Bound excitons in low dimensional halide perovskites

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2017

Chong, W. K. (2017). Bound excitons in low dimensional halide perovskites. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/72894>

<https://doi.org/10.32657/10356/72894>

NANYANG
TECHNOLOGICAL
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**BOUND EXCITONS IN LOW DIMENSIONAL
HALIDE PEROVSKITES**

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2017

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HALIDE PEROVSKITES**

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A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for
the degree of

Doctor of Philosophy

2017

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

Chong Wee Kiang

2017

Abstract

Lasers and light emitting diodes are found in numerous applications in our daily lives. The performance and applications of these diodes are very dependent on the choice of light emitting material. Ideally, these materials should be brightly emitting, solution-processible, low cost, and tunable. Among the vast variety of light emitting materials, three dimensional organic-inorganic halide perovskites are found to inherit these characteristics. As such, their light emitting and optical gain properties have been in the limelight over the past few years. On the contrary, not much attention was given to their low dimensional counterparts, which exhibit bright excitonic emission. In these low dimensional systems, the role of bound excitons cannot be neglected as they are an important species that influences light emitting and optical gain properties. In particular, this work explores the role of bound excitons in these perovskites for optical gain and white emission, which could be attractive for electrically pumped gated laser and white LEDs respectively.

Bound excitons, in particular defect-bound excitons, were found to be one of the problems in limiting low temperature biexcitonic optical gain in $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4$ two dimensional perovskites. In this material, biexcitonic states were found to be populated through free-to-bound excitonic relaxation followed by bound-to-biexcitonic relaxation. Through these relaxation pathways, both free and bound excitonic recombinations can take place, which effectively compete with biexcitonic population inversion build up. Theoretical modelling

revealed a high biexcitonic optical gain threshold, which is consistent with the presence of strongly competing relaxation channels. Low optical damage threshold is another problem that is inherent in this material. This threshold, which is ~ 1 order of magnitude lower than the theoretical biexcitonic optical gain threshold, could impede the path to achieving optical gain.

On the other hand, bound excitons, in the form of self-trapped excitons, are responsible for white emission from low dimensional perovskites, such as $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbCl}_4$ and $(\text{NH}_3\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3)\text{PbBr}_6$. Notably, white emission is only observed in the latter thin films fabricated with excess PbBr_2 . Importantly, these excitons were found to undergo self-trapping at different locations in the two materials, with exciton self-trapping at the organic framework for the former and at the inorganic framework for the latter. Nonetheless, large exciton-phonon coupling strength, which is indicative of self-trapped excitons, was measured from both materials. Self-trapping phenomenon at the organic framework provide a new perspective on the origin of white emission in these systems, which deviates from conventional understanding of self-trapping in inorganic semiconductor systems. These two findings suggest that judicious selection of both organic and inorganic precursors are crucial for developing high efficiency white emitting perovskites.

In retrospect, the presence of bound excitons in low dimensional perovskites serves as a double-edged sword, which either limits optical gain or gives rise to white emission.

Acknowledgements

I would like to express my thanks to Nanyang Technological University Interdisciplinary Graduate School (IGS) for providing me with the scholarship and opportunities that made this work possible.

I would like to express my greatest appreciation and thanks to my supervisor, Associate Professor Sum Tze Chien. I would like to thank him for recruiting me into the group since my undergraduate years. I have gain a lot, especially on optical spectroscopic knowledge, during my six years of research in his lab. I would also like to thank him for his guidance and spending his precious time with me on numerous discussions over these years. He have provided me with valuable advice and new ideas, which have help me a lot through my PhD candidature.

I would like to express thanks to my co-supervisor Professor Subodh Gautam Mhaisalkar on the advices given to my project despite his exceptionally busy schedule as Executive Director of the Energy Research Institute @ NTU (ERI@N). I would also like to thank him for allowing me to use the laboratories in ERI@N for sample preparations and characterizations.

I would like to express thanks to my mentor Assistant Professor Nripan Mathews on guiding me on my research and imparting valuable advices and knowledge on the perovskite system I am working on. I would also like to thank him for the wonderful samples, which made this work possible.

I would like to thank the former Postdoctoral researchers in my lab, Professor Xing Guichuan and Professor Liu Xinfeng. They are the ones that imparted me

Acknowledgements

with essential knowledge and experimental skills on optical spectroscopy since my undergraduate years. I would also like to thank them for the numerous consultation sessions on experimental techniques, data analysis, and literatures during these years. The guidance from them has helped me improved as an experimentalist.

I would like to express my thanks to Mr. Krishnamoorthy Thirumal for spending his time to fabricate the samples and making this project possible. I would also like to thank him for showing and explaining to me on the sample fabrication procedures. He have helped me to understand the perovskite materials in a greater detail.

I would like to thank all the members in my lab and folks in ERI@N who have help me in one way or the other and making this project possible.

Lastly, I would like to thank my parents. They are the most important person in my life and are always there for me. Thank you for taking care of me and being so supportive of what I do these years.

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Abbreviations

2D-OMHP	Two-Dimensional Organometallic Halide Perovskites
3D-OMHP	Three-Dimensional Organometallic Halide Perovskites
ASE	Amplified Spontaneous Emission
BE	Biexcitons
CaTiO₃	Calcium Titanium Oxide
CCD	Charge-Coupled Device
CCT	Correlated Colour Temperature
CIE	Commission Internationale de l'Eclairage
CPA	Chirped-Pulse Amplification
CW	Continuous Wave
DBE	Defect Bound Excitons
DMF	Dimethylformamide
DMSO	Dimethyl Sulfoxide
E_B	Exciton Binding energy

Abbreviations

FE	Free Excitons
FETs	Field-Effect Transistor
fs	Femtosecond
FWHM	Full Width at Half Maximum
GM	Gifford-McMahon
HOMO	Highest Occupied Molecular Orbital
ITO	Indium Tin Oxide
LBO	Lithium Triborate
LEDs	Light-Emitting Diodes
LUMO	Lowest Unoccupied Molecular Orbital
MCP	Micro-channel Plate
meV	Millielectronvolts
<i>m</i>-XDLB	<i>Meta</i> -Xylylenediammonium Lead Bromide
PbBr₂	Lead (II) Bromide
PEPB	Phenethylammonium Lead Bromide
PEPC	Phenethylammonium Lead Chloride
PEPI	Phenethylammonium Lead Iodide
PIA	Photo-induced Absorption
PL	Photoluminescence
PMMA	Poly(methyl methacrylate)

Abbreviations

PMT	Photomultiplier Tube
rpm	Revolutions Per Minute
SE	Spontaneous Emission
SEM	Scanning Electron Microscopy
STE	Self-Trapped Excitons
TAS	Transient Absorption Spectroscopy
TRPL	Time-Resolved Photoluminescence
UV	Ultraviolet
XPS	X-ray photoelectron spectroscopy
XRD	X-ray Diffraction

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[†] These authors contributed equally to this work.

Chapter 1

Introduction

In this chapter, the motivation behind this thesis will first be covered. Two scientific hypotheses to be tested will also be covered. They serve as a beacon to the focus and outcome of this thesis, and will be presented in the objectives and scope sections. Next, the thesis organization will be elaborated to give a clear outline of this thesis. Lastly, novel findings of this work will be summarized.

1.1 Motivation

Light emitting applications and properties of perovskites have been of great interests to the scientific community over the past few years. This interest has led to innumerable literature and achievements from this excellent light emitting material (Figure 1.1). In particular, optical gain and white emitting properties of perovskites (Chapter 2) have been extensively investigated by the community. The biggest motivation behind these studies is attributed to perovskites' potential for technological applications, such as lasers and white light emitting diodes (LEDs). However, to date, a clear understanding of the photophysics behind their optical gain and white emitting properties is still lacking. As such, there is a need to address the knowledge gaps in these properties. These deficiencies will be

Figure 1.1: Timeline depicting notable light emitting achievements in perovskites.

described in the following sections and Chapter 2, and will be addressed in this thesis.

1.1.1 Perovskite Lasers

Semiconductor lasers have a vast variety of applications in areas such as optical storage, sensors, displays, and communications. The demands for these lasers are still surging with their market expected to grow from ~USD 6.12 billion to ~USD 9.52 billion in the next ten years [1, 2]. As such, this has led to extensive efforts in research and development of lasers. The basic requirement for these lasers is the presence of optical gain (Chapter 2.5). In the perovskite family, optical gain phenomenon is by far exclusive to three-dimensional organometallic halide

perovskites (3D-OMHP), with hardly any mention from their two-dimensional counterpart. While lasing action from two-dimensional organometallic halide perovskites (2D-OMHP) cannot be ruled out, it is still surprising that lasing reports from this system are scarcely available. 2D-OMHP, which can exhibit a strong excitonic green emission, could be a potential solution for overcoming the “green gap” or green “valley of death” in semiconductor lasers [3]. In particular, this material system has been extensively investigated for LEDs applications in the 1990s and early 2000 [4, 5]. The “green gap” problem refers to the extreme difficulties in directly obtaining electrically-pumped green lasers without the need for frequency doubling. As of now, emission from most green lasers are generated indirectly via frequency doubling of an infra-red (*e.g.*, 1064 nm) laser emission. Even though a direct green laser diode has been realized and commercialized in 2012 [6–8], its market is generally still in its infancy with untapped opportunities to discover more novel green lasing mediums, such as OMHP.

If lasing can be realized for 2D-OMHP, devices such as electrically pump gated green lasers could be fabricated. The excellent in-plane mobility experienced by charge carriers in 2D-OMHP quantum well is also expected to be better than four-level conjugated organic semiconductor systems exhibiting optical gain [9]. This is especially advantageous for charge carriers injection and recombination. In addition, these low cost materials are easily solution-processible, which is also a plus for keeping device fabrication costs down.

1.1.1.1 Hypothesis I

The difficulty in achieving optical gain could be due to an inherent problem in 2D-OMHP. For all lasing media, population inversion is required to induce optical gain, and it occurs at level 2 in a classical four-level system (Figure 1.2 [10]). Since 2D-OMHP is an excitonic system, level 2 is likely to be an excitonic level.

In excitonic systems, single excitonic gain can only be triggered under certain conditions *e.g.*, presence of carrier-induced Stark effect [11]. On the other hand, biexcitonic gain (Chapter 2.3) has fewer pre-requisites and is commonly observed in excitonic systems. This is also the type of gain that should be expected for conventional 2D-OMHP. Therefore, the lack of optical gain in 2D-OMHP is likely due to a fundamental problem that restrict biexcitons population build-up.

For net optical gain to occur, optical gain must exceed loss. The loss channel in 2D-OMHP could be attributed to the presence of defects and traps, which promotes non-radiative recombination. In particular, defects can be detrimental since localization of excitons at defect sites, *i.e.* formation of defect bound excitons (Chapter 2.3), could limit biexcitons formation and population inversion. On the other hand, one might also attribute exciton-phonon scattering as a limiting factor to obtain net optical gain in 2D-OMHP. However, given the small exciton-phonon coupling strength in narrow emitting 2D-OMHP [12] compared to ZnO quantum well [13] and white emitting 2D-OMHP [14], the possibility of dominant exciton-phonon scattering losses can be eliminated. As such, one can hypothesize that the lack of biexcitonic gain is due to loss channel caused by defects. Consequently, there exists a motivation to investigate the role of defects on biexcitonic recombination kinetics in 2D-OMHP.

1.1.2 White Perovskite Emitters

White emitting light sources are of paramount importance in our daily lives. There are several technologies, such as incandescent, fluorescent, and solid-state lighting, which are capable of generating white light. Out of these technologies, solid-state lighting devices (or LEDs) are gaining popularity over the past few years. In addition, the popularity of white LEDs are still expected to grow with forecasted contribution of 50% to all lighting sale worldwide by 2020 [15]. White LEDs generate less heat, give better quality light output, and are more durable.

Figure 1.2: Classical four level energy level scheme used to describe lasing action. Population inversion occurs at level 2 (also known as the metastable state) with stimulated emission represented by a thick arrow. Figure adapted from Reference [10].

They are also more energy saving and have been forecasted to reduce lighting energy consumption in the United States by 40% in 2030 [15]. This is particularly important since energy is considered as humanity's top 10 Problems for next 50 years [16]. Therefore, great efforts have been devoted to the study and development of white emitting materials.

