursors at 85°C and 160°C respectively in separate crucibles. XPS and UPS showed good quality of the perovskite surface without observable surface contaminants shown in Figure 5.1. The characteristics of the grown perovskite surface corresponds well with those in reported literature[1].

Figure 5.1: XPS ((a)-(e)) and UPS ((f) and (g)) of evaporated MAPbI₃ film: (a) wide scan, (b) N 1s, (c) I 3d, (d) Pb 4f, (e) C 1s, (f) SECO and (g) VBM region.

Interpretation of 2PPE signals

Figure 5.2: (a) Steady-state 2PPE spectra of evaporated MAPbI₃ film on Cu(111) for pump only (black), probe only (blue) and total pump-probe signal at time-zero (red). The inset shows the pump-induced difference spectra which is the TR-2PPE signal representing the non-equilibrium carrier distribution. (b) TR-2PPE signal probed at ~ 1 eV above E_F , with a fitted lifetime about 0.24 ± 0.01 ps.

Figure 5.2(a) shows the energy spectra for TR-2PPE with various configurations of pump and probe energies of 2.38 eV (520 nm) and 4.59 eV (270 nm) respectively with the sample cooled down to 173K. The fluence was $4.5 \mu\text{J}/\text{cm}^2$ and $0.2 \mu\text{J}/\text{cm}^2$ for the pump and probe respectively. The probe itself contributes a background signal as the double of its photon energy is larger than the ionisation potential of the evaporated perovskite, as illustrated by the energy level diagram shown in Figure 5.3. When both pump and probe pulses arrive the sample at time-zero, there is additional pump-induced signal contribution. The pump-probe spectrum was subtracted with the probe only signal to give the difference spectrum shown in the inset of Figure 5.2(a) in 0.0 - 1.5 eV $E-E_F$ region which represents the non-equilibrium carrier distribution. This spectrum has two spectra features, one in

0.0 - 0.5 eV near the conduction band edge and another in the 0.5 - 1.5 eV at the hot electron region. Dynamics at 1.0 eV shows a fitted lifetime of 0.24 ± 0.01 ps in Figure 5.2(b) similar to the reported results[2].

Figure 5.3: Photoionisation scheme for evaporated MAPbI₃ film showing: (a) background process where two probe photons excite and ionise the electron through the conduction band region and (b) additional pump induced TR-2PPE signal contribution where the pump photon excites the valence band electron to the conduction band region and the probe photon ionises the electron into the vacuum state.

Instability of Evaporated MAPbI₃ under Irradiation

Figure 5.4: Initial scan 2PPE signal of evaporated MAPbI₃ film with pump-probe (brown), probe only (purple) and pump only (black) configurations and repeated scan after 10 minutes with pump-probe (red), probe only (blue) configurations. Inset: Difference spectra between pump-probe and probe only configurations for initial scan (red) and repeated scan (black).

However, prolonged UV irradiation causes drastic changes in the intensity and features of the 2PPE spectra in evaporated MAPbI₃ as shown in Figure 5.4. A shift of 0.06 eV towards lower kinetic energy and ~ 20 fold increase in peak intensity occurs within 10 minutes. The difference spectra of the repeated scan in the inset shows similar shift of the low kinetic energy region towards lower energies together with the appearance of a negative signal in the 0.0 - 0.5 eV $E - E_F$ region. Negative signals can occur in TR-2PPE signifying the depletion of electrons from occupied states by the pump as demonstrated with a study performed on double-wall carbon nanotubes[3]. This negative difference signal occurs in the negative

E-E_F region. However, the negative signals in this case occur in the positive E-E_F region. Besides, the shift to negative E-E_F shows large positive difference. These are indications that the difference spectra obtained during the repeated experiment contain some artefacts, likely due to photodegradation which occurred under prolonged light exposure, particularly under UV light.

The presence of this UV induced change poses great concerns, as it not only affects device performance but can also introduce artefacts when performing spectroscopy. The experiment conditions in this experiment closely replicate those of current literature[2], but the sample was unstable to the irradiation despite lowering the sample temperature down to above ~160K, following the established work. Sample temperature is constrained to above 160K to prevent structural phase transition so that the tetragonal phase of MAPbI₃ can be measured. This highlights an inherent UV stability issue in MAPbI₃, to which a more comprehensive discussion on improving the UV stability of MAPbI₃ and other solution-processed perovskites shall be presented in Chapter 6. The next section shall cover some preliminary TR-2PPE results for lead bromide single crystals, which were more stable towards UV light, to examine hot carrier properties.

5.2.2 Lead Bromide Single Crystal Studies

Photostability of Lead Bromide Single Crystals

Before going into the study proper, 2PPE experiments were performed on three lead bromide perovskite single crystals with different cations (FA⁺, MA⁺ and Cs⁺) under prolonged UV exposure, to determine their photostability by examining the change in photoemission spectra over time. The single crystals were irradiated under 400 nm excitation at 8 nJ/cm² for six minutes. The results shown in Figure 5.5(a), (c) and (e) for FAPbBr₃, MAPbBr₃ and CsPbBr₃ respectively show that the single crystals are stable under 400 nm irradiation at this low fluence, and the

photoemission signal from FAPbBr₃ and CsPbBr₃ single crystals show a squared dependence with fluence, due to the action of two photons to generate the signals. However, the photoemission intensity of MAPbBr₃ deviates from the supposed squared dependence with fluence, which might suggest its poor photostability under high fluence with 400 nm excitation.

Figure 5.5: 2PPE spectra at initial condition (red), after 3 minutes (blue) and after 6 minutes (black) of under 400 nm irradiation for FAPbBr₃ (a), MAPbBr₃ (c) and CsPbBr₃ (e) single crystals. Fluence dependence between 6.0 - 30.0 nJ/cm² for FAPbBr₃ (b), MAPbBr₃ (d) and CsPbBr₃ (f) single crystals.

Figure 5.6: 2PPE spectra at initial condition (red), after 3 minutes (blue) and after 6 minutes (black) of under 272 nm irradiation for FAPbBr₃ (a), MAPbBr₃ (b) and CsPbBr₃ (c) single crystals.

Under 272 nm irradiation at low fluence of $1 \text{ nJ}/\text{cm}^2$ for the single crystals, MAPbBr₃ and CsPbBr₃ showed good photostability as the photoemission spectra in 5.6(b) and (c) remains unchanged, while gradual increase of the spectra for FAPbBr₃ over time indicates its instability under prolonged 272 nm irradiation in 5.6(a). From these results, CsPbBr₃ single crystal was deemed the most stable among the three and thus TR-2PPE experiment was carried out with CsPbBr₃.

Electron Dynamics in CsPbBr₃ Single Crystal

Figure 5.7: Figure (a): 2PPE spectra of CsPbBr₃ single crystal under 515 nm pump at 5 $\mu\text{J}/\text{cm}^2$ and probed at 270 nm at 1 nJ/cm^2 and (b): deconvoluted pump-induced difference spectra at 2.6 ps, with four spectra features 1, 2, 3, and 4 in ascending order.

TR-2PPE experiment was performed at 515 nm pump wavelength and probed at 272 nm wavelength at 5 $\mu\text{J}/\text{cm}^2$ and 1 nJ/cm^2 respectively. The 2PPE spectra collected at various delay times are shown in Figure 5.7(a). As described in Section 5.2.1, the TR-2PPE signal appears as an additional pump-induced contribution to the steady-state probe background signal shown in Figure 5.7(b) for the difference spectrum at 2.6 ps. The deconvolution contains four conduction band states labelled 1, 2, 3 and 4 after deconvolution. The conduction band minimum located 0.58 eV above E_F in this work is consistent with a published study using inverse photoemission spectroscopy[4] which reported it to be 0.6 eV above E_F . This n-type surface contradicts with the expected Fermi level position near midgap[5] of 1.11 eV from conduction band minimum due to the observed low carrier concentration of $\sim 10^9 \text{ cm}^{-3}$ [6] in CsPbBr₃ single crystals. Therefore, it is likely that surface defects have changed the surface doping level supported by the XPS measurements

shown in Figure 5.8, where elemental composition analysis in Table 5.1 shows a halide deficient surface which makes the surface more n-type[7].