White emission typically requires a combination of either primary (red, green, and blue) or complementary colors (*e.g.*, blue and orange) to ensure sufficient coverage of the whole visible spectrum (Figure 1.3(a)-(e)). As most semiconductors typically emit over a narrow range, a combination of emitters is therefore required for white emission. Disadvantages of creating white light using multiple emitters are: (i) problem of self-absorption due to spectral overlap (reducing emission efficiency), and (ii) different ageing rate of emitters (evolution of emission profile with time). These problems could be mitigated by using a single

white emitter (Figure 1.3(f)), such as 2D-OMHP [17–20].

Even though 2D-OMHP exhibit white emission, there is still no report of white emitting diodes from this system. Despite this, fundamental studies on intrinsic properties and origins of white emission are still on going. These studies are important as they could potentially guide the fabrication of better perovskite white emitters for devices.

1.1.2.1 Hypothesis II

As of now, self-trapped excitons are widely accepted to be responsible for white emission from 2D-OMHP. In addition, there is also a general consensus that these excitons are self-trapped to the inorganic framework (Chapter 2.3). Albeit this, one could still observe white emission from 2D-OMHP by changing only the organic precursor ([17, 22]). Therefore, one could hypothesize that the organic framework does have a role to play in white emission. Since both organic and inorganic precursors could play a role in white emission, one can also postulate that changing the ratio of either precursor should also have an impact on white emission. Therefore, there exist motivation to study the role of organic precursors, and varying precursors ratio for white emission. Such studies could lead to new insights and design rules for synthesizing newer white emitting perovskites.

1.2 Objectives and Scope

Two main objectives of this work are:

- To understand the role of bound excitons in limiting amplified spontaneous emission (ASE) from 2D-OMHP.
- To understand the role of bound excitons in white emission from perovskite fabricated with stoichiometric and non-stoichiometric precursors ratio.

Figure 1.3: White emission created with different configurations by (a) using a single white emitting layer comprising of different colored emitters, (b) stacking together different coloured LEDs, (c, d) using multiple layers of colored emitters, (e) exciting a red emitter with a blue LED, and (f) using a single white emitting layer. Figure adapted from Reference [21].

These objectives will be fulfilled using ultrafast optical spectroscopy to understand the photophysical properties of selected perovskites. The details of these perovskites can be found in Chapter 3.1. The following aspects are beyond the scope of the thesis and will not be covered:

- Realization of optical gain in 2D-OMHP.
- Optimization of white emitting perovskites (e.g. improving photoluminescence quantum yield).
- Fabrication of light emitting diodes.

1.3 Thesis Organization

This thesis addresses and highlights the roles of bound excitons in low dimensional perovskites for optical gain and white emission. The outline of this thesis is as follows:

Chapter 2 gives an overview and discusses the recent progress or developments in the perovskite family. Excitonic species and the general role of bound excitons in 2D-OMHP will be covered. In addition, optical gain and white emission phenomenon will be discussed. Lastly, the relevance of this thesis in the context of literature will be covered.

Chapter 3 introduces the sample fabrication methods and optical spectroscopic techniques used in this thesis. The rationale for sample selection and optical characterization techniques will also be covered.

Chapter 4 discusses the impact and role of defect bound excitons in limiting optical gain for 2D-OMHP thin film. In addition, several solutions are proposed in this chapter, which may help to achieve optical gain in 2D-OMHP.

Chapter 5 and 6 will cover the role of self-trapped excitons in white emitting perovskites. These two chapters demonstrate that self-trapping of excitons at

both organic (Chapter 5) and inorganic (Chapter 6) frameworks are responsible for white emission from low dimensional perovskites. These chapters also provide insights to new strategies for perovskite white emission.

Chapter 7 concludes this thesis and discusses possible directions to future works. A schematic of the flowchart, which summarizes the thesis outline, can be found in Figure 1.4.

Figure 1.4: Thesis Outline.

1.4 Originality of Findings and Outcomes

The novel outcomes highlighted in this thesis are:

1. Establishing the dominating factors limiting ASE from 2D-OMHP thin film. These factors include:
 - Photodamage threshold which is ~ 1 order of magnitude lower than the calculated ASE threshold.
 - Presence of competing relaxation channels, which limit biexcitonic population inversion build-up.

These findings highlight the challenges in obtaining biexcitonic ASE from 2D-OMHP.

2. Establishing that excitons self-trapping is the main mechanism for white emission from low dimensional perovskites, and white emission from thin film can be influenced by:
 - Perovskite organic framework
 - Excess lead (II) bromide (PbBr_2).

These factors could be overlooked during analysis (since general consensus points to contributions from inorganic framework) and/or sample fabrication (since stoichiometric precursors ratio are usually used). In addition, these findings could lead to new design strategies and also emphasize the importance of both organic and inorganic precursors for perovskites white emitter.

These novel outcomes have been published or are in-preparation for manuscript submission.

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Chapter 2

Literature Review

In this chapter, an overview of the developments in the perovskite field will first be covered. Next, the different types of organometallic halide perovskites, and the dominant charge carrier species in two dimensional perovskites will be presented. The physics behind these species will also be covered. Lastly, questions on the contributions of these species to the optical properties of perovskites, and its relevance to this thesis will be discussed.

2.1 Overview of the Organometallic Halide Perovskites

Perovskite mineral was first discovered in 1839, and was traditionally referred to calcium titanium oxide mineral (CaTiO_3). The structure that CaTiO_3 possesses is known as the perovskite structure. Consequently, compounds having a general formula of ABX_3 , and similar structure as CaTiO_3 were also referred to as perovskites. More recently, perovskites also lend its name to an emerging class of semiconductor known as three-dimensional organometallic halide perovskites (3D-OMHP). This class of semiconductor were found to possess favourable and versatile optoelectronic properties, with potential applications for solar cells [1–

3], LEDs [4–6], lasers [7–9], photodetectors [10, 11], and field-effect transistors (FETs) [12, 13]. Notable achievements from 3D-OMHP include solar cell power conversion efficiency of 22.1 % [1] (from 3.8 % [14] in just 7 years), high LED external quantum efficiency of 11.7 % [15], and ultralow nanowire lasing threshold of 220 nJ/cm² [9]. These are made possible due to their superb properties, such as long charge carriers diffusion length [16], low traps densities, and high gain coefficient [7]. While 3D-OMHP are often in the limelight for superior optoelectronic applications, increasing attention has also been placed on two-dimensional organometallic halide perovskites (2D-OMHP), having a general chemical formula of A₂BX₄ or ABX₄, as an alternative candidate with good optoelectronic properties for solar cells [17], LEDs [18], and photodiodes [19] applications.

2.2 2D-OMHP

The structure of OMHP is made up of two constituents: an organic cation (A⁺) and an inorganic octahedra (BX₆^{4−}), and varies according to their structural dimensionality. The structure of 3D-OMHP consists of repeating units of six corner sharing BX₆^{4−} (blue), with A⁺ (green) embedded within the inorganic cage (Figure 2.1(a)). These constituents form a continuous 3D structural network. On the other hand, the constituents of 2D-OMHP form a 2D layered network of alternating organic and inorganic layers having thicknesses typically of the order of sub-to a few nanometers [20]. This layered configuration gives rise to characteristic periodic X-ray diffraction peaks [20]. The inorganic layers consist of four corner sharing BX₆^{4−} octahedra while the organic layers are made up of organic cations (Figure 2.1(b)). Compared to typical cations found in 3D-OMHP (e.g. Cs⁺, HC(NH₂)₂⁺, CH₃NH₃⁺), the organic cations for 2D-OMHP are generally much larger in size [20, 21]. In addition, 2D-OMHP with chemical formula of either

Figure 2.1: Crystal Structure of (a) $\text{CH}_3\text{NH}_3\text{PbI}_3$ (3D-OMHP), and (b) $(\text{CH}_3\text{NH}_3)_2\text{PbI}_4$ (2D-OMHP). Figure adapted from Reference [22].

A_2BX_4 or ABX_4 could be obtained, depending on the number of ammonium side chains in organic cation. (Figure 2.2).

A variety of methods can be employed to fabricate 2D-OMHP samples. These include mechanical exfoliation [24], solution-processed growth, single source thermal ablation, and thermal evaporation [25]. Solution-processed method, which are facile and most common, allows formation of 2D-OMHP microdisks [26], single crystals, and thin films [27]. In addition, these methods can also result in growth of 2D-OMHP in the $\langle 001 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ direction (Figure 2.3) [28]. In particular, the BX_6^{4-} octahedra for $\langle 111 \rangle$ -orientated 2D-OMHP are isolated but still arranged in layers. These perovskites could also be loosely referred to having a 0D perovskite structure [25], or dimensionless. Compared to 3D-OMHP, 2D-OMHP are also generally better moisture resilience [29–31].

Depending on the choice of organic and inorganic precursors, the energy alignment in 2D-OMHP could resembles either a type I (Figure 2.4(a) and (b)) or type II semiconductor (Figure 2.4(c)). Despite this, type I alignment are most commonly found in 2D-OMHP. In type I 2D-OMHP quantum well, dielectric and

Figure 2.2: Schematic of 2D-OMHP with organic cation (red) possessing (a) a single (A_2BX_4) or (b) double (ABX_4) ammonium side chain(s). Figure adapted from Reference [23].

Figure 2.3: Schematic of 2D-OMHP orientated in the (a) $\langle 001 \rangle$ ($(R-NH_3)_2MX_4$), (b) $\langle 110 \rangle$ (A'_3AMX_5), and (c) $\langle 111 \rangle$ (A'_2MX_6) directions. Figure adapted from Reference [28].

quantum confinement effects are very dominant [32]. This leads to discernible room temperature excitonic spectral features since excitons in this system possess large binding energy, typically of the order of hundreds millielectronvolts (meV) ([18, 33–36]). These features include distinct sharp excitonic absorption and emission peaks [20, 21]. Consequently, their optical properties are very much governed by excitons. This is different from weakly confined 3D-OMHP with exciton binding energy of tens of meV [22] and optical properties generally determined by free carriers.

In general, optical transitions in OMHP are influenced by inorganic components; the valence band maximum consists of hybridizations between B ns orbital and X (n-1)p orbitals while the conduction band minimum consists of hybridizations between B np and X (n-1)s orbitals [37]. An example would be $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$ 2D-OMHP, where its valence band maximum and conduction band minimum consists of hybridization between Pb 6s and I 5p orbitals and hybridization between Pb 6p and I 5s respectively (Figure 2.5). However, there are also exceptions where optical phenomena are governed by organic framework in 2D-OMHP, such as triplet emission from naphthalene-based 2D-OMHP [38], and broadband emission from optically active organic layers in 2D-OMHP [39].

2.3 Excitons in 2D-OMHP

An exciton consists of a coulombically bound electron and hole pair. Compared to free electron-hole pair, the energy level of excitons are situated within the bandgap. The energy difference between bandgap and exciton energy is also known as exciton binding energy (E_B). In general, there are three different types of excitons: (1) Frenkel excitons, (2) Wannier-Mott excitons, and (3) charge transfer excitons [40].

Figure 2.4: Schematic of energy alignments in 2D-OMHP with (a) a narrower bandgap (E_g) in inorganic layers, (b) a wider E_g of inorganic layers, and (c) a relative shifting in electron affinity of organic layers. Figure adapted from Reference [23].

Figure 2.5: Bonding diagram of 3D ($\text{CH}_3\text{NH}_3\text{PbI}_3$) and 2D ($\text{C}_4\text{H}_9\text{NH}_3$)₂ PbI_4 perovskite crystals. Figure adapted from Reference [37].

Frenkel excitons are tightly bounded excitons with highly localized wavefunction, and are commonly found in molecular crystals. Their Bohr radius is smaller than the dimensions of a unit cell [41], and they typically possess large exciton binding energy of the order of 0.1 to 1 eV [42]. Wannier-Mott excitons (or also known as Mott excitons) possess binding energy typically around 0.01 eV [42]. These excitons have highly delocalized wavefunctions and possess Bohr radius that spans over many unit cells. This enables them to move freely within the crystal [40]. As such, they are also known as free excitons (FE) [42]. Charge transfer excitons form due transfer of charged species across a semiconductor interface. The electrons and holes in these excitons are spatially separated, but coulombically bounded, across the interface.

In 2D-OMHP, the species responsible for characteristic excitonic absorption and emission peaks are free excitons [43]. Despite having a large E_B , their in-plane excitonic wavefunctions continue to span over several unit cells and resemble that of FE. This discrepancy is due the strong out-of-plane excitonic confinement, which contributes to a large E_B .