Figure 5.8: XPS of CsPbBr₃ single crystal: (a) wide scan, (b) Cs 3d^{5/2}, (c) Pb 4f and (d) Br 3d.

Table 5.1. Elemental composition in CsPbBr₃ single crystal.

% element	Cs	Pb	Br
Stoichiometric	20.0	20.0	60.0
Measured	21.3	22.2	56.5

Figure 5.9: (a): Time-resolved kinetics of CsPbBr₃ single crystal probed at 1.07 eV above E_F , (b): Area representing the population of states 1, 2, 3 and 4 against delay time.

Time-resolved kinetics probed at 1.09 eV above E_F is shown in Figure 5.9(a). The dynamics showed a slow rise of 19 ps, which is attributed to differences between the regions excited by the pump and probe together with the diffusion of carriers towards the top surface for the photoelectrons to escape the surface. The optical excitation volume is dependent on the material's absorption coefficient which is a function of wavelength. In this case, the pump photon energy used was close to the band edge of CsPbBr₃ hence penetrates deeper to the bulk of the crystal, therefore initial photocarriers were generated in that region. On the other hand, short wavelength UV light having shorter penetration depth is absorbed primarily

at the surface region[8]. Furthermore, the effective sample probing depth for the TR-2PPE experiment is confined to near surface region of ~ 5 nm which is limited by the inelastic mean free path of electrons in solids[9]. Considering differences between the sample probing depth and typical optical penetration depths in ~ 100 nm where photoexcited carriers are generated, it is reasonable to assume part of the photogenerated carrier population diffuses to the near surface and interact with the probe before escaping the surface unimpeded by inelastic collisions within the solid. The subsequent dynamics showed a long decay lifetime fitted to be 4 ± 3 ns. The large error was attributed to excessive noise from instrumental limitations and therefore the 2PPE spectra at various delay times were taken to look at their state dynamics in more detail. For each delay time, the pump-induced spectra was deconvolved and the area representing each state was calculated to determine its population at the particular delay time. The data points are plotted in Figure 5.9(b), which show that state 2 maintains steady population within ~ 200 ps while states 1, 3 and 4 continued to rise, thereafter all four states exhibited similar dynamics as shown in Figure 5.9(a). The extremely slow cooling of hot carrier states 3 and 4 arising from carrier-carrier scattering is rather surprising compared to the findings of a similar study[10] which reported hot carrier cooling time constant of 0.7 ± 0.1 ps with above band gap excitation. Despite the large noise, the obtained experimental value of 4 ± 3 ns lifetime probed at 1.09 eV above Fermi level is appreciably longer than most previously reported values which are in picoseconds regime or shorter.

To explain the long lifetime observed in this work, the widely reported hot phonon bottleneck might not be a suitable, as the lack of quantum confinement of carriers in single crystal results in more available phonon modes as loss channels for hot carriers which makes the hot phonon bottleneck effect less dominant, thus

hot carriers would be expected to cool quickly. Rather, this would be better associated with strong band filling of band edge carriers which inhibits carrier cooling, similar to that reported by Fang *et al.*[11] on FASnI₃ thin films, but with a major difference of pumping under resonant excitation in this work. Band edge states are instantaneously populated under resonant excitation, unlike after a delay associated with carrier relaxation processes such as phonon emission or hot-phonon bottleneck effect when exciting well above the band gap. Owing to longer carrier lifetimes[12] of perovskite single crystals compared to their polycrystalline thin film counterparts, band edge states remain occupied longer as their carriers take a longer time to recombine. Therefore, hot carriers generated either through carrier-carrier scattering or band filling are unable to relax to the occupied band edge states leading to a prolonged cooling process.

Present research on hot carrier dynamics in perovskites has largely focused on the cooling of hot carriers generated by above-gap excitation on solution-processed perovskite films or nanocrystals[10, 11, 13–22]. This work differs from the reported ones by studying hot carrier dynamics in single crystals pumped at resonance excitation. Existing single crystal studies on hot carrier dynamics do not involve pumping the sample at resonance[10, 16, 17]. Although some measurements of hot carrier dynamics under resonance excitation were performed[23–28], such studies in single crystals are not investigated in detail to the best of knowledge. Even though the effect of band filling on hot carriers has been elucidated[11], its significance towards hot carrier dynamics is still less understood in perovskites. The carrier cooling process in quantum confined systems is typically observed to be much slower compared to its bulk system, for instance by up to two orders of magnitude in GaAs[29]. Therefore, the observation of long hot carrier lifetimes of CsPbBr₃ single crystal in the nanosecond regime is surprising and suggests that the effects of band filling on carrier cooling dynamics become pivotal for such systems. It

is also crucial that band edge carriers are long-lived to hinder the relaxation of hot carriers. This work, though preliminary at this stage, explores an alternative mechanism of prolonged hot carrier cooling which may give rise to the possibility of harnessing hot carriers from single crystals.

At this stage, the TR-2PPE system is limited by poor energy resolution and signal-to-noise ratio. These limitations pose challenges in performing pump fluence dependence measurements which are important to determine the extent of band filling in the cooling dynamics. More experiments can be performed to investigate this with improvements to the present equipment such as upgrading the electron analyser with improved energy resolution down to ~ 1 meV which facilitates fitting the high energy tails of 2PPE spectra with a Boltzmann distribution to determine carrier temperature and improving the sensitivity of the instrument so that short time decay dynamics can be resolved clearly.

5.3 Summary

In this chapter, hot electron lifetime of 0.26 ± 0.1 ps in evaporated MAPbI₃ was successfully replicated through TR-2PPE on evaporated MAPbI₃ pumped at 520 nm, $4.5 \mu\text{J}/\text{cm}^2$ fluence and probed at 270 nm, $0.2 \mu\text{J}/\text{cm}^2$ fluence, which corresponds well with published results. However, an unaddressed issue of rapid degradation by light was inadvertently observed from changes in photoemission spectra in a span of ten minutes. A study to resolve this photodegradation issue shall be discussed in the subsequent chapter. The family of APbBr₃ (A=Cs⁺, MA⁺ or FA⁺) single crystals was then chosen for resonantly pumped TR-2PPE study with anticipation of better stability under light. A photodegradation test using UV light ($\lambda=400$ nm or 272 nm) showed that CsPbBr₃ was the most stable among the three, which was then chosen for the TR-2PPE experiment. CsPbBr₃ was pumped using 515 nm at $5 \mu\text{J}/\text{cm}^2$ fluence and probed at 272 nm wavelength using $1 \text{ nJ}/\text{cm}^2$ fluence. The

conduction band region of CsPbBr₃ showed four band states, with the conduction band edge and two uppermost excited states having a slow rise of 19 ps, likely due to carrier diffusion from deeper regions towards the crystal surface before it could be probed. Subsequent decay dynamics with 4 ± 3 ns lifetime were observed for all states, which is surprisingly long compared to reported TR-2PPE hot carrier cooling lifetimes in the range of ~ 1 ps. The long decay dynamics of hot electron states possibly arises from strong band filling of the characteristically long-lived band edge carriers of perovskite single crystals under resonant excitation. This band filling effect inhibiting carrier cooling was reported by Fang *et al.*[11] on FASnI₃ thin films and could be prolonged in single crystals owing to longer band edge carrier lifetimes compared to polycrystalline thin films[12], causing the hot electrons to cool more slowly in this case. This preliminary finding of long-lived electron dynamics of CsPbBr₃ single crystal at resonance excitation demonstrates the influence of sample configuration and excitation energies towards the dynamics of hot electrons, which complements optical studies which do not distinguish electron and hole dynamics of hot carriers. Future work to perform better systematic study to investigate the origin of this anomalous phenomenon would open up a branch of hot carrier dynamics in the presence of low lying band edge carriers.

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Mitigating Light-Induced Instability in MAPbI₃ Perovskites

The issues of photostability encountered during the TR-2PPE experiment in chapter 5 are addressed in more detail here. The wide ranging effects of photodegradation shall be first put into context for both perovskite device research and fundamental optical studies followed by the attempts to improve photostability in devices. However, these solutions are not suitable to improve the photostability, as the materials involved are either reactive towards the harsh deep UV light in optical experiments or change the intrinsic property of perovskites which obscure accurate measurements during the experiments. A solution is proposed here using Hindered Amine Light Stabilisers (HALS), a class of compounds which are derivatives of 2,2,6,6-tetramethylpiperidine, originally used to stabilise organic polymers to enhance their durability under UV light. Extensive film characterisation and optical studies were performed to investigate the physical and chemical effects on solution-processed MAPbI₃ films by doping four different representative HALS compounds through the antisolvent washing step, followed by UV photodegradation studies of the doped films. The influence of chemical functional groups and structures of the

HALS compounds on the crystallinities and morphologies of their resultant films is discussed, as well as their impact on UV photostability to determine the mechanism which HALS can enhance UV photostability. Optoelectronic enhancements of the doped films and possible mechanism are also discussed.

6.1 Introduction

Throughout the development of perovskite solar cells, photostability is a major concern that needs to be addressed for further progress towards commercialisation. This phenomenon appears to affect the lead iodide materials more than the other perovskites like those in the bromide family, which is likely due to weaker chemical bonds from the larger iodide ion. However, only the lead iodide perovskites are suitable for photovoltaics due to their smaller band gaps of ~ 1.55 eV. Therefore, there is a need to mitigate light induced degradation in lead iodide perovskites as much as possible, particularly in the prototypical MAPbI₃. Studies have shown that light-induced degradation can either occur by itself, or in combination with moisture, oxygen, heat or vacuum[1–8], whereas others indicate that interfaces between MAPbI₃ and the mesoporous TiO₂[9] or Al₂O₃[10] also play a role in the degradation process. A spectral dependence study shows that the more energetic UV-B band is more damaging towards MAPbI₃ films as compared to UV-A[11]. Another similar study[12] demonstrates that MAPbI₃ undergoes photobrightening effects under irradiation wavelengths above 520 nm while it undergoes photodegradation under light irradiation of wavelengths below 520 nm which likely involves the photoexcitation of residual PbI₂ and goes to show that UV damage is more pronounced with increasing photon energies. Therefore, studies to elucidate the mechanism of photodegradation as well as slowing its process in devices becomes crucial. Initial studies proposed that the desorption by light of oxygen adsorbed at MAPbI₃/meso-TiO₂ interface creates an instability in standard DSSC type solar

cells, and proposed to use mesoporous Al₂O₃ to circumvent this problem[9]. However, study also shows that MAPbI₃ also decomposes under light even with the mesoporous Al₂O₃ interface[10]. Several mechanisms of light-induced degradation were proposed, such as the formation of polaronic states from lattice strains and molecular orientations[13], formation of free radical species like superoxides[1, 4, 10], localised traps[14], and ion migration[15]. Furthermore, this problem is apparently not restricted to MAPbI₃, which has also been found to extend towards mixed halide perovskites[14]. It is apparent that the problem of photodegradation has to be resolved for perovskites to be used practically in devices.

Furthermore, photodegradation of perovskites also affects optical measurements of perovskite as evidenced in the preceding chapter of this work, where TR-2PPE studies on MAPbI₃ showed drastic changes of photoemission spectrum under prolonged exposure to deep UV probe even at low excitation fluence in the nJ/cm² regime. Thus, results of optical measurements should be placed under scrutiny, particularly those involving UV light. On the other hand, solutions which enhance UV stability of perovskites in optical measurements without unintentionally modifying its intrinsic properties as much as possible would be extremely desirable for subsequent engineering of stable perovskite devices.

Studies conducted to overcome UV degradation problems have placed more emphasis toward practical devices. In general, the photocatalytic property of TiO₂ where formation of deep traps due to the reaction between photogenerated holes and oxygen at surface oxygen vacancies appears to be a major cause of UV degradation in perovskite solar cells. Therefore, various strategies were implemented to circumvent this issue through interface modification or using UV downconverters to reemit UV photons in the visible region before reaching the perovskite layer.

UV stability of perovskite solar cells can be improved by replacing the mesoporous TiO₂ with other suitable electron extraction layers, such as an insulating mesoporous Al₂O₃ scaffold[9] and mesoporous SnO₂[16] which also enhances electron injection from perovskite to the mesoporous SnO₂ layer. Ga-doped SnO₂ which drastically reduces the trap density in SnO₂ enhances its solar cell performance besides it being UV stable[17]. Shin *et al.* replaced TiO₂ with lanthanum-doped BaSnO₃ perovskite in a planar heterojunction configuration due to its unusually high room temperature electrical mobility and poor UV photocatalytic activity[18]. The use of 2D atomically stacked titania having less oxygen vacancies as a transport layer was shown by Chen *et al.* to be effective at reducing UV degradation in solar cell devices[19]. Liu *et al.* found processed Li-doped C₆₀ electron transport layer having better interface energetic matching and enhanced electron mobility enhances the UV stability in air[20].

Several works highlight the use of interlayer materials between perovskite and the electron extraction layers to prevent direct contact, thus mitigating UV degradation. Interlayer compounds such as SrO[21], sinapoyl malate[22] and SnO₂[23] were used in devices with DSSC configuration to enhance their UV stability. Cesium halides[24, 25] and silane coupling agents[26] as interlayers have been also shown to enhance UV stability in planar perovskite solar cell devices.

UV downconversion materials are used in perovskite solar cells to convert UV light into the visible to overcome the problem of UV stability of perovskite. Materials like Sr₂CeO₄:Sm³⁺[27], YVO₄:Eu³⁺[28], phosphor-in-glass[29] and photocurable fluoropolymers[30] were used for such purposes which enhances the UV stability in perovskite solar cells. However, this particular approach is not relevant to this work as the main focus is to improve photostability of perovskites to study its intrinsic properties under light exposure.

In addition, current interlayer materials can create additional problems, such

as photodegradation of UV absorbers[31] and changing the surface properties of the perovskite absorber layer. Therefore, an effective solution to the issue of photostability should address its underlying cause without such additional problems.

Figure 6.1: Chemical structure of 2,2,6,6-tetramethylpiperidine.

To this end, we propose a solution to tackle the photostability issue using Hindered Amine Light Stabilisers (HALS), a class of compounds which are derivatives of 2,2,6,6-tetramethylpiperidine, originally used to stabilise polymers and plastics from UV damage by free radical formation[32]. The chemical structure of 2,2,6,6-tetramethylpiperidine is shown in Figure 6.1. In this aspect, HALS can be a suitable class of candidate to reduce the photodegradation process from superoxide free radical formation caused by the addition of photoexcited electrons of perovskite to available oxygen, forming O_2^- free radical. This class of compounds has other advantages which make HALS desirable, one of which is being durable due to its mechanism of action by the Denisov cycle[33], therefore it only needs to be introduced by a small amount (~ 0.1 to 1 wt%) and still remains stable for a long time. Additionally, HALS compounds do not absorb in UV region, which makes HALS useful in spectroscopy as this class of dopants should not interfere with the UV light used in TR-2PPE experiments[34–36]. At present, there has been a report of implementing HALS to improve stability of MAPbI₃[37]. However, the influences of chemical and structural characteristics of these compounds on the films’ physical and optoelectronic properties along with identifying factors to enhance film photostability have not been studied in detail, hence significant

avenues exist to improve the use of HALS for greater photostability of perovskite films.