The interaction of exciton with itself or other species can leads to new excitonic species or quasiparticles, such as defect bound excitons (DBE) [35, 44], self-trapped excitons (STE) [45–47], and biexcitons (BE) [33, 48]. The former two can also be referred to as bound excitons. DBE arise due to defects or impurities in the system. These defects or impurities can induce potential wells for FE. Subsequently, FE lose their kinetic energies and can localize at these wells. As such, DBE will have lower energy than FE. Subsequently, photoluminescence from DBE are expected to red shift from FE. In general, spectral signatures from DBE are expected to be less pronounced at higher temperature due to overcoming of DBE binding energy (de-trapping process).

STE arise in systems with large exciton-phonon interactions. The interactions result in trapping of FE at the lattice and produce large lattice distortions. In

Figure 2.6: Relative energy position of free and bound excitonic state with respect to free electron and hole states. The notation E_g and E_b represents bandgap and free exciton binding energy respectively.

general, there are two different types of self-trapping processes: self-trapping at intrinsic host crystal is known as intrinsic self-trapping while self-trapping aided by defects is known as extrinsic self-trapping. Extrinsic self-trapping is driven by localization effect due to a combination effect of weak defect potential and exciton-phonon coupling, such that neither one of them are capable to cause localization [49]. The energy positions of FE and bound excitons, with respect to free electrons and holes, are depicted in figure 2.6.

The formation of BE occurs due to significant exciton-exciton interactions at high exciton density with each electrically neutral BE originating from two excitons. Similar to DBE, spectral signatures from BE could be less pronounced at higher temperature depending on BE binding energy. While their binding energies are usually positive, there are instances where negative binding energies are measured [50, 51]. In systems with negative binding energies, the BE energy level is lower than the energy sum of two individual excitons. When BE recombines, an exciton and a photon are released.

2.4 Optical Phenomena in Perovskite Systems

There is an increasing number of reports on optical phenomena from OMHP systems in the recent years. In particular, two phenomena that should be given special mentions are: optical gain and white light emission. They are crucial for important applications such as electrically pumped lasers and white LEDs. The following sections will cover the theoretical framework and recent progress in terms of optically pumped lasing (Section 2.5 and 2.6) and white light emission (Section 2.7 and 2.8) from the perovskite systems. In additions, gaps in current understanding of these phenomena will also be presented since they will serve as a basis for problem statements in this thesis (Section 2.6.1 and 2.8.2).

2.5 Optical Gain Phenomena: ASE and Lasing

Amplified spontaneous emission (ASE) is the amplification of spontaneous emission (SE) due to stimulated emission in absence of a laser cavity. This amplification process, also known as optical gain, is governed by population inversion. As such, there is a minimum threshold for ASE onset. Compared to SE, the emission linewidth for ASE is narrower. While ASE has a low temporal coherence, its spatial coherence can be either high [52] or low [53]. In addition, its emission wavelength is usually red-shifted from SE due to the balance between optical gain and self-absorption [7].

In the presence of a laser cavity, lasing phenomenon takes place. Similar to ASE, stimulated emission is the main mechanism behind lasing. In contrast to ASE, lasing usually occurs at a much lower threshold with a much narrower emission linewidth. In addition, its emission wavelength very is dependent on cavity features. Materials that exhibit optical gain (regardless of ASE or lasing) are known as optical gain medium. The main similarities and differences between ASE and lasing are summarized in table 2.1.

Table 2.1: Main similarities and differences between ASE and lasing.

	ASE	Lasing
Cavity	Not required	Required
Mechanism	Stimulated Emission	Stimulated Emission
Optical Gain	Yes	Yes
Threshold	Exists an ASE threshold	Usually lower than ASE
Temporal Coherence	Low	High
Spatial Coherence	Could be either high or low	High
Emission Wavelength	Usually red-shifted	Dependent on cavity
Emission FWHM	Narrower than SE	Narrower than ASE

2.5.1 Signatures of lasing

In addition to the lasing properties mentioned in the previous section, a more stringent and comprehensive set of lasing signatures have been provided by Samuel *et al.* [54] (Figure 2.7). They can be used to distinguish lasing from other optical phenomena with spectral features similar to lasing. Examples of these phenomena are ASE, waveguiding effect [55, 56], and luminescent microcavity effect [57]. In short, there are four signatures to confirm a lasing phenomenon. The first signature is the presence of a strong and narrow emission linewidth (Figure 2.7(a)), typically less than 1 nm. Depending on the lasing cavity, single (single-mode lasing) or several (multi-mode lasing) lasing peak(s) can be measured. As optical gain bandwidth (range of wavelength in which optical gain is possible) is largely influence by laser cavity, one should also expect lasing wavelength to be

Figure 2.7: Four main signatures of lasing [54]: (a) strong and narrow lasing linewidth with wavelength dependent on cavity and gain medium. The gain bandwidth should also lie within the broad spontaneous emission region (signature I and II), (b) presence of threshold associated with integrated emission intensity and FWHM (signature III), and (c) lasing output should consists of a beam (signature IV).

dependent on cavity length. The second signature is the overlap of lasing wavelength (i.e. gain bandwidth) with the broad spontaneous emission region (Figure 2.7(a)). The third signature is the presence of well-defined transition (threshold) for emission intensity and full width at half maximum (FWHM) from SE to lasing (Figure 2.7(b)). The last signature is the presence of a laser beam output from laser cavity. A strong beam output is possible due to optical feedback provided by highly reflecting laser cavity (Figure 2.7(c)). These four signatures also highlight the importance of the optical cavity for lasing.

2.6 Recent Progress in Optically Pumped 3D-OMHP ASE and Lasing

Over the past few years, 3D-OMHP have been tagged with the reputation of having excellent optical gain properties. Ever since the first few studies of ASE and lasing from solution processed 3D-OMHP thin films in 2014 [7, 58], their

optical gain research has grown substantially, with numerous reports following on (Figure 2.8). In particular, these pioneering works have also led to the first demonstration of 3D-OMHP nanoplatelets (in 2014) [59], nanowires (in 2015) [9], and quantum dots lasing (in 2015) [8]. The intrinsic properties which make them a good optical gain medium, even in polycrystalline thin film form, are their large absorption coefficient, slow Auger recombination, and ultralow bulk defect density [7]. Notably, Xing *et al.* [7] have demonstrated an ASE threshold of $12 \mu\text{Jcm}^{-2}$, which is comparable to ASE from state-of-the-art polymer thin film [60] and super yellow [61], using $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film. Their ASE/lasing wavelengths also showed great tunability across the whole visible region upon changing halide composition [7, 62, 63]. In addition, their lasing wavelengths could also be tuned into near infrared region ($\sim 1 \mu\text{m}$) using CsSnI_3 based 3D-OMHP [64]. In 2016, a great leap towards electrically pumped 3D-OMHP lasing was also shown with the demonstration of low temperature perovskite laser pumped with an InGaN laser diode [65].

2.6.1 PhD in context of literature - Optical gain challenges in 2D-OMHP

While 2D-OMHP had dominated limelight in the past for potential LEDs applications [18, 119–122], not much progress was observed in term of optical gain as compared to their 3D counterparts. As of 2016, optical gain reports for 2D-OMHP are few and far between: out of 63 reports from the OMHP family, there is only 1 early report by Kondo *et al.* claiming low temperature (16K) biexcitonic lasing from $(\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4$ 2D-OMHP planar waveguide sample [48] (Figure 2.9). Although an emission linewidth narrowing to 1.1 nm was reported by Kondo *et al.* (partial fulfilment of Signature III - Figure 2.7(b)), the light-in-light-out graph presented did not show a clear transition from SE to lasing (Figure 2.7(b)). In addition, while the narrow emission overlap with the broad spontaneous emission (fulfilment of Signature II - Figure 2.7(a)), wavelength

Figure 2.8: Histogram depicting the number of optical gain reports from 3D-OMHP during 2014 to 2016 [7–9, 58, 59, 62–118], with 3D-OMHP optical gain field growing substantially since pioneering works in 2014 [7, 58].

tunability by varying cavity length was not demonstrated (Signature I - Figure 2.7(a)). The emission far-field pattern from the waveguide samples was found to be elliptical, and could suggest a beam output (fulfilment of Signature IV - Figure 2.7(c)). In view of limited data available from Kondo *et al.*, it is difficult to precisely confirm the presence of biexcitonic lasing based on the four lasing signatures. Furthermore, this “lasing” phenomenon could even be a case of a luminescent microcavity and/or waveguiding effect (Section 2.5.1), which could lead to emission linewidth narrowing and a beam output.

Even though optical gain from 2D-OMHP cannot be totally ruled out, it is still surprising their reports are scarcely available. The present scenario could depict an inherent challenge for 2D-OMHP in achieving optical gain. Therefore, detailed photophysical insights into the relaxation mechanism of excitonic species, as well as possible dominant factors limiting optical gain in 2D-OMHP, are urgently required.

Statistics of Optical Gain Reports from 1997 to 2016

Figure 2.9: Statistics of optical gain reports from 2D perovskites [48] (cyan), 3D perovskites quantum dots [8, 66–69, 113] (red), 3D perovskites nanowires [9, 62, 63, 70–74, 108, 114, 115, 118] (green), and the rest of 3D perovskites system [7, 58, 59, 64, 65, 75–107, 109–112, 116, 117] (blue) from 1997 to 2016. Compared to 3D-OMHP optical gain reports, the number from 2D-OMHP is greatly disproportionate. The usage of 3D and 2D here refers to the degree of PbI_6^{4-} octahedron corner sharing in the perovskite, also referred to structural dimensionality. For example, 3D means that the PbI_6^{4-} exhibit sharing corner in all three directions. The usage of quantum dots and nanowire refers to growth refers to growth dimensionality, which is different from structural dimensionality.

Figure 2.10: CIE 1931 standards. (a) Schematic of CIE 1931 color space. Chromaticity coordinates are represented in the color space [123]. (b) A graph of CIE 1931 standard observer color matching functions used to calculate chromaticity coordinates [124].

2.7 Quantifying Colors using CIE 1931 Color Space

The CIE (Commission Internationale de l'Eclairage) 1931 color space (Figure 2.10(a)) color space correlates pure colors in the visible spectrum to human perceived colors. It can be a useful tool to quantify color using numbers (either chromaticity coordinates or tristimulus values). Since color sensitivity of the eyes is dependent on angle of view, CIE 1931 X , Y and Z tristimulus values are therefore defined using a 2° field of view. The tristimulus values can be calculated using following integrals:

$$X = \int_{380}^{780} I_{PL}(\lambda) \bar{x}(\lambda) d\lambda, \quad (2.1)$$

$$Y = \int_{380}^{780} I_{PL}(\lambda) \bar{y}(\lambda) d\lambda, \quad (2.2)$$

$$Z = \int_{380}^{780} I_{PL}(\lambda) \bar{z}(\lambda) d\lambda, \quad (2.3)$$

where I_{PL} represents spectral radiance, λ represents wavelength, and $\bar{x}$, $\bar{y}$ and $\bar{z}$ are

the color matching functions (Figure 2.10 (b) [123]). In addition, the respective CIE 1931 chromaticity values (x , y , and z) could be calculated from tristimulus values using following equations:

$$x = \frac{X}{X + Y + Z}, \quad (2.4)$$

$$y = \frac{Y}{X + Y + Z}, \quad (2.5)$$

$$z = \frac{Z}{X + Y + Z}. \quad (2.6)$$

with

$$z = 1 - x - y, \quad (2.7)$$

it would be sufficient to represent colors using two of the chromaticity values. Conventionally, colors are quantified using chromaticity coordinates instead of tristimulus values. In addition, only chromaticity coordinates x and y are used in CIE 1931 color plot.

2.7.1 White Light

White light comprises of a combination of lights with different wavelengths. The CIE 1931 standard defines pure white as having a chromaticity coordinates of $(x, y) = (\frac{1}{3}, \frac{1}{3})$. Region around this coordinates is defined as the white region, and is illustrated in Figure 2.11. In general, the degree of whiteness can be described using a parameter known as correlated color temperature (CCT). White light with CCT over 5000 K and between 2700 K to 3000 K is known as cool and warm white light respectively (Figure 2.12). Both types of white light are actively employed in real life applications. A cool white light provides a cleaner and brighter atmosphere while a warm white light provides a warm and welcoming atmosphere. CCT value can be calculated from CIE 1931 chromaticity coordinates. In addition, the calculations can be simplified using a MATLAB[®]

Figure 2.11: Schematic of CIE 1931 color space showing the white region (white color). Figure adapted from Reference [128].

script, which is based on Robertson's method [125], provided by Lighting Research Center [126]. In this method, chromaticity x and y values are converted into chromaticity u and v of CIE 1960 color space. Subsequently, linear interpolation is used to find the isotherm lines corresponding to respective u and v values [127] (Figure 2.13).

2.8 Recent Development of 2D-OMHP white emitting material

Over the past few years, a handful of studies on 2D-OMHP broad emission have been reported [39, 45–47, 130]. In particular, some of these broad emissions were found to lie in the white region of CIE 1931 color space [45–47, 130]. In addition, both cold and warm white light were reported from these studies. The white emission spectra for selected 2D-OMHP are depicted in Figure 2.14(a) to (e). These emissions are from a single material and should be distinguished from white emission using perovskite phosphor excited with a blue chip (Figure 2.14(f))

Figure 2.12: Schematic of CCT scale with examples to illustrate the respective CCT values. Figure adapted from Reference [129].

Figure 2.13: Calculations of CCT values. (a) CIE 1960 chromaticity diagram showing both blackbody locus (Planckian locus) and isothermperature lines (with CCT labelled) [127]. (b) CCT values are obtained by linear interpolation of known CCT values. In the schematic, T_j and T_{j+1} correspond to isothermperature lines with known CCT values [125].

Figure 2.14: Broadband emission from (a) $(\text{C}_6\text{H}_{13}\text{N}_3)\text{PbBr}_4$ [39], (b) $(\text{C}_6\text{H}_{11}\text{NH}_3)_2\text{PbBr}_4$ [46], (c) $(\text{N-MEDA})[\text{PbBr}_4]$ [130], (d) $(\text{EDBE})\text{PbCl}_4$ [47], and (e) $(\text{EDBE})\text{PbBr}_4$ [47] 2D-OMHP. N-MEDA and EDBE refers to N^1 -methylethane-1,2-diammonium and (ethylenedioxy)bis(ethylammonium) respectively. (f) Alternative approach to obtain a broad (white) emission using bluechip/ $\text{CH}_3\text{NH}_3\text{PbBr}_3$ quantum dots/ $\text{K}_2\text{SiF}_6:\text{Mn}^{4+}$ (KSF) configurations [131].

[131]). Importantly, these studies highlight the potential of 2D-OMHP as white emitter for LEDs.

2.8.1 Mechanisms of Broad Emissions Proposed in Literature

To date, there has been no demonstration of white perovskite LEDs. Albeit this, recent studies have been focusing on identifying the main mechanism responsible for broadband emission from 2D-OMHP. Several proposed mechanisms are illustrated in Figure 2.15. As of now, exciton self-trapping is widely agreed to be the mechanism for 2D-OMHP white emission (Figure 2.15 (a) and (b)). The formation of self-trapped excitons occurs when free excitons overcome a small

self-trapping energy barrier (typically tens of meV). To date, two different types of self-trapping processes have been assigned to 2D-OMHP broad emitters: (i) self-trapping into several states with different trapping depth (Figure 2.15 (a)), and (ii) self-trapping into a single state (Figure 2.15 (b)).

Deep-level defect emission is another mechanism proposed to explain the broad emission (Figure 2.15 (c)). This mechanism is very dependent on defect concentration; at higher excitation density, defects are depleted and emission intensity should saturate. Furthermore, this mechanism should also be very dependent on particle size with varying surface defect concentration. However, such behaviour are not observed in some of these white emitting perovskites, with no emission intensity saturation at higher excitation density [46, 47] and insensitivity of emission spectrum to particle size [47, 130]. As such, it is not likely that emission from deep-level defect emission has any contribution to the broad emission.

The last mechanism proposed is broad emission from an optically active organic framework mediated by energy transfer from inorganic framework (Figure 2.15 (d)). This mechanism has been observed in $(\text{C}_6\text{H}_{13}\text{N}_3)\text{PbBr}_4$ perovskite [39] and is also the only unique mechanism from 2D-OMHP to date. This conclusion is derived from photoluminescence excitation studies of $(\text{C}_6\text{H}_{13}\text{N}_3)\text{PbBr}_4$, and wavelength-dependent emission studies of $(\text{C}_6\text{H}_{13}\text{N}_3)\text{PbBr}_4$ and its organic precursor $(\text{C}_6\text{H}_{11}\text{N}_3)\cdot 2\text{HBr}$.

2.8.2 PhD in context of literature - Origins of white light emission in 2D-OMHP

As of now, general consensus for broad emission from 2D-OMHP points to radiative recombination of self-trapped excitons at the inorganic framework. Despite the important role of inorganic framework, one should also not neglect possible effects of organic framework on white emission; changes from

Figure 2.15: Mechanisms proposed to explain broadband emission from 2D-OMHP. These mechanisms include (a, b) emission from Self-trapped excitons [45, 46], (c) emission from deep-level defect [46], and (d) emission from optically active organic components mediated by energy transfer mechanism [39].

violet to white emission are observed when only the organic framework is changed from $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbBr}_4$ [43, 132] to $(\text{C}_6\text{H}_{11}\text{NH}_3)_2\text{PbBr}_4$ [46], (N-MEDA) PbBr_4 (N-MEDA = N^1 -methylethane-1,2-diammonium) [130], and (EDBE) PbBr_4 (EDBE = 2,2'-ethylenedioxy)bis(ethylammonium) [47]. These suggest that the role of organic framework on white emission should be investigated.

Inspired by the sensitivity of both organic and inorganic framework for white emission from stoichiometric 2D-OMHP, one should also investigate the influence of excess precursors for white emission. Specifically, this thesis will also investigate the role of excess inorganic precursors for white emission.

The results from these studies could be used to motivate new design strategies for white emitting 2D-OMHP.

2.9 Summary

In this chapter, an overview of the OMHP field was given, with emphasis on 2D-OMHP. Optical properties and different types of excitons in 2D-OMHP were covered. Optical gain and white emission in 2D-OMHP were also introduced in this chapter. In addition, recent literature and progress for optical gain and white emission from perovskites were covered. Based on the gaps in knowledge from literature, problem statements relating to these two fields were formulated and presented.

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Chapter 3

Experimental Methodology

In this chapter, the rationale behind the choice of samples for this thesis will first be presented. The sample fabrication methods will also be covered in detail. In addition, rationale behind the choice of sample characterization techniques will be discussed. Specifically, this chapter will be mainly focusing on optical spectroscopy principles and techniques. The techniques involved are steady-state and transient absorption spectroscopy, steady-state and time-resolved photoluminescence spectroscopy and X-ray photoelectron spectroscopy.

3.1 Rationale for selection of Materials

The rationale for sample selection in this thesis are derived from the two hypotheses in Chapter 1.1.1.1 (hypothesis I) and Chapter 1.1.2.1 (hypothesis II). In short, hypothesis I states that defects and traps could be limiting biexcitons population build-up in 2D-OMHP while hypothesis II states that self-trapped excitons formation for white emitting perovskites can be influenced by both organic precursor and excess precursors.

Figure 3.1: Photograph of green photoluminescence from PEPI under UV laser excitation, adapted from Reference [1].

3.1.1 Samples for Hypothesis I

A suitable candidate for testing hypothesis I would be phenethylammonium lead iodide - $(C_6H_5C_2H_4NH_3)_2PbI_4$ (hereafter referred to as PEPI) 2D-OMHP. The organic precursor for PEPI is shown in Figure 3.2(a). PEPI exhibits strong excitonic emission with ultraviolet (UV) laser excitation [1] (Figure 3.1), and has been extensively investigated for light emitting applications and photophysical properties in the 1990s to early 2000 [2–4]. Therefore, it could be considered one of the famous representative and archetypal material in the 2D-OMHP family. Furthermore, no optical gain has been reported from PEPI and therefore, it is purposeful to employ this material for this study.

3.1.2 Samples for Hypothesis II

Two suitable candidates can be used for testing hypothesis II:

(a) The role of organic framework for white emission can be investigated using

phenethylammonium lead chloride - $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbCl}_4$ (hereafter known as PEPC) 2D-OMHP. The organic precursor for PEPC is shown in Figure 3.2(b). This study is a first report of white emission from PEPC despite its existence in the 1990s [5, 6]. It is also surprising that while several photoluminescence studies has been reported from PEPC, none of them had emission spectrum taken across the visible wavelength, and only an excitonic emission peak at ~ 343 nm was reported [7, 8]. In contrast to PEPC, most two dimensional chloride perovskite only exhibit a single excitonic emission peak [9]. As such, PEPC is a suitable system to investigate the role of organic framework for white emission. The use of PEPC is also meaningful since its organic torsional motion is different from those non-white emitting PEPI and phenethylammonium lead bromide - $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbBr}_4$ (hereafter known as PEPB) [6].

(b) The dependence of excess precursor on white emission can be investigated using *meta*-xylylenediammonium lead bromide - $(\text{NH}_3\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3)_2\text{PbBr}_6$ (hereafter referred to as *m*-XDLB, where *m* denotes *meta*). The organic precursor for *m*-XDLB is shown in Figure 3.2(c). This material is unique since white emission from *m*-XDLB thin film is only observed upon using excess lead bromide (PbBr_2) precursor. This is also a first report of white emission from perovskite thin film using excess (non-stoichiometric) inorganic precursors. As such, it is meaningful to investigate the effects of varying PbBr_2 precursor concentrations for white emission from *m*-XDLB thin film.

3.2 Perovskites Fabrication

The low dimensional perovskite samples used in this study was provided and fabricated by Mr. Krishnamoorthy Thirumal from Energy Research Institute @ NTU (ERI@N). The perovskite structure and formula was also confirmed by Mr. Krishnamoorthy Thirumal prior to measurements.

Figure 3.2: Organic precursors (a) $\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3\text{I}$, (b) $\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3\text{Cl}$, and (c) $\text{BrNH}_3\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3\text{Br}$ employed for perovskites fabrication in this thesis.

3.2.1 Perovskite Precursors

The precursors $\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3\text{X}$ and PbX_2 ($\text{X} = \text{Cl}$ and I) were employed for perovskites fabrication. $\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_2\text{X}$ powders were fabricated by adding HX to a mixture of $\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_2$ in methanol at 0°C . The resulting mixture was stirred for an hour at room temperature with excess solvent subsequently removed using a rotatory evaporator at 50°C to obtain a powder mass. This powder mass was then washed with cold ether several times to obtain $\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3\text{X}$ powder.

3.2.1.1 PEPI Thin Films

PEPI thin films were fabricated from solution with stoichiometric ratio (2:1) of $\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_2\text{I}$ (Figure 3.2(a)) and PbI_2 , mixed in dimethylformamide (DMF). The weight concentration of two precursors in DMF was fixed at 25 %. Thin films was obtained by spin coating the solution on cleaned quartz substrates at 4000 revolutions per minute (rpm) and 30 seconds, and subsequently annealed at 100°C for 30 minutes.

3.2.1.2 PEPC Thin Films

PEPC thin films were fabricated from solution with stoichiometric ratio (2:1) of $\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_2\text{Cl}$ and PbCl_2 , mixed in dimethyl sulfoxide (DMSO). The concentration of pervoskite solution was fixed at 1 M (mol/dm^3). Thin films were obtained by spin coating the solution on cleaned quartz substrates at 4000 rpm and 30 seconds, and subsequently annealed at 100 °C for 30 minutes.

3.2.2 PEPC Powders

PEPC powders were obtained by drop casting PEPC solution on cleaned glass substrates, and drying at 100°C for 30 minutes. The dried PEPC mass was subsequently finely ground to obtain the powders.

3.2.3 PEPC Nanoparticles Solution

PEPC nanoparticles solution was initially prepared using a solution mixture consisting of 27.8 mg of PbCl_2 , 29.0 mg of $\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_2$, 26.4 μl of octylamine, and 26.4 μl of DMF, followed by the addition of 50 μl of HCl. The function of octylamine is to create capping ligands for the nanoparticles. This mixture was then sonicated for a few minutes to obtain a clear solution. A $\sim 200 \mu\text{l}$ volume of this solution was then slowly added to 2 ml of hexane under rigorous stirring at room temperature for 5 minutes. PEPC nanoparticles were obtained by quick addition of acetone in this mixture, and subsequently centrifuging to remove the supernatant.