6.2 Results and Discussion

6.2.1 Selection Criteria of Dopants

Since HALS is a class of compounds which are derivatives of 2,2,6,6-tetramethylpiperidine, four of them are selected and tabulated in Table 6.1, along with two UV absorbers which were chosen as a comparison of stability under UV light. The compounds are abbreviated for easy reference and chemical structures for both the HALS and UV absorbers are shown in Figures 6.2 and 6.3 respectively. These HALS compounds were ingeniously chosen for considerations of geometry and functional groups of compounds which might influence the doping process of the perovskite. The compounds H-1 and H-2 are largely similar in a sense that both are elongated, having two 2,2,6,6-tetramethyl-4-piperidyl type side chains. However, the hindered amine groups in H-2 are substituted with the long octyloxy side chains, which might enhance the hydrophobicity of the film. The compound H-3 is a polymer which has a physical passivation effect on the film. Lastly the compound H-4 is 4-amino-2,2,6,6-tetramethylpiperidine, which has an additional amine group which could enhance the chemical bonding with [PbI₆]⁴⁻ octahedral much like the ammonium groups in MA⁺ and FA⁺. H-4 is the HALS used in the single published study. These compounds shall then be screened for photostability under UV irradiation.

Table 6.1. Chemicals used as dopants for this work.

Chemical Name	Sample	HALS/UV absorber
Bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate	H-1	HALS
Bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl)- sebacate	H-2	HALS
Poly[[6-[(1,1,3,3-tetramethylbutyl)amino]- -s-triazine-2,4-diyl]-[(2,2,6,6-tetramethyl-4- piperidyl)imino]-hexamethylene-[(2,2,6,6-tetra- methyl-4-piperidyl)imino]	H-3	HALS
4-Amino-2,2,6,6-tetramethylpiperidine	H-4	HALS
2-(2H-Benzotriazol-2-yl)-4,6-di-tert-pentylphenol	A-1	UV absorber
2-(2H-Benzotriazol-2-yl)-4-methyl-6-(2- propenyl)phenol	A-2	UV absorber

Figure 6.2: Chemical structure of HALS compounds used in the experiment.

Figure 6.3: Chemical structure of UV absorber compounds used in the experiment.

6.2.2 Screening of Suitable Dopants

To screen suitable dopants for MAPbI₃, a preliminary experiment using UV light irradiation over 15 minutes was performed on each of them to determine their photostability through changes in photoemission spectra. The wavelength of the UV light was 270 nm, with fluence of 3 nJ/cm² from a regenerative amplifier after third harmonic generation. The results in Figure 6.4 show that the HALS compounds are practically inert to UV light irradiation compared to those of the UV absorbers. Therefore, subsequent experiments shall be performed with only HALS compounds to study their effects on photostability enhancements in MAPbI₃.

Figure 6.4: Changes in photoemission signal over 15 minutes for: (a) H-1, (b) H-2, (c) H-3, (d) H-4, (e) A-1 and (f) A-2.

6.2.3 Film Preparation and Sample Quality

These HALS compounds were individually doped into single step solution-processed MAPbI₃ samples via the antisolvent treatment using toluene. The MAPbI₃ concentrations were 40wt% and 10wt% in DMF to make samples for non-optical and optical experiments respectively. The dopants were dissolved at 2wt% concentration in toluene as the antisolvent, and the doped antisolvents were dropped at the third second during twelve-second spincoating processes at 5000 rpm. Subsequently, the films were annealed at 100°C for 30 minutes which complete the fabrication process. The whole fabrication process is illustrated by Figure 6.5.

Figure 6.5: Schematic of the fabrication process of HALS-doped MAPbI₃ films.

Basic film characterisation techniques were performed on the HALS-doped films to determine their film quality. Firstly, linear absorption spectra in Figure 6.6(a) show that the doped films have similar absorption features as the control sample and the Tauc plots in Figure 6.6(b) show that the doped films have slightly larger band gaps.

Figure 6.6: Linear absorption of the HALS-doped MAPbI₃ samples showing: (a) absorbance and (b) normalised Tauc plot with the obtained band gap values shown in the legend.

XRD was performed to characterise crystallinity of the HALS-doped films. The XRD spectra of doped samples at the top of Figure 6.7 show prominent peaks of

the various orientations of MAPbI₃ unlike the control MAPbI₃ sample which has predominant (110) orientation. The peak assignments were verified with reported literature[38] and shown at the bottom of Figure 6.7. Here, it can be deduced that HALS compounds cause the perovskite crystallites to form at various orientations, perhaps due to the additional viscosity of the antisolvent with doping affecting film formation. The presence of (110) peak orientation in all samples shows that these HALS compounds do not alter the lattice structure of MAPbI₃ significantly by the doping process.

Figure 6.7: XRD pattern of HALS-doped and control MAPbI₃ samples (top) and that of ground MAPbI₃ single crystals (bottom)(Adapted from Ref. [38] with permission from *The Royal Society of Chemistry*). Inset: (110) orientation of HALS-doped and control MAPbI₃ samples.

The surface morphologies of HALS-doped samples were determined using AFM

in Figures 6.8(a)-(e), which show that doping with HALS generally gives larger grain size compared to the control, with the exception of H-2, likely due to long octyloxy side chains breaking up the perovskite crystallites during the spincoating step. It is worth noting that H-4 doped sample provides rough surface morphology as seen by the wide range of depth of ~ 90 nm. The SEM images in Figures 6.9(a)-(e) correspond relatively well to the AFM images, as surfaces of H-1 and H-3 doped samples appear relatively smoother than those of H-2 and H-4. Furthermore, bright features in SEM imaging associated with strong backscattering from heavy elements[39] appear on the rough surface of H-4 doped sample, suggesting the presence of heavy elements from uncoated perovskite on the surface which are studied in detail in the next section.

Figure 6.8: AFM morphology of (a) control MAPbI₃, (b) H-1, (c) H-2, (d) H-3, (e) H-4 samples.

Figure 6.9: SEM images of (a) control MAPbI₃, (b) H-1, (c) H-2, (d) H-3, (e) H-4 samples.

Surface elemental composition was characterised using XPS. The results in Figure 6.10 show that the peaks belonging to perovskite are greatly diminished in general for the sample doped with H-3. This could either be due to the polymer washing away the perovskite or it acting as a passivating layer on top of it. The plot of XRD (110) peak in Figure 6.7 inset shows that the (110) peak for H-3

Table 6.2. Elemental ratios and binding energy positions for I 3d^{5/2}, Pb 4f^{7/2} and N 1s of MAPbI₃ for the HALS-doped and control samples. Values for H-3 could not be determined due to complete physical passivation of the perovskite surface by dopant.

Sample	Elemental ratio		Binding Energy (eV)		
	I/Pb	Pb/N	I 3d ^{5/2}	Pb 4f ^{7/2}	N 1s
Control	3.3	1.1	619.6	138.8	402.9
H-1	3.2	0.6	619.8	139.1	402.6
H-2	3.9	0.9	619.6	138.8	402.8
H-4	3.6	0.9	619.7	139.0	402.6

doped sample does not disappear which confirms that H-3 polymer does not wash away the perovskite, but has formed a physical passivation layer on top of the perovskite. The H-3 polymer is able to have almost complete coverage over the perovskite film, likely due to its large molecular size which makes it immobile during the antisolvent treatment. The elemental compositions and binding energy positions for various elements are tabulated in Table 6.2. Some differences of the HALS-doped samples compared to the control are attributed to interactions between dopants with the perovskite during washing and result in different surface characteristics. The difference in binding energies observed might point towards the creation of additional interface dipoles which deserves further study. In summary, doping with HALS compounds creates widely varying surface characteristics which is sensitive to their geometric and chemical structure.

Figure 6.10: XPS characterisation of HALS-doped and control MAPbI₃ samples: (a) wide scans, (b) Pb 4f, (c) I 3d, (d) C 1s, (e) N 1s and (f) O 1s.

The characterisation performed on the HALS-doped samples shows generally decent film qualities, and the next section shall be devoted to determine the photodegradation properties of HALS-doped samples. Subsequently, the interplay of

various factors such as film surface quality, crystallinity, along with the chemical structure and functionality of HALS compounds shall be discussed in further detail, followed by their effects on the films' optoelectronic properties.

6.2.4 Photodegradation of HALS-doped MAPbI₃

Photostability of the HALS-doped samples were benchmarked using photoemission signals under UV light and compared to the control sample by irradiating them at 270 nm wavelength at 3 nJ/cm² over the span of 60 minutes using the same regenerative amplifier source. Figure 6.11(b)-(f) describes the photoemission changes of the samples over first 15 minutes. Intensity changes throughout 60 minutes of UV irradiation is summarised in Figure 6.12. The intensity changes were referenced to the initial photoemission spectra in each sample. This is justified as the initial spectra of all samples shown in the inset of Figure 6.11(a) are similar, thus likely represent the characteristic photoemission features of CH₃NH₃PbI₃. Hence, the characteristics of HALS being inert towards UV light is demonstrated. Differences in energy positions of photoemission signals are attributed to differences in work function by applying HALS compounds. From there, it can be seen that for samples doped with H-1 and H-3 compounds showed smaller intensity changes than that of the control sample, whereas it is the opposite for H-2 and H-4. To quantify such changes, the values after 60 minutes of irradiation are summarised in Table 6.3 and compared against the control sample. Samples doped with H-1 and H-3 showed decent improvements of 39.1% and 59.2% respectively, whereas those doped with H-2 and H-4 showed more severe photodegradation compared to the control sample. The interplay between sample characteristics and photodegradation shall be discussed in the subsequent section to investigate such widely varying stabilisation effects by from doping the various HALS compounds.

Figure 6.11: Photoemission spectra changes showing: (a) initial states for each of the samples, and the inset overlapping all spectra to compare spectral features, and photoemission spectra changes over fifteen minutes for control sample (b), H-1 doped sample (c), H-2 doped sample (d), H-3 doped sample (e) and H-4 doped sample (f).

Table 6.3. Intensity changes and comparison with the control sample for each sample after 60 minutes of UV irradiation. (Uncertainty attributed within 5% for Intensity ratio.)

	Control	H-1	H-2	H-3	H-4
Intensity ratio	1.62	0.99	3.40	0.66	7.42
Comparison with control	-	0.61	2.10	0.41	4.58
Improvement (%)	-	39.1	-110.3	59.2	-358.1

Figure 6.12: Area intensity changes over 60 minutes of UV irradiation for control sample (red circle), H-1 doped sample (yellow square), H-2 doped sample (grey down triangle), H-3 doped sample (cyan side triangle) and H-4 doped sample (purple diamond). Uncertainty of the data points are within 5% of the intensity ratio values.

6.2.5 Discussion

The enhancements in photostability from samples doped with H-1 and H-3 compounds coincide with smoother film surfaces observed with AFM in these two samples, which indicate some correlation between sample morphology and photostability. Doping of HALS compounds on MAPbI₃ reduces the crystallinity of the films in general and appears to have no direct correlation towards the photostability. This shows that film crystallinity has little impact on the chemical nature of photodegradation but may have some significance towards device applications as will be discussed further below. The comparison between surface morphological and bulk crystal structure against the films' photostability above implies that surface characteristics of the films play a more significant role in enhancing the photostability of films using HALS. The chemical structures of these HALS compounds play a critical role towards sample morphologies. The elongated planar structure of the H-1 compound enables it to conform appropriately to the perovskite surface. In contrast, the long octyloxy groups of H-2 compound might disrupt the surface film formation as well by breaking up the crystallites into fine grains. The coverage of H-2 compound on the perovskite surface is poor which adversely affects its photostability. On the other hand, the almost complete coverage owing to large molecular size of polymeric H-3 compound leads to greater contact between the hindered amine groups and perovskite film to achieve desired stabilisation effect while preserving the perovskite bulk in the process. Hence, proper coverage of the perovskite film is important in improving photostability using dopants of large molecular sizes like H-3. Chemical passivation effects also exist by chemical interaction between protic amine groups in HALS compounds and Pb²⁺ forming Pb-alkylamide bonds[40, 41] induced by the soft Lewis acidity of Pb²⁺. On the other hand, the effect of small molecular size in the case of films

doped with H-4 compound, may have caused the influence of Pb-alkylamide bonding to over dominate and detrimentally affecting film formation to produce the rough morphology in Figure 6.8. Hence, H-4 doped sample exhibits poorer photostability than control by 358.1% due to the large surface exposure of the film to UV light from poor coverage. At this point, it should be noted that the mentioned physical and chemical passivation effects are distinct from the photostabilisation process of the hindered amine functional groups, and a balance between the two passivation effects maximises the photostabilisation potential. Functionality wise, it would suggest that physical passivation nature of H-3 compound is required to achieve the best photostability among the four HALS compounds compared to possible benefits bought upon by the other HALS compounds. From this work, the intricate interplay between chemical and structural characteristics of these HALS compounds, together with surface/bulk film characteristics, and surface morphology affecting the outcome of photostability is demonstrated which has not been studied, but is crucial in enhancing the photostability of perovskites. Similar spectra features observed across all samples as shown in the inset of Figure 6.11(a) is also a good indication that these HALS compounds have little interfere with the photoemission process.

Film crystal orientations measured with XRD can provide some idea on the practical implications of doping perovskite film with HALS compounds. It has been reported that oriented perovskite films are generally preferred for favourable charge extraction for photovoltaic devices, due to enhancements of carrier mobilities and the lowering of trap densities[42] resulting in higher J_{sc} and lower series resistance R_s [43, 44]. This is also evidenced for 2D perovskite layers[45–47] where the fabrication of vertically aligned perovskite layers enhances the solar cell efficiency significantly. Therefore, oriented MAPbI₃ films which give rise to enhanced mobilities are not suitable for light emitting devices (LEDs), as the free carrier

dominant nature along with their high mobilities would result in high probability for non-equilibrium carriers to be captured by rare non-radiative centers in MAPbI₃[48]. The XRD results of Figure 6.7 show that the perovskite becomes less oriented as various peaks aside from (110) plane are prominent in the doped films as compared to the undoped films. This suggests that the doped films are suited for LED instead of solar cell application.

In order to investigate the influence of HALS compounds on the photoluminescence properties of MAPbI₃ which is relevant for LEDs, PL-based measurements were performed to compare the best (H-3) and worst (H-4) samples against the control to elucidate various aspects of doping on their PL lifetimes, trap densities, PL quantum yield and diffusion lengths.

The radiative properties of the samples were determined with TR-PL spectroscopy using a streak camera setup. The results in Figure 6.13 show significant lifetime enhancements by doping MAPbI₃ with HALS compounds H-3 and H-4 from 7.2 ± 0.1 ns to > 50 ns for the doped samples. This is likely due to the reaction between PbI₂ and protic amine groups of the HALS compounds to form Pb-alkylamide impurities which passivates the non-radiative Pb⁰ defect formation during the doping process leading to the enhancements in PL lifetimes[41].

Figure 6.13: TR-PL spectra of control MAPbI₃ (black squares), H-3 doped (blue upward triangles) and H-4 doped (red circles) films.