3.2.4 PEPC Single Crystals

Single crystals of PEPC were grown by nitromethane vapor diffusion into a solution with stoichiometric ratio (2:1) of $\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3\text{Cl}$ and PbCl_2 in DMF at

room temperature. The purpose of nitromethane is to act as anti-solvent, such that its diffusion into perovskite solution sets supersaturation conditions to promote PEPC seed crystals formation [10]. Importantly, nitromethane (anti-solvent) is miscible in DMF (solvent) but hardly dissolve PEPC crystals. Similarly, high supersaturation conditions can be achieved even with low addition rates of anti-solvent [11]. PEPC single crystals were then allowed to grow from these seed crystals at room temperature, with good quality crystal platelets obtained after one week. The lateral dimensions of these crystals are typically of a few millimetres.

3.2.5 *m*-XDLB Thin Films

m-XDLB thin films were fabricated from solution of $\text{BrNH}_3\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3\text{Br}$ and PbBr_2 mixed in DMSO. Thin films without excess PbBr_2 were fabricated from solution with $\text{BrNH}_3\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3\text{Br}$ and PbBr_2 in 2:1 molar ratio. Those films with excess PbBr_2 were fabricated using different PbBr_2 amount during solution preparation. *m*-XDLB thin films were obtained by spin coating the solution on cleaned quartz substrates at 4000 rpm and 30 seconds, and subsequently annealed at 100 °C for 30 minutes.

3.2.6 *m*-XDLB Single Crystals

Single crystals of *m*-XDLB were prepared using vapor-assisted crystallization (Section 3.2.4), where diethyl ether is used as the anti-solvent. *m*-XDLB crystals were grown by allowing diethyl ether to slowly diffuse into the perovskite solution, which consists of equal $\text{BrNH}_3\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3\text{Br}$ and PbBr_2 in weight dissolved in DMF. The crystallization process lasted for two months.

3.3 Femtosecond Laser Spectroscopy

Optical gain and white emission properties of perovskites are closely linked to their charge-carrier dynamics. These dynamical information could reveal excitonic processes, and are crucial for testing the two hypotheses. Therefore, it is important to use short pulse excitation lasers, such as femtosecond (fs) lasers, for these studies. Some advantages of using fs lasers include:

- Allowing high excitation fluence. This is useful for observing any optical gain and trap saturation phenomenon.
- Tuning of excitation wavelength via non-linear effects. This is useful for exciting different electronic states.
- Enabling time-resolved measurements. Temporal studies can only be carried out with pulse laser.
- Allowing high temporal resolution. This is useful for revealing ultrafast charge-carrier dynamics of the order of few hundreds fs.

Common spectroscopic techniques compatible with fs laser excitations include time-resolved photoluminescence and transient absorption spectroscopy.

3.3.1 Femtosecond Laser Pulses

The duration of a femtosecond laser pulse is on the femtosecond scale (1 fs = 10^{-15} s). The spectral and temporal profile of a laser pulse is usually represented by a symmetrical "bell-shaped" function, such as Gaussian or Lorentzian profile. The electric field of a pulse can be represented in frequency ($E(\omega)$) or time domain ($E(t)$), with $E(\omega)$ and $E(t)$ being Fourier transform of each other:

$$E(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} E(\omega) e^{-i\omega t} d\omega \quad (3.1)$$

Figure 3.3: Illustration of laser pulses.

$$E(\omega) = \int_{-\infty}^{+\infty} E(t) e^{-i\omega t} dt \quad (3.2)$$

A laser pulse duration (Δt) can be defined as the time width in which laser intensity (proportional to $[E(t)]^2$) is half of its maximum value (Figure 3.3). A similar definition can be derived for laser spectral bandwidth ($\Delta \nu$, where $\omega = 2\pi\nu$). These quantities (Δt and $\Delta \nu$) are also known as full width at half maximum (FWHM) values. The product of Δt and $\Delta \nu$, which is also known as time-bandwidth product (K), yields the inequality:

$$\Delta t \Delta \nu \geq K \quad (3.3)$$

The inequality dictates that it is impossible to obtain a laser pulse with narrow pulse duration and spectral width simultaneously. The K values for some symmetrical functions are found in table 3.1 [12]. A laser pulse is also known as transform limited when the equality in equation 3.3 is satisfied. Deviations away from transform limited behaviour are usually caused by pulse chirping, with frequencies components in a pulse possessing time-dependent values. A positively

Table 3.1: Time-bandwidth products for some symmetrical functions [12].

Function	$E(t)$	$\Delta t \Delta \nu$
Gaussian	$\exp[-(t/t_0)^2/2]$	0.441
Lorentzian	$[1+(t/t_0)^2]^{-1}$	0.142
Hyperbolic Secant	$1/\cosh(t/t_0)$	0.315
Exponential function	$\exp[-(t/t_0)/2]$	0.140

and negatively chirped pulse possesses instantaneous frequency that increases and decreases with time respectively.

3.4 Femtosecond Laser Systems

The optical studies were mainly conducted using Coherent Libra titanium:sapphire (Ti:sapphire) regenerative amplifier laser system. The 800 nm laser pulses from this system possess a pulse width and repetition rate of ~ 50 fs and 1 kHz respectively (Figure 3.3). The pump and seed lasers for regenerative amplification processes was provided by Coherent Evolution and Vitesse pulse laser respectively. Chirped-pulse amplification (Section 3.4.3) is the main technique behind regenerative amplification in Coherent Libra.

3.4.1 Seed Laser - Coherent Vitesse

The pulse laser from Coherent Vitesse seed laser system has a wavelength of 800 nm with pulse width and repetition rate of ~ 100 fs and 80 MHz respectively. Two main components, namely Coherent Verdi and Verdi-pump ultrafast (VPUF) laser head, can be found in this system. Coherent Verdi is a 532 nm continuous wave (CW) laser with yttrium vanadate (Nd:YVO_4) as gain medium

(Chapter 2.5). The lasing action of Nd:YVO₄ produces wavelength of 1064 nm when optically pumped with a 808 nm laser. The 1064 nm laser emission is then converted to 532 nm via second harmonic generation using a lithium triborate (LBO) nonlinear optical crystal. The 532 nm CW verdi laser subsequently acts as a pump laser for Ti:sapphire gain medium in VPUF laser head. The pulse generation in VPUF employs Kerr-lens mode-locking, which uses optical Kerr effect for mode-locking.

3.4.1.1 Kerr-lens Mode-locking

Ti:sapphire is a gain medium with large gain bandwidth, and can support large number of lasing modes when optically pumped. The pumping of Ti:sapphire crystal with Coherent Verdi laser in a laser cavity initially produces multiple laser modes. Kerr-lens mode-locking does not self-start and initiation requires changing cavity length at proper speed to introduce high power fluctuation to these CW laser modes. When a large instantaneous power is achieved for the modes, optical kerr effect takes place at Ti:sapphire crystal. These high power modes then self-focused and undergo interference, giving rise to a laser pulse. The pulse laser beam are allowed to pass through an aperture, while non-focused CW beam are attenuated by it (Figure 3.4 [13]). Kerr-lens mode-locking is a self-sustaining process once a large number of lasing modes are formed. The pulse output from VPUF is responsible for Coherent Vitesse laser output.

3.4.2 Pump Laser - Coherent Evolution

Coherent Evolution laser is a 527 nm laser with pulse width and repetition rate of 204 ns and 1 kHz respectively. Its gain medium is a Neodymium-doped yttrium lithium fluoride (Nd:YLF) crystal, which lases at 1053 nm when pumped by 805 nm aluminium gallium arsenide laser diode. The pulse formation takes place via

Figure 3.4: Schematic of Kerr-lens mode-locking using a non-linear optical medium (Ti:Sapphire). Self-focusing effect in the crystal is a result of intensity (I) dependent non-linear refractive index changes (Δn), where $\Delta n \propto I$. Figure adapted from Reference [13].

Q-switching. In Q-switching, an attenuator is used to vary laser feedback in the cavity. The gain medium is initially pumped while cavity feedback is reduced (low Q). During this period, lasing action is prevented while gain (population inversion) continues to build-up. Cavity feedback is then increased (high Q) once maximum gain is reached (gain saturation). Laser action is then resumed with depletion of large amount of energy from the gain medium, giving rise to intense short pulses. These 1053 nm pulse laser is subsequently converted to 527 nm via second harmonic generation using a LBO nonlinear optical crystal.

3.4.3 Coherent Libra Regenerative Amplifier

Coherent Libra is a Ti:sapphire regenerative amplifier system which uses Coherent Vitesse and Evolution as seed and pump laser respectively. Chirped-pulse amplification CPA is the main technique behind regenerative amplification process (Figure 3.5). The initial process of CPA involves pulse stretching of 800 nm

Figure 3.5: Schematic of chirped-pulse amplification process in Coherent Libra system. Figure adapted from Reference [14].

seed laser using a stretcher. The stretching process ensures that pulses can be safely amplified without damage to sensitive optical components in the system. The stretched pulses then undergo many round trips through a ti:sapphire crystal (pumped using 527 nm Coherent Evolution), extracting energy for amplification. The cavity round trips are maintained with pockel cells. The broad amplified pulses are then released from the cavity and directed into a pulse compressor, where pulse narrowing takes place. This results in a 800 nm laser with pulse width and repetition rate of ~ 50 fs and 1 kHz respectively.

3.4.4 Coherent OPerA Solo

The 800 nm output from Coherent Libra limits the choice of excitation wavelength. However, an optical parametric amplifier can be used to overcome this limitation. This output can be directed into Coherent OPerA Solo optical parametric amplifier, which allows wavelength tunability from 290 to 2600 nm.

Both optical parametric generation and optical parametric amplification are involved in wavelength tuning. Optical parametric generation involves creation of two beams from the 800 nm beam. However, these beams are relatively weak.

Optical parametric amplification is then used to amplify one beam while making the other weaker, and generating a third beam in the process. Both optical parametric generation and amplification obey energy conservation and phase matching conditions.

3.5 Characterization Techniques

The follow sections introduce the optical spectroscopic techniques and equipment used in this thesis. The techniques are steady-state photoluminescence PL, temperature-dependent PL, time-resolved PL, steady-state absorption, and transient absorption spectroscopy.

3.5.1 Steady-State PL Spectroscopy

PL spectroscopy can be used to investigate optical properties of light emitting samples, *e.g.* perovskite samples in this thesis. It employs a light source, such as fs lasers, for photo-excitation of samples. The schematic of our homemade PL spectroscopy setup is shown in (Figure 3.6). The excitation wavelength is very dependent on absorption band gap of samples, and can be tuned easily using Coherent OPerA Solo. These wavelengths are typically in ultraviolet (UV) region for 2D-OMHP samples. The excitation laser is first passed through a short pass filter to remove residual 800 nm before directing at the sample. The diverging PL is then collected using a collimating lens pair. The collected emission is passed through a UV long pass filter before directing into a monochromator, and subsequently at a charge-coupled device CCD (Princeton Instruments). The diffraction grating inside a monochromator is responsible for spatially separating emission wavelengths. The separated wavelengths are then directed out of monochromator exit slits into a CCD. A CCD consists of an array of light sensitive pixels which convert light into electrical signal for data acquisition. The ultimate resolution

Figure 3.6: Schematic of homemade PL spectroscopy setup.

of a spectrograph consisting of a monochromator and CCD, is dependent on slit width, diffraction grating resolution (in lines per millimeter), monochromator focal length, and CCD pixel size.

3.5.1.1 PL Spectrum Correction

The PL spectra for white emitting perovskites are broad with spectral features sensitive to response functions of detectors (Figure 3.7). As such, there is a need to perform PL spectrum correction to obtain an accurate spectrum. This is carried out by dividing measured spectrum by the response functions (Appendix A).

3.5.1.2 Time-Resolved PL Spectroscopy

Time-resolved PL (TRPL) spectroscopy can be used to investigate PL decay kinetics after pulse laser excitation. The setup is similar to Figure 3.6, except the emission is now directed into a monochromator coupled to a streak camera. The emission is first spatially separated into photons of different wavelengths using a monochromator (Princeton Instruments). It is subsequently sent into a streak

Figure 3.7: (a) Digitized response functions for Princeton Instruments monochromator and CCD from Reference [15] and [16]. (b) Detector response function for Horiba Fluoromax-4 Spectrofluorometer.