Although doping the perovskite with HALS compounds increases their carrier lifetime, it is not a good measure of the potential for optoelectronic applications by itself as it has to be correlated with quantum yield measurements. The enhancement in radiative lifetimes of the doped samples suggests similar trend in their quantum yields. The quantum yield measurements were performed using an integrating sphere which collects all scattered excitation and emission light. Samples were excited with 532 nm CW laser source at 5 mW for the doped samples, and 15 mW for the control sample due to the absence of PL emission signal at 5 mW. The exceedingly low PL emission of the control sample requires high excitation power which caused blooming in the CCD. Therefore, the spectrometer response was calibrated against laser power using a blank quartz substrate as shown in Figure 6.14(a). Calibrated counts were proportional to their corresponding integrated

counts in the linear regime within 0.5 mW, and had a cubic relation at high power. Spectra of the scattered laser and sample emission were taken under identical experimental conditions. The PL quantum yield was calculated by the formula of Equation 6.1:

$$\text{PLQY} = \frac{N_{\text{em}}}{N_{\text{abs}}} \times 100, \quad (6.1)$$

where the number of photons absorbed by the sample, N_{abs} is proportional to the difference in integrated intensity between laser light scattered off quartz and that of sample, while the number of photons from sample fluorescence, N_{em} is proportional to the integrated PL intensity. The laser spectra obtained from these samples shown in Figure 6.14(b) were fitted with Voigt profiles. The saturated spectra were fitted using the intensity calibration under high power in Figure 6.14(a). Areas of these fitted profiles were subtracted off from those of the quartz substrates in Figure 6.14(a) at corresponding laser power. The fluorescence spectra of samples are shown in Figure 6.14(c) where counts were integrated for each sample. The calculated quantum yields are summarised in Table 6.4.

Figure 6.14: Results obtained from PL quantum yield experiment: (a) Calibration curve of laser power intensity against measured counts, (b) scattered laser light from the sample (coloured dots) and their fitted curves (solid lines) for control sample at 15 mW (black), H-3 at 5 mW (red) and H-4 at 5 mW excitation (blue), (c) PL emission (coloured dots) and their fitted spectra (solid lines) for control sample at 15 mW (black), H-3 at 5 mW (red) and H-4 at 5 mW excitation (blue) with inset: magnified spectra of the weak PL signal of MAPbI₃.

These results show that doping the perovskite films with HALS compounds increases its PL quantum yield significantly. It is worth noting that despite the

Table 6.4. Quantum yield values for control, H-3 and H-4 samples.

	Control	H-3	H-4
Quantum yield (%)	<1.0	1.9	9.5

possibly small differences between the control sample and H-3, there is no fluorescence observed for the control sample at 5 mW laser power. This indicates that the PL quantum yield of control sample is significantly smaller than 1.0% at 5 mW power excitation. The increase in PL quantum yield correlates well to the radiative lifetime enhancement in the doped films.

Interestingly, the decrease in bulk traps leading to enhancement in PL quantum yield come about despite poor film crystallinity likely points toward the wide ranging benefits of Pb-amine chemistry in enhancing optoelectronic properties of perovskites.

Consequently, trap density study was performed using fluence-dependent time-integrated PL. The results were fitted using a trap density model to obtain the films' bulk trap density n_{TP}^F and that of its surface, n_{TP}^S [49] in Equation 6.2:

$$n_c(0) = \sum_i n_{\text{TP}}^i(0)(1 - e^{-\frac{a_i \tau_0 I_{\text{PL}}}{k}}) + I_{\text{PL}}/k, \quad (6.2)$$

where $n_{\text{TP}}^i(0)$ and k represent the trap density of the i -th state and a fitting constant respectively, τ_0 the radiative lifetime, I_{PL} the integrated PL intensity and a_i the product of the trapping cross section and the carrier velocity.

The fitted data in Figure 6.15 show that doping with H-3 compound decreases both n_{TP}^F from $8.40 \times 10^{16} \text{ cm}^{-3}$ to $5.24 \times 10^{16} \text{ cm}^{-3}$ and n_{TP}^S from $1.30 \times 10^{18} \text{ cm}^{-3}$ to $9.60 \times 10^{17} \text{ cm}^{-3}$ respectively. On the other hand, doping with H-4 compound does not improve n_{TP}^S , but n_{TP}^F decreases from $8.40 \times 10^{16} \text{ cm}^{-3}$ to $1.76 \times 10^{16} \text{ cm}^{-3}$. This might mean that the small molecular size of H-4 compound plays a role

in influencing the bulk trap properties through Pb-amine chemistry during the nucleation process, however the small size of H-4 molecule is unable to improve the films' surface properties. Correlating with the photostability measurements again suggests that reducing the bulk trap density is insufficient to improve the films' photostability, while passivating surface traps to improve surface characteristics is important to enhance the UV stability of MAPbI₃.

Figure 6.15: Fitting of carrier densities against PL intensity using trap density model of Equation 6.2 for (a): MAPbI₃, (b): H-3 doped MAPbI₃, and (c) H-4 doped MAPbI₃.

Even though the doping process suppresses trap states in perovskite, optoelectronic properties are also influenced by other important factors such as charge extraction and diffusion as reported in this section. However, it is worth noting

that the litmus test of optoelectronic properties would be to make real devices after film optimisation procedures, which is beyond the scope of this thesis and shall be pursued in a future work.

With superior film properties of having lower trap density and larger quantum yield by doping the perovskite film with HALS compounds, it is compelling to understand the effects of doping on charge extraction properties of photoexcited electrons and holes in these samples and determine their diffusion lengths. Carrier diffusion length of the samples were determined through TR-PL quenching. An additional PCBM or spiro-OMeTAD extraction layer was spincoated onto each of the control, H-3 and H-4 samples to determine their electron or hole extraction properties respectively. The TR-PL experiment was performed using 600 nm excitation at 0.1 $\mu\text{J}/\text{cm}^2$ fluence. Transients were fitted with either monoexponential or biexponential decay function, where the instantaneous decay rate of photoexcited carriers is assumed to be proportional to its corresponding population of each state. For cases where biexponential function were fitted, the average lifetime is determined using equation 6.3

$$\bar{\tau} = \frac{\alpha_1\tau_1^2 + \alpha_2\tau_2^2}{\alpha_1\tau_1 + \alpha_2\tau_2}, \quad (6.3)$$

where the α_i 's are the pre-exponential factors for their respective lifetimes τ_i .

Figure 6.16: Representative TR-PL plots for: (a) control sample, (b) H-3 and (c) H-4. The uncoated samples are plotted with black squares, samples coated with PCBM plotted with red circles and those coated with spiro-OMeTAD plotted with blue upper triangles.

A representative plot of lifetime quenching is shown in Figure 6.16 and the values obtained for TR-PL lifetimes, film thickness, electron and hole diffusion lengths are summarised in Table 6.5. The results show that doping the perovskite with HALS compounds causes significantly less quenching of its TR-PL lifetime. Therefore, the carrier diffusion lengths for the doped samples are generally shorter than those of the control sample. The electron diffusion length of the doped samples are 90 ± 10 nm and 41 ± 2 nm for H-3 and H-4 respectively, compared to that of

Table 6.5. Values of TR-PL lifetimes, film thickness, electron and hole diffusion lengths for control sample, H-3 and H-4.