Figure 3.8: Operating principles of a streak camera. Figure adapted from Reference [17].

camera (Optronis) to measure variations of PL intensity with time. The Optronis Optoscope streak camera system used in this thesis possesses an ultimate resolution of ~ 10 ps at the fastest scan speed, and its operating principles are shown in Figure 3.8 [17]. The spatially separated photons are first directed at a photocathode for photoelectrons generation. Next, these photoelectrons are subjected to a pair of electrodes with time varying potential. This leads to a time-dependent photoelectrons deflection, which allows extraction of time information (PL kinetics). In addition, the deflected electrons are multiplied using a micro-channel plate (MCP) before forming streak image on the phosphor screen.

3.5.1.3 Temperature Dependent PL Spectroscopy

Temperature dependent PL spectroscopy is conducted using the same homemade PL spectroscopy setup (Figure 3.6), with samples mounted in an evacuated cryostat. The cryostat is connected to a continuous flow cryocooler (CRYO Industries) fed with high purity helium (He) gas (99.9997 %). Cryogenic temperatures as low as ~ 10 K can be obtained with this system.

The cooling process takes place in a Gifford-McMahon (GM) refrigerator. Each cooling cycle consists of four steps. The first step involves opening a high pressure path to allow high pressure He gas (at constant temperature) to pass through a regenerator material into an expansion space. The regenerator is made up of solid porous material, which periodically stores/releases heat from/to the gas. The volume in the expansion space is variable and can be controlled by a displacer. The second step involves expansion of He gas. The high pressured He gas moves the displacer to increase chamber volume, which subsequently leads to expansion and cooling for He gas. This is a crucial step since main cooling takes place. The third step involves opening of low pressure path, which allows cooled He gas to pass through regenerator material again. This process cools the material and removes heat from the cryostat. The last step involves returning of displacer to its original position, which completes the whole cycle.

The cryocooler in this study employs a two-stage GM refrigerator, where cooling is done using a series of two regenerator materials. The first material ensures that He gas is cold enough for cooling the second material. This allows lowering of temperature to ~ 10 K.

In this study, the samples are mounted in an evacuated cryostat using carbon tape and thermally conductive silver paste, which ensures good thermal contact between samples and sample mount. The temperature is adjusted and monitored using a temperature controller (Lake Shore Cryotronics, Inc.). In addition, the

samples are allowed to reach steady temperature before acquisition of PL spectrum.

3.5.2 Steady-State Absorption Spectroscopy

Steady-state absorption spectroscopy is conducted using Shimadzu UV3600 spectrophotometer, which is capable of measuring absorbance in wavelength range of 185 nm to 3.3 μm . Measurements across such broad range are possible due to three detectors: (i) photomultiplier (PMT tube for ultraviolet and visible wavelengths, and (ii) indium gallium arsenide and (iii) lead sulfide detectors for infrared wavelengths. The substrate spectrum is also collected to correct for any contributions from it. The absorbance (A) and transmittance (T) can be calculated from incident (I_0) and transmitted (I) light intensity. These quantities are related by the expressions:

$$T = \frac{I}{I_0} = 10^{-A} \quad (3.4)$$

3.5.3 Transient Absorption Spectroscopy

Femtosecond transient absorption spectroscopy (TAS) is performed using HELIOS setup from Ultrafast Systems. It is carried out using two fs laser beams (pump and probe), which are delayed with respect to each other. The schematic of a typical TAS setup is shown in Figure 3.9. The fs beams originate from Coherent Legend regenerative amplifier, which is a system similar to Coherent Libra regenerative amplifier. The pump and seed laser for Coherent Legend regenerative amplifier are from Coherent Vitesse and Coherent Evolution respectively. The output from Coherent Legend regenerative amplifier is a 800 nm laser with pulse width and repetition rate of ~ 150 fs and 1 kHz respectively.

The 800 nm laser is split into two beams for generation of pump and probe beams.

Figure 3.9: Schematic of a typical fs TAS setup.

The pump beam is directed into Coherent TOPAS optical parametric amplifier to obtain desired excitation wavelength, while the probe beam is directed into a Sapphire crystal to obtain a white light continuum. The delay between these two beams is adjusted using an optical delay line stage. Both beams are directed and spatially overlapped at the sample. The time where pump and probe beams overlap temporally is known as time zero. The transmitted probe beam is then directed into a spectrophotometer to determine pump-induced probe transmission change (ΔT) after time zero, and is given by the expression:

$$\Delta T = T_{withpump} - T_{withoutpump}, \quad (3.5)$$

where $T_{withpump}$ and $T_{withoutpump}$ is the probe transmission with and without pump laser respectively. Equivalently, pump-induced probe absorption change (ΔA) can be calculated using expression from Equation 3.4.

Typical features in a transient absorption spectrum are shown in Figure 3.10(a). A

negative ΔA (or positive ΔT) signal is either assigned to photobleaching or stimulated emission signal, while a positive ΔA (or negative ΔT) signal is assigned to photoinduced absorption (PIA) signal. The mechanisms responsible for photobleaching, stimulated emission, and PIA signals are shown in Figure 3.10(b).

Prior to pump pulse arrival, a small fraction of carriers are excited (absorbed) by the weak probe pulse (Figure 3.10(bi)). However, this action gives rise to no change in ΔT , since $T_{withpump} = T_{withoutpump}$ (Equation 3.5).

The arrival of a stronger pump pulse promotes more carriers into excited state, leaving lesser of them in ground state (increased $T_{withpump}$). This results in reduced probe absorption (compared to before time zero), giving rise to increased $T_{withpump}$ and a positive ΔT **photobleaching** signal (Figure 3.10(bii)). The photobleaching peak should also coincide with steady-state absorption peak.

A positive ΔT signal can also arise due to stimulated emission of carriers (excited by pump pulses) by probe pulses (Figure 3.10(biii)). The additional photons due to stimulated emission (compared to before time zero) gives rise to increased $T_{withpump}$, which leads to a positive ΔT **stimulated emission** signal.

A negative ΔT signal can occur due to excited state absorption of carriers (excited by pump pulses) by probe pulses (Figure 3.10(biv)). The increased probe absorption (compared to before time zero) gives rise to reduced $T_{withpump}$, which leads to a negative ΔT **photoinduced absorption** signal.

3.6 Summary

In this chapter, the various perovskite samples used in this thesis were first introduced. Next, the rationale of samples selection and fabrication methods were covered. The various optical spectroscopic techniques involved in samples characterization were also listed. Lastly, key equipment and theories behind these techniques were covered in details.

Figure 3.10: (a) Typical spectroscopic features in a transient absorption spectrum [18]. Photobleaching signal is represented by dashed line, stimulated emission is represented by dotted line, and photoinduced absorption is represented by solid line. The net signal from these three process is shown by bold line. (b) Interaction of charge carriers with probe pulse (i) before, and (ii, iii, and iv) after time zero. Non-zero ΔT (and ΔA) signal occurs after time zero as (ii) photobleaching, (iii) stimulated, and (iv) photoinduced absorption signal.

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Chapter 4

Optical Gain Challenges in PEPI Perovskites

In this chapter, the role of bound excitons in limiting amplified spontaneous emission in PEPI thin film will be covered. Firstly, the difficulty in obtaining ASE from this perovskite will be highlighted. In addition, the presence of competing excitonic relaxation channels in PEPI will be emphasized. Lastly, calculations of theoretical biexcitonic ASE threshold will be presented. This threshold was found to be ~ 1 order of magnitude higher than the material damage threshold.

4.1 Introduction

PEPI (Figure 4.1) is a 2D-OMHP that has been previously employed in the 1990s and early 2000 as light emitting layers for LEDs [1, 2], with high luminance achieved at cryogenic temperature [1]. In addition to LEDs integration, the excitonic optical properties of PEPI have also been widely studied during that period [3, 4]. Its popularity in the scientific community has therefore made it a representative member of the 2D-OMHP family. Although the possibility of obtaining lasing from PEPI cannot be totally eliminated, it is still surprising that optical gain reports from 2D-OMHP family are scarcely available (Chapter 2.6.1). If

Figure 4.1: Schematic showing the structure of PEPI, which consists of alternating organic $\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3^+$ and inorganic $[\text{PbI}_6]^{4-}$ layers. The naturally formed quantum well structure enables the formation of tightly bound excitons in the inorganic layers.

the optical gain problem is resolved, green emitting PEPI (or other 2D-OMHP) could be a potential gain material for addressing the “green gap” in semiconductor lasers. This is particularly attractive for integration into electrically pumped gated green lasers.

As such, detailed photophysical insights into the relaxation processes of excitonic species, as well as the dominant factors limiting optical gain in PEPI, are needed. In subsequent sections, detailed photophysical studies on solution processed PEPI thin films using pump-fluence and temperature dependent PL spectroscopy are presented. Room temperature PL spectroscopy of PEPI using high laser pump fluence (of the order of $100 \mu\text{J}/\text{cm}^2$) showed a free excitonic emission peak (peak 1), with an absence of ASE. Low temperature PL of this material revealed two more emission peaks: a bound excitonic peak (peak 2), and a biexcitonic peak (peak 3), with peak 3 appearing at higher laser excitation fluence ($\sim 30 \mu\text{J}/\text{cm}^2$). Similarly, no optical gain (*i.e.* ASE) can be observed from PEPI at low

temperatures using high laser fluence (of the order of $100 \mu\text{J}/\text{cm}^2$). Furthermore, irreversible PL intensity reduction, indicating photodegradation of sample, was observed at much higher laser fluence. The Arrhenius plot from temperature dependent PL measurements revealed a small energy difference ($\sim 10 \text{ meV}$) between peak 1 and peak 2 emission, and suggest dependencies between these levels. In addition, significant PL quenching of peaks 2 and 3 were observed upon surface passivation of PEPI, which suggests the surface origin of these two peaks. Importantly, these findings show the interplay between competing relaxation channels in PEPI thin film, which could potentially limit biexcitonic optical gain. This limitation concurs with theoretical modelling, which shows a large biexcitonic ASE threshold beyond photodamage threshold of PEPI. Lastly, from these findings, suggestions to overcome optical gain challenges in 2D-OMHP were proposed.

4.2 Results and Discussion

4.2.1 Excitonic Absorption

The steady-state absorption spectrum of PEPI thin film from 280 to 900 nm is shown in Figure 4.2. Three distinct peaks (labelled A, B, and C) can be observed in the spectrum. Peak A ($\sim 325 \text{ nm}$) and B ($\sim 400 \text{ nm}$) correspond to transition from Pb 6s and I 5p hybridization orbital to Pb 6p orbital [3], while peak C ($\sim 517 \text{ nm}$) corresponds to free excitonic absorption peak. Such distinct excitonic absorption peak is characteristic of 2D-OMHP systems [5]. The excitonic nature of PEPI is also reflected from its large exciton binding energy of $\sim 180 \text{ meV}$ (Figure 4.2 inset). This value is also consistent with reported values [3, 6, 7]. The large value also suggests strong excitonic confinement with low thermal dissociation probability of excitons into free carriers at room temperature (equivalent to 25 meV). Therefore, steady-state absorption measurements highlight the excitonic nature of PEPI thin film.

Figure 4.2: Room temperature steady-state absorption of PEPI thin film. Inset shows the estimation of free exciton binding energy of PEPI. The estimate for bandedge and free excitonic energy are 2.42 and 2.24 eV respectively.

4.2.2 2D Layered Structure

The X-ray diffraction (XRD) pattern of PEPI thin film is shown in Figure 4.3. There exists a prominent diffraction peak from (002) plane at $2\theta \approx 5.5^\circ$. In addition, the sharp and narrow feature of this peak suggests preferred orientation in (002) direction (parallel to substrate). The 2D layered structure of PEPI thin film is reflected in the diffraction pattern as periodic (002n) peaks, where $n = 1, 2, \dots, 5$. Therefore, XRD measurements ensures formation of layered PEPI thin film, which is consistent with the schematic in Figure 4.1.

4.2.3 Film Morphology

Figure 4.4 shows the scanning electron microscopy (SEM) image of PEPI thin film. The spin coated film shows good morphology with good substrate coverage.

Figure 4.3: XRD pattern of PEPI thin film. Smaller XRD peaks can be observed when the pattern is zoom into 2θ range of $\sim 15^\circ$ to 35° . The periodic features are representative of a layered structure and are typical for 2D perovskite [5].

Altogether, steady-state absorption, XRD, and SEM measurements show that the spin coated sample possesses good quality for optical studies.

4.2.4 Absence of ASE in PEPI

The excitation fluence dependent PL spectrum of PEPI thin film measured at room temperature is shown in Figure 4.5(a). A narrow emission peak can be observed in the spectrum using 400 nm pulse excitation.

Origin of peak 1. This emission peak, labelled as peak 1, has wavelength of ~ 525 nm and FWHM of ~ 15 nm. The origin of this peak can be assigned to free excitonic emission (Chapter 2.3), given good correspondence with free excitonic absorption peak in Figure 4.2.

The room temperature PL spectrum does not exhibit any spectral narrowing and superlinear increase in intensity, when excitation fluence is increased from 0.9 to

Figure 4.4: SEM image of spin coated PEPI thin film, showing a flat surface, indicating good film morphology.

$105.2 \mu\text{J}/\text{cm}^2$. These spectral changes are not representative of ASE phenomenon (Chapter 2.5), and clearly shows the absence of ASE in PEPI thin film up to $105.2 \mu\text{J}/\text{cm}^2$. The PL spectrum of PEPI thin film is also investigated at low temperature where ASE threshold is expected to be lower. The 10 K emission spectrum of PEPI consists of three spontaneous emission peaks centered at ~ 525 (peak 1), 535 (peak 2), and 545 nm (peak 3) (Figure 4.5(b)). Although the intensity of peak 3 surpasses peak 1 and 2 at higher laser fluence, no superlinear increase in PL intensity could be observed up to $127.3 \mu\text{J}/\text{cm}^2$. Importantly, both room temperature and low temperature PL measurements were stopped at laser fluence just below the damage threshold (of the order of $100 \mu\text{J}/\text{cm}^2$, or 10^{19} cm^{-3} incident photon density). Above this threshold, the samples are optically damaged, and PL emission diminishes irreversibly (Figure 4.6). In short, these PL measurements demonstrate and confirm the difficulties in obtaining ASE from PEPI thin film at both room and low-temperatures.

Optical gain and thickness of PEPI thin film. The thickness of PEPI thin film is an important parameter that can influence ASE properties. In this thesis, the

Figure 4.5: Excitation fluence dependent PL spectrum of PEPI thin film at (a) 298 K (room temperature), and (b) 10 K. The PL experiments were conducted using 400 nm excitation laser pulses (50 fs, 1 kHz).

thickness of PEPI thin film is fixed at ~ 100 nm. The rationale of not using a thinner film (*e.g.* few tens of nm) is to prevent the problem of insufficient gain volume. In addition, the rationale of not choosing thick micron film is to prevent the problem of self-absorption, which would further increase ASE threshold (if any). Furthermore, the thickness of PEPI thin film used in this experiment is also similar to typical thickness (~ 100 nm [8]) required to obtain ASE from 3D perovskites thin film.

4.2.5 PL Peaks Assignment

The low fluence temperature dependent PL spectrum of PEPI thin film is shown in Figure 4.7(a). The identity of peak 1 was assigned in previous section as free excitonic emission. The wavelength of peak 1 exhibits a slight unconventional red shift with decreasing temperature, and can be attributed to effects from negative Varshni parameter. This red shifting behavior has also been previously observed in 3D-OMHP [9]. Unfortunately, the origins of peak 2 and 3 in Figure 4.5(b) are

Figure 4.6: Steady-state PL spectrum of PEPI thin film excited with 400nm, taken at excitation fluence of $1.3 \mu\text{J}/\text{cm}^2$, before and after exposure to high laser fluence of $177 \mu\text{J}/\text{cm}^2$. The optical damage threshold is defined here as the laser fluence that diminishes PL intensity. The typical damage fluence found in PEPI thin film is of the order of $100 \mu\text{J}/\text{cm}^2$ (excited with 400 nm laser pulses).

still unclear, and are a matter of debate in the literature. Their origins must be established for the modelling of recombination kinetics in PEPI.

Origin of peak 2. The origin of peak 2 could be attributed to either a phonon replica or bound excitonic emission. Gauthron *et al.* [4] has previously observed two low temperature PL peaks from PEPI thin film at 2.355 eV (526.5 nm - peak 1) and 2.337 eV (530.5 nm - peak X) (Figure 4.7(b)). The 526.5 nm emission peak is consistent with peak 1 while the 530.5 nm emission peak is red shifted from peak 2. They found significant interaction between peak 1 and optical phonons using a phenomenological model, and subsequently assigned peak X as a phonon replica of peak 1. However, the PL spectrum lacks characteristic features of phonon replicas (multiple evenly spaced peaks), which have been observed in PL spectrum of PEPI at 2 K [7]. Importantly, peak X observed by Gauthron *et al.* need not correspond to peak 2 in this study. In addition, TRPL measurement revealed different decay kinetics for peaks 1 and 2, which suggests that peak 2 is unlikely a phonon replica of peak 1 (Figure 4.8).

On the other hand, Kitazawa *et al.* attributed a bound excitonic (Chapter 2.3) origin to peak 2 [3]. Two activation energies of ~ 10 and 200 meV were extracted from their temperature dependent integrated PL intensity plot. The larger energy of 200 meV can be attributed to free exciton binding energy of PEPI, which is consistent with the value extracted from steady-state absorption measurement (Figure 4.2 inset). On the other hand, the much smaller energy of ~ 10 meV can be attributed to trapping–detrapping energy of bound excitons. This energy is equivalent to a temperature of ~ 120 K, and also corresponds well to the temperature where peak 2 becomes prominent (Figure 4.7). Similar bound excitonic emission can also be observed in $(\text{C}_{10}\text{H}_{21}\text{NH}_3)_2\text{PbI}_4$ 2D-OMHP [10].

These activation energies are also consistent with values obtained from fitting the integrated PL intensity (peak 1 and 2) against temperature plot using Equation 4.1 (Figure 4.9(a)). The fitting employs a biexponential Arrhenius equation with

Figure 4.7: (a) Temperature dependent PL spectrum of PEPI measured in this study. There are two distinct emission peaks (peaks 1 and 2), with peak 2 appearing at lower temperature. The PL experiments were conducted using 400 nm excitation laser pulses (50 fs, 1 kHz) with a fluence of $2.6 \mu\text{J}/\text{cm}^2$. (b) Temperature dependent PL spectrum of PEPI measured by Gauthron *et al.* [4]. (c) 2 K and 300 K PL spectrum measured by Hong *et al.* [7].

Figure 4.8: TRPL kinetics of peak 1 and 2 measured at 10 K. The TRPL measurement was conducted using 400 nm excitation laser pulses (50 fs, 1 kHz) with a fluence of $7.0 \mu\text{J}/\text{cm}^2$.

expression:

$$I = \frac{I_0}{1 + A_1 e^{-\frac{E_1}{k_B T}} + A_2 e^{-\frac{E_2}{k_B T}}}, \quad (4.1)$$

where I represents PL intensity, I_0 represents integrated PL intensity at 0 K, A_1 and A_2 represent pre-exponential amplitudes, E_1 and E_2 represent activation energies, k_B represents Boltzmann constant, and T represents temperature. The fitting yield $E_1 = 8.2 \pm 0.7$ meV, and $E_2 = 160 \pm 20$ meV. The smaller energy is also consistent with value obtained from fitting integrated PL intensity of peak 2 only against temperature plot with a single exponential Arrhenius equation (Figure 4.9 (b)):

$$I = \frac{I_0}{1 + A_1 e^{-\frac{E_1}{k_B T}}}. \quad (4.2)$$

The fitting yields $E_1 = 13.7 \pm 0.7$ meV. These evidence suggest that the origin of peak 2 is linked to bound excitons, which are formed from free excitons after overcoming a trapping barrier of ~ 10 meV.

Evidence of bound excitons are also reflected in surface passivation PL studies

Figure 4.9: Integrated PL intensity at different temperatures for (a) peak 1 and peak, and (b) peak 2 only. The activation energies are extracted using Arrhenius equations. The PL experiments were conducted using 400 nm excitation laser pulses (50 fs, 1 kHz) with a fluence of $2.6 \mu\text{J}/\text{cm}^2$.

of PEPI thin film. Surface passivation is carried out by spin coating a layer of poly(methyl methacrylate) (PMMA, 10 mg/ml in chloroform) above PEPI. The presence of PMMA overlayer gives rise to a reduction in peak 2 intensity (Figure 4.10(a)), which suggests surface contributions. The degree of surface quenching also varies across different sample batches (Figure 4.10(b)), and suggests significant surface trapping with some bulk contributions. Therefore, these two findings imply a large surface bound excitons contribution to peak 2.

Furthermore, effects of surface traps passivation are also evident from (i) a broadening of free excitonic PL peak (peak 1) (Figure 4.10(a)), and (ii) a 37 % increase in the overall integrated PL intensity (Figure 4.10(c)). In addition, there is also a lifetime lengthening of peak 1 (Figure 4.10(d)), which is consistent with fewer free exciton trapping due to trap reduction. As such, both steady-state and time-resolved measurements correspond well with surface bound excitons assignment of peak 2.

Origin of peak 3. The origin of peak 3, which appears at higher laser fluence (Figure 4.5(b)), can similarly be elucidated using PMMA surface passivation

Figure 4.10: Effect of PMMA overlayer on emission properties of PEPI thin film. (a) 10 K PL spectrum of PEPI with and without PMMA overlayer. (b) 77 K PL spectrum of PEPI with and without PMMA layer showing variable degree of quenching for peak 2. (c) Integrated PL intensity of PEPI at 10 K with and without PMMA, measured from 60 equally distributed spots across a $\sim 0.75 \times 0.75 \text{ cm}^2$ sample area. The averages (horizontal lines) and standard deviations (vertical bars) are also included in the plot. (d) 10 K TRPL kinetics of peak 1 with and without PMMA. The effect of traps reduction is reflected in lifetime lengthening of peak 1. All experiments were conducted using 400 nm excitation laser pulses (50 fs, 1 kHz) with a fluence of $7.0 \mu\text{J}/\text{cm}^2$.

studies. Figure 4.11(a) shows the effect of PMMA overlayer on PEPI PL spectrum. The presence of PMMA overlayer leads to quenching of both peak 2 and 3 at high excitation fluence, and suggests dependencies between the two peaks. This result also highlights a surface origin to peak 3. It is likely that peak 3 originates from biexcitonic (Chapter 2.3) recombination given quadratic increase ($m_3 = 2.2 \pm 0.2$) in its emission intensity with laser fluence (Figure 4.11(b)). The reduction of m_3 to m_4 at higher laser fluence can be attributed to increase exciton-biexciton scattering [11]. Importantly, this quadratic behavior is not observed for peak 1 and 2. Therefore, these findings suggest that peak 3 originates from bound biexcitons residing at PEPI surface.

Biexciton binding energy (E_{bx}) can be expressed as:

$$\begin{aligned} E_{bx} &= 2E_x - E_{xx} \\ &= E_x - (E_{xx} - E_x), \end{aligned} \tag{4.3}$$

where E_x and E_{xx} represent exciton and biexciton energy respectively. Here, E_x corresponds to peak 2 energy. The radiative recombination of a biexciton gives rise to an exciton formation and a photon release. In this case, the energy of photon released ($E_{xx} - E_x$) corresponds to peak 3 energy. Therefore, the bound biexciton binding energy in PEPI can be calculated from the energy difference between peak 2 and 3, i.e. ~ 40 meV.

In summary, these PL measurements show that peak 1, 2, and 3 originates from free excitons, surface bound excitons, and surface bound biexcitons respectively.

4.2.6 Identity of Surface Defect in PEPI

The bound excitons responsible for peak 2 and 3 can be classified as defect bound excitons (Chapter 2.3). Therefore, it is important to identify the defect species that promotes bound excitons formation. Surface sensitive techniques, such as X-ray photoelectron spectroscopy (XPS), can be used to probe species responsible

Figure 4.11: (a) PL spectrum of PEPI thin film with and without PMMA overlayer measured at high fluence of $\sim 92 \mu\text{J}/\text{cm}^2$. (b) A plot of integrated PL intensity of the three peaks with excitation fluence. The data points are fitted using power law ($y_i = k_i x^{m_i}$). The exponent m_i indicates the behavior of respective species under different excitation fluence. All experiments were conducted using 400 nm excitation laser pulses (50 fs, 1 kHz) at 10 K.

defect formation in PEPI. XPS is a technique based on photoelectric effect, where photoelectrons are emitted from sample upon x-ray irradiation in ultra-high vacuum environment. The kinetic energies (E_k) of photoelectrons are measured by an electron analyzer to determine its binding energy (E_{binding}). These parameters are related via the expression:

$$E_{\text{binding}} = E_{\text{photon}} - (E_k + \phi), \quad (4.4)$$

where E_{photon} and ϕ are x-ray energy and work function induced by electron analyzer respectively. The binding energies of photoelectrons are unique to elements, and can be employed for elemental composition studies. XPS signal are mainly contributed by surface photoelectrons, since bulk photoelectrons are greatly attenuated via recombination, recapture, and inelastic collision before escaping into vacuum.