	L (nm)	L_D^e (nm)	L_D^h (nm)	τ_0 (ns)	τ_{PCBM} (ns)	$\tau_{\text{spiro-OMeTAD}}$ (ns)
Control	290±6	320±50	170±20	20.0±0.4	4.8±0.2	10.6±0.3
H-3	315±6	90±10	130±20	16.8±0.8	14.1±0.4	12.0±0.2
H-4	385±6	41±2	undeterminable	34.2±0.3	33.2±0.4	37.7±0.4

the control sample at 320±50 nm. The hole diffusion length for H-3 is 90±10 nm, which is shorter than that of the control sample at 170±20 nm. However, the hole diffusion length of H-4 could not be determined as lifetime enhancement was observed at 37.7±0.4 ns from 34.2±0.3 ns for the uncoated H-4 sample. This indicates that hole extraction across H-4:MAPbI₃/spiro-OMeTAD interface is not efficient. It should be noted that the charge extraction process from perovskites, which is used to determine carrier diffusion length, is dependent on the film morphology[50]. Good film morphology optimises charge extraction as the contact interface between perovskite and its adjacent charge extraction layer is enhanced. Therefore, the exceedingly rough surface of H-4 (~23% of film thickness) could have caused in poorer charge extraction across the interface which might have contributed towards the poor PL lifetime quenching, and in turn producing an apparently short diffusion length.

The series of fluorescence experiments show that doping with HALS compounds reduces overall trap density and provided better PL quantum yields. However, film morphology, which plays an important role in carrier extraction, influences the measurement of carrier diffusion lengths in MAPbI₃ doped with H-4 compound. Despite having lower PL quantum yield of films doped with H-3 compared to H-4, H-3 demonstrates superior surface properties of having lower surface trap density owing to good surface coverage which enhances chemical passivation of

non-radiative defects by protic amine groups. These factors influencing surface morphology facilitate charge extraction across its interfaces as shown by its decent diffusion length of at least 90 nm compared to that of H-4. The protic amine functional group in H-4 molecule sacrifices surface property of films although it is able to passivate bulk traps, due to its small molecular size making it more mobile to interact with Pb²⁺ during the antisolvent treatment. Hence, it results in rough surface morphology and poor carrier extraction across the interfaces. The strong correlation between structural/functional group of the HALS compounds and their resulting surface characteristics is reflected well from this series of PL experiments.

6.2.6 Implications of Work

The instability of MAPbI₃ under UV light is a critical issue to overcome, and the solutions sought thus far mostly focus on adding UV absorber materials to block the UV light from reaching the perovskite layer. However, a subtle caveat to this being that UV absorbers can also be susceptible to UV degradation as evidenced in our photostability measurements. Due to this, unwanted side-effects such as unintended chemical reactions could occur during the operation of solar cells. Not only this affects solar cell operations, photostability issues also affects fundamental studies particularly in those which requires UV light such as TR-2PPE. Hence, a class of materials which is chemically inert towards UV light that does not interfere with spectroscopic measurements such as HALS is desirable to resolve the photostability issues of perovskites. An important detail to keep in mind is that photodegradation experiments done in this work is in the UV-C region, whereas the light of AM1.5 starts beyond ~ 300 nm. Therefore, the benchmark used in this work is more harsh compared to solar simulator experiments. We believe that enhancement of photostability by doping HALS compounds in solar cells should be even better. This work highlights the generality of application

and remarkable characteristics of doping HALS in perovskites, and that polymeric HALS should provide the best photostability enhancements.

6.3 Summary

For this chapter of this present work, the UV stability of various HALS and UV absorber compounds were compared to look at their suitability for use under UV light at wavelength of 270 nm using the photoemission spectra over fifteen minutes. It was found that these HALS compounds are practically inert towards UV light, whereas UV absorbers showed severe degradation as the photoemission spectra showed large changes. Thus, the effect of doping different HALS compounds with different chemical structures on the material characterisation such as crystallinity, film morphology, surface chemical property, optical absorption and photoluminescence was investigated. The interplay between the material characteristics and chemical structure contributes to the eventual photostability of the HALS-doped films, which was determined using the photoemission spectra change over one hour. The photoemission spectra in the initial stage of irradiation show insignificant changes across all samples, demonstrating the characteristic inertness of HALS to the UV irradiation. It was found that doping with polymeric HALS H-3 provides the best photostability with 59.2% improvement in photostability compared to the control sample. This is likely due to effective physical passivation of the film surface by the polymer which provides a smooth surface with good coverage without compromising the bulk of the perovskite. In contrast, the use of small molecular HALS with additional amine groups appears to be unsuitable in terms of UV stability due to excessive unwanted strong lead-amine interactions during doping which result in rough films with poor coverage of the HALS compounds. Systematic comparison using PL and TR-PL studies was done between the control sample, best (H-3) and worse (H-4) films to elucidate the influence of HALS compounds on

their photophysical properties. Trap density modelling reveals that doping with H-3 compound reduces bulk trap density from 8.40×10^{16} to 5.24×10^{16} and surface trap density from 1.30×10^{18} to 9.60×10^{17} . Doping with H-4 compound reduces its bulk trap density from 8.40×10^{16} to 1.76×10^{16} , but there is a marginal increase in surface trap density from 1.30×10^{18} to 1.34×10^{18} . These variations in surface and bulk trap densities correlate well to the functionalities of the HALS compounds by their chemical structure and functional groups. PL quantum yield of HALS-doped samples also showed enhancements from $<1\%$ to 1.9% and 9.5% for H-3 and H-4 respectively, which correlates with reduction of bulk trap densities. The doped samples have shorter carrier diffusion lengths compared to the control sample. The electron and hole diffusion lengths of films doped with H-3 compound are 90 ± 10 nm and 130 ± 20 nm respectively, which are shorter than those of the control at 320 ± 50 nm and 170 ± 20 nm. Sample doped with H-4 compound also has shorter electron diffusion length of 41 ± 2 nm compared to the control, but the hole diffusion length could not be determined due to enhancement of its PL lifetime, likely due to poor hole extraction with its rough surface morphology evidenced with the AFM. Doping perovskite with HALS compounds enhances the films' photophysical properties, however the lower crystallinity likely hinders charge extraction which makes these doped films more suited for LED's. This work elucidates the effects of chemical and geometrical structure of HALS compounds on the film quality to improve UV photostability in optical studies.

References

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Conclusions and Future Work

7.1 Conclusions

In this thesis, major issues in surface and interface properties of perovskites are addressed. In the first work of this thesis, apparent upward band bending up to 0.1 eV in FAPbI₃-based perovskites was observed during evaporation of charge extraction layers spiro-OMeTAD and PCBM. Band bending has traditionally been known to arise from the formation of space charge layers to compensate net surface charges. However, this work shows that this factor is not the reason of this apparent upward band bending but it is due to the presence of surface δ -FAPbI₃. This presence of surface δ -FAPbI₃ also causes charge extraction of low lying photoexcited electrons to PCBM to be less efficient, but photoexcited electrons with higher energies get extracted as efficiently as that of holes. It was also found that using the triple cation mixture does not eliminate the presence of surface δ -FAPbI₃, even though this mixture stabilises the α -FAPbI₃ to give one of the highest performing solar cells at present. The presence of surface δ -FAPbI₃ in the interfaces of FAPbI₃-based materials highlight a critical issue to be addressed, as it negates the potential of using FAPbI₃ as a small band gap material.

In the second part of this thesis, the technique of TR-2PPE which incorporates the advantages of time and energy resolution was implemented. In order for the system to be operational, a homemade *LabView* interface was built to link the electron analyser system to the delay stage. The system was calibrated using the image potential state of Cu(111) pumped at 520 nm, $10.5 \mu\text{J}/\text{cm}^2$ and probed at 270 nm, $0.5 \mu\text{J}/\text{cm}^2$, which produced a system resolution of 230 ± 10 fs. This setup was then used to replicate the hot carrier dynamics of evaporated MAPbI₃ at 170K, with a fitted lifetime of 240 ± 10 fs. However, a drastic change of the photoemission spectrum was observed after ten minutes of irradiation by light. Besides, the positive signature of the non-equilibrium carrier distribution at negative $E-E_F$ shows that this is likely to be photodegradation which has been widely known in the research community. Hence, various perovskite materials were sought to select those which showed reasonable photostability during the measurement timeframe. APbBr₃ (A=Cs+, MA+ or FA+) single crystals may be more appropriate due to their lower surface to volume ratio and their relatively stronger Pb-Br bonds, hence systematic studies were performed to determine their dynamics using TR-2PPE. The photodegradation characteristics of the single crystals were done using either 272 nm excitation, $1 \text{ nJ}/\text{cm}^2$ or 400 nm excitation, $8 \text{ nJ}/\text{cm}^2$ irradiation over six minutes. CsPbBr₃ was deemed to be the most stable amongst them and TR-2PPE was performed with resonance pumping with 515 nm, $5 \mu\text{J}/\text{cm}^2$ and probed at 272, $1 \text{ nJ}/\text{cm}^2$. The TR-2PPE signals showed four distinct conduction band states after deconvolution, with the presence of two hot carrier states up to ~ 1 eV above the conduction band edge due to strong carrier-carrier scattering. The conduction band edge and these hot carrier states showed long lifetimes of 4 ± 3 ns, likely due to strong band filling effect of long-lived band edge carriers of single crystal which hinders hot carrier cooling. The large uncertainty is due to instrumental limitations. However, the lifetime obtained for the hot carrier states contrasts

with most reported values of less than 1 ps. It is worth noting that in the reported literature, the CsPbBr₃ single crystal was pumped at 3.1 eV excitation whereas the excitation energy is 2.4 eV in this work. We posit that excitation using a near band gap resonant energy could induce an instantaneous population of band edge carriers whereby any hot carriers generated would experience a bottleneck effect when cascading down to the band edge. This opens a new direction of understanding the dynamics of hot carriers in presence of band edge carriers and would play a crucial role in manipulating hot carriers for prototypical hot carrier solar cells.

The final part of this thesis addresses the challenge of light-induced, particularly UV instability of perovskites by doping MAPbI₃ with HALS. HALS has long been used as an additive in polymers and plastics to overcome degradation by UV light through photo-oxidation. In this work, we look at the intricate interplay between chemical structure, film formation and photodegradation characteristics in HALS doped films. The solution-processed MAPbI₃ films were prepared through a single-step deposition method with toluene antisolvent treatment. Four different HALS compounds were each dissolved in 2 wt% concentration in toluene and introduced in the antisolvent treatment step for the doping process. They were judiciously selected for their geometry and chemical properties: H-1 and H-2 are elongated compounds with two 2,2,6,6-tetramethyl-4-piperidyl end groups, but H-2 has the hindered amines substituted with octyloxy groups which may have added benefit of making the films more hydrophobic; H-3 is a polymeric HALS which enhances physical passivation due to its large molecular size while H-4 possesses an additional amine side group which could enhance the bonding with the [PbI₆]⁴⁻ octahedral like the cations in MAPbI₃. Material characterisation techniques, namely linear absorption, XRD, AFM, XPS and TR-PL were performed to discern the properties of the HALS-doped films. In general, the HALS-doped films gives up to 23 meV

larger band gaps compared to the control film. XRD shows that doping with HALS preserves the crystallinity of MAPbI₃ as evidenced by the (110) crystal orientation, however the films become amorphous shown by the pronounced presence of other orientations. The surface morphologies of HALS-doped films are highly dependent on the chemical structure of the dopants. It was found that doping with H-1 and H-3 give large grains with small roughness, but the grains were finer than the control in H-2 likely due to the overly long molecule disrupting the nucleation process while H-4 gives large pinholes with depth variation about 90 nm likely due to uneven film formation from strong interactions with the reactants. Surface chemical composition using XPS shows slight variation with the control sample in terms of elemental ratios and binding energy positions. However, sample doped with H-3 shows almost indiscernable signals of the perovskite peaks due to good physical passivation of the film surface when analysed together with the corresponding XRD data. TR-PL with 600 nm excitation and 0.15 $\mu\text{J}/\text{cm}^2$ fluence shows lifetime enhancement of all HALS-doped films compared to the control. It might be possible that the piperidine groups in HALS may have the reported benefit of activating dark grains in the perovskite films like the deprotonated pyridine groups. Photodegradation experiments were performed using the change in photoemission signals by exciting the samples using 270 nm light at 3 nJ/cm^2 over one hour. The similar spectra features of all films shows the inertness of the HALS toward the harsh UV light. Films doped with H-1 and H-3 showed improvements in photodegradation by 39.1% and 59.2% respectively compared to the control sample, whereas H-2 and H-4 showed more severe photodegradation by 110.3% and 358.1%. The comparison of the photodegradation characteristics in HALS compared to the control sample correlates well with the film morphology. H-3 performed the best due to the additional factor of superior physical passivation from its polymeric nature. From these results, we have found that polymeric HALS should be used for this method

of doping of MAPbI₃ films, and it is useful in optical experiments involving UV light to prolong the duration to obtain useful data. Due to the harsh UV light exposure in our experiment, we expect HALS to enhance the photostability of solar cells much more, as the solar spectrum only start to extent beyond ~ 300 nm. We also foresee potential for more applicability of HALS in hot carrier cells where excitation photon has higher energy which is more damaging to these devices.

7.2 Future Work

7.2.1 Formation Processes at CH₃NH₃PbI₃ Interfaces

There is currently a research gap in the study of interface energetics. So far, most of the surface and interface studies conducted are performed with an organic overlayer evaporated on top of solution-processed perovskite samples. This configuration has limited the scope of research in the sense that only the interactions between mobile organic functional groups and rigidly fixed ions of perovskites are considered. However, solar cell devices follow a sandwich architecture, whereby the perovskite absorber is sandwiched between an electron and hole extraction layer so that charges can be extracted at the opposite ends. At some point of fabrication, there would be a step where the perovskite is spincoated, thus unintended chemical interactions could happen as the mobile ions of perovskite form at the interface which could affect the charge extraction of photoexcited carriers in perovskite. The procedure with the evaporated devices is also similar. Therefore interface energy level alignment studies with perovskite overlayers by evaporation is proposed to observe species formed at the instance of interface formation along with its energetics to correlate with any effects with charge extraction. Results of these studies would facilitate systematic optimisation of the interface to tune its charge extraction properties.

7.2.2 Hot Carrier Extraction Interfaces

Perovskite has recently been shown to possess long hot carrier lifetimes, which has potential as light absorbers for hot carrier solar cells. However, the extraction of hot carriers in perovskites would require good energy selectivity of the extraction layer and interface charge extraction processes should occur at very short timescales before the hot carriers decay. Thus the selection of suitable hot carrier extraction layers requires additional complexity compared to that of conventional solar cells. A recent work by Li *et al.* demonstrated hot electron extraction at nanocrystal MAPbBr₃/BPhen interface within 1 ps[1]. Here, we propose to study the interface of nanocrystal MAPbBr₃/BPhen to understand why this interface is suitable for hot electron extraction, through determining the type of adsorption BPhen is on the nanocrystal surfaces, and if presence of interface states would be beneficial for extraction of hot carriers. Results gathered from this study would go a long way in making optimal hot carrier extraction interfaces for hot carrier solar cells.

7.2.3 Multifunctional Device Applications using HALS

The potential in applying HALS to MAPbI₃ thin films was demonstrated in chapter 6. The physical passivation effects of H-3 providing the best photostability of MAPbI₃ films, can serve greater usage if H-3 also functions as a charge transport layer. The feasibility of this prospect would be determined using a combination of UPS and device measurements to elucidate interface energetics and carrier transport properties in a real device. A successful demonstration of the multi-functionality of H-3 would save costs of applying additional charge extraction layers to extract the photogenerated charges in addition to prolonging device lifetime which solves this long-standing issue.

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Publications and Presentations

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