Table 4.1: Surface elemental composition ratio of PEPI thin film derived from area under respective XPS elemental peaks in Figure 4.12(b) to (e).

Element	C	N	Pb	I
Stoichiometric Ratio	16	2	1	4
XPS Results	11.2	1.7	1.0	4.0

The XPS wide scan spectrum of PEPI thin film spin coated on indium tin oxide (ITO) substrate is shown in Figure 4.12(a). A conductive ITO substrate is used to prevent surface positive charge accumulation (or positive potential) due to ejected photoelectrons, which would artificially modify the binding energies. The wide scan spectrum revealed four elemental peaks (C, N, I, and Pb), which are consistent with elements in PEPI. The ratio between these elements can be calculated using the area under respective elemental peaks in Figure 4.12(b) to (e). The calculated XPS elemental ratio is shown in Table 4.1. The deviation from ideal values for C and N suggests presence of organic surface vacancies, which could be responsible for surface trapping and bound excitons formation in PEPI thin film.

The excitonic processes responsible for peak 1, 2, and 3 in low temperature PL spectrum of PEPI thin film can be summarized in Figure 4.13.

These findings suggest that surface bound excitons in PEPI cannot be neglected and could potentially have an adverse effect on biexcitonic optical gain. The adverse effect of traps might also be more apparent in 2D-OMHP compared to 3D-OMHP, given higher trap densities observed as dimensionality of perovskites reduces [12, 13].

Figure 4.12: Room temperature XPS scans of PEPI thin film grown on ITO substrate. (a) XPS wide scan spectrum labelled with respective elements and orbitals. XPS narrow scan spectrum of respective elemental peaks: (b) C 1s, (c) N 1s, (d) Pb 4f, and (e) I 3d.

Figure 4.13: (a) Free excitons, (b) bound excitons, and (c) biexcitons relaxation channels in PEPI thin film.

Figure 4.14: Electronic alignment of different semiconductor heterojunctions. These heterojunctions can give rise to a (a) type I, (b) type II, or (c) type III alignment.

4.2.7 Theoretical Biexciton ASE Threshold

The strongly quantum confined nature of PEPI is a result of type I alignment as shown in Figure 4.14(a). Achieving single exciton gain in a type I system is challenging as symmetry between absorption and emission process limits population inversion. Nonetheless, this symmetry can be broken with the formation of biexcitons. This also indicates that biexcitonic optical gain is easier to achieve in a type I semiconductor. Unfortunately, this type of gain is still not observed in PEPI (Figure 4.5(b)), and is likely due to competing relaxation channels present in the material. These channels could in turn increase the threshold required for biexcitonic ASE.

This motivates a calculation of biexcitonic ASE threshold based on a model developed for charge carriers and emission dynamics in PEPI. This model was modified based on a well-established model of ASE in semiconductor nanostructures [14] to account for our peaks assignment. The schematic of the model, which is consistent with Figure 4.13, is shown in Figure 4.15. This model considers

Figure 4.15: Proposed schematics of exciton (open circles) relaxation channels in PEPI. These channels includes both radiative and non-radiative processes.

relaxation processes subsequent to carriers excitation into the free carrier band $|C\rangle$: ① formation of free excitons $|X\rangle$ and bound excitons $|X_B\rangle$, ② capture of free excitons into bound excitonic state, ③ non-radiative relaxation of free and bound excitons, ④ radiative recombination of free excitons, ⑤ radiative recombination of bound excitons, ⑥ formation and emission of biexcitons $|XX_B\rangle$, ⑦ non-radiative exciton–exciton annihilation. A set of rate equations describing these seven processes are shown in Equations (4.5) to (4.10). The description of the terms in these equations are also listed in Table 4.2.

$$\frac{dN_c}{dt} = \underbrace{\frac{\alpha F}{\tau_L \sqrt{\pi \hbar \omega}} \exp\left(-\frac{t^2}{\tau_L^2}\right)}_{\text{Laser Excitation}} - \underbrace{\frac{N_c}{\tau_{CX}}}_{\text{Relaxation to } |X\rangle} - \underbrace{\frac{N_c}{\tau_{CX_B}}}_{\text{Relaxation to } |X_B\rangle} + \underbrace{\frac{1}{2} \gamma (N_X^2 + N_{X_B}^2)}_{\text{Exciton-exciton annihilation}} \quad (4.5)$$

$$\frac{dN_X}{dt} = \frac{N_c}{\tau_{CX}} - \underbrace{k_{Xnr} N_X}_{\text{Non-radiative recombination}} - \underbrace{\frac{N_X}{\tau_{Xr}}}_{\text{Radiative recombination}} - \underbrace{V_{gX} g_X S_X}_{\text{Photon gain}} - \underbrace{\frac{C_X N_X}{\tau_{CX}}}_{\text{Surface traps capture}} - \underbrace{\frac{\gamma N_X^2}{2}}_{\text{Exciton-exciton annihilation}} \quad (4.6)$$

$$\begin{aligned}
\frac{dN_{XB}}{dt} = & \frac{N_C}{\tau_{CX_B}} + C_X N_X - \underbrace{k_{X_B nr} N_{X_B}}_{\text{Non-radiative recombination}} - \underbrace{\frac{N_{X_B}}{\tau_{X_B r}}}_{\text{Radiative recombination}} - \underbrace{v_g X_B g_{X_B} S_{X_B}}_{\text{Photon gain}} \\
& - \underbrace{\gamma N_{X_B}^2}_{\text{Exciton-exciton annihilation}} - \underbrace{\frac{B_{XX_B} N_{X_B}^2}{\tau_{X_B r}}}_{\text{Biexciton emission}} - \underbrace{V_{g_{XX_B}} g_{XX_B} S_{XX_B}}_{\text{Biexciton photon gain}}
\end{aligned} \tag{4.7}$$

$$\frac{dS_X}{dt} = V_g g_X S_X + \frac{N_X}{\tau_{Xr}} \tag{4.8}$$

$$\frac{dS_{X_B}}{dt} = V_{g_{X_B}} g_{X_B} S_{X_B} + \frac{N_{X_B}}{\tau_{X_B r}} \tag{4.9}$$

$$\frac{ds_{XX_B}}{dt} = V_{g_{XX_B}} g_{XX_B} S_{XX_B} + \frac{B_{XX_B} N_{X_B}^2}{\tau_{XX_B r}} \tag{4.10}$$

In addition, the optical gain (g_X , g_{X_B} , and g_{XX_B}) is modelled from the competition between absorption and stimulated emission as shown in Equations (4.5) to (4.10). The factor of 2 in Equations (4.11) to (4.13) is to account for contributions from both electrons and holes. The description of terms in these equations are also listed in Table 4.2.

$$g_X = g_{X0} \left(\frac{2N_X}{D_X} - 1 \right) \tag{4.11}$$

$$g_{X_B} = g_{X_B0} \left(\frac{2N_{X_B}}{D_X} - 1 \right) \tag{4.12}$$

$$g_{XX_B} = g_{XX_B0} \left(\frac{2B_{XX_B} N_{X_B}^2}{D_X} - 1 \right) \tag{4.13}$$

The initial gain (g_{X0} , g_{X_B0} , and g_{XX_B0}) are estimated from linear absorption measurements since gain = -absorption when $N = 0$. The density of states (D_X) are estimated from density of valence electrons in Pb^{2+} . These valence electrons

Table 4.2: Description and values of terms used in Equations (4.5) to (4.13).

Term	Description	Value
$\hbar\omega$	Pump photon energy	3.1 eV
α	Absorption coefficient at pump energy	$2.086 \times 10^5 \text{ cm}^{-1}$
τ_{Xr}	Exciton radiative lifetime	100 ps
k_{Xnr}	Exciton non-radiative relaxation rate	0.011 ps^{-1}
$\tau_{XB r}$	Bound exciton non-radiative relaxation rate	150 ps
$k_{XXB nr}$	Bound biexciton non-radiative relaxation rate	0.04 ps^{-1}
$\tau_{XX r}$	Bound biexciton radiative relaxation rate	50 ps
τ_{CX}	Free carrier to exciton relaxation time	50 fs
τ_{CX_B}	Free carrier to bound exciton relaxation time	10 fs
τ_L	Laser time constant	100 fs
C_X	Bound exciton trapping	9 ns^{-1}
B_{XX_B}	Bound biexciton formation coefficient	$8 \times 10^{-21} \text{ cm}^3$
γ	Exciton-exciton annihilation coefficient	$3.38 \times 10^{-12} \text{ cm}^3/\text{s}$
V_{gX}	Group velocity at exciton emission energy	$1.14 \times 10^8 \text{ m/s}$
V_{gX_B}	Group velocity at bound exciton emission energy	$1.25 \times 10^8 \text{ m/s}$
V_{gXX_B}	Group velocity at bound biexciton emission energy	$1.31 \times 10^8 \text{ m/s}$
g_X	Free exciton optical gain	$1.038 \times 10^5 \text{ cm}^{-1}$
g_{X_B}	Bound exciton optical gain	$6.603 \times 10^4 \text{ cm}^{-1}$
g_{XX_B}	Bound biexciton optical gain	$4.964 \times 10^4 \text{ cm}^{-1}$
D_x	Density of states	$4 \times 10^{21} \text{ cm}^{-3}$

contribute mainly to the valence state in PEPI. The parameters used in Equations (4.5) to (4.13) are either taken from experimental parameters or data, and are summarized in Table 4.2. These equations are solved numerically using Euler's method in MATLAB[®], and their solutions concur with experimental findings in this thesis. The free exciton lifetime (peak 1) can be well-fitted with numerical solution of Equation 4.6. In addition, experimental results in Figure 4.11(b) can also be well-fitted with numerical solutions of Equations (4.11) to (4.13) at various excitation fluence. Importantly, no ASE onset has been predicted from the numerical solutions. However, an ASE onset from peak 3 is observed as the range of calculations is extended beyond damage threshold of PEPI thin film (Figure 4.11(b) inset). The theoretical ASE threshold was found to be $\sim 1.4 \text{ mJ/cm}^2$, which is ~ 1 order of magnitude higher than experimental damage threshold (Figure 4.6).

Excitation wavelength is also an important parameter that can affect biexcitonic ASE threshold. Herein, biexcitonic ASE threshold is also calculated for different excitation wavelengths (Figure 4.17). As shown in Figure 4.17 (a), biexcitonic ASE occurs at different threshold when excitation wavelength is changed from 350 to 525 nm. The threshold as a function of excitation wavelength is also shown in Figure 4.17 (b). Notably, no clear trend was observed from Figure 4.16 (b). Instead, ASE threshold is more dependent on absorption coefficient (or absorbance). The lowest ASE threshold occurs at 525 nm (compared to 350, 400, 450, and 500 nm), where absorbance is the largest (Figure 4.2). A high absorbance (or absorption coefficient) leads to more biexcitons formation, and hence a lower threshold. However, excitation wavelength of 525 nm may not be suitable for this study as it overlaps with the emission wavelengths. A good choice of excitation wavelength would be 400 nm since one of the lowest ASE thresholds is calculated at this value. This is also in good agreement with the excitation wavelength used in this chapter. One might also point out that excitation

Figure 4.16: Rate equation analysis of kinetics and energetics in PEPI thin film. (a) TRPL kinetics of peak 1 emission measured at 10 K, fitted with numerical of solution 4.6. Inset shows the 2D time-wavelength image of the PL emission with peak 1 labelled. The TRPL measurement were conducted using 400 nm excitation laser pulses (50 fs, 1 kHz) with fluence of $7 \mu\text{J}/\text{cm}^2$. (b) Integrated PL intensity of respective PL peaks as a function of excitation intensity, which are extracted from Figure 4.11(b). The data points can be well-fitted with numerical solutions of Equations (4.11) to (4.13). Inset shows the integrated PL intensity modelled at higher excitation fluence with a calculated biexciton ASE threshold of $\sim 1.4 \text{ mJ}/\text{cm}^2$.

Figure 4.17: Behaviour of biexcitonic emission as a function of wavelength. (a) Calculated biexcitonic emission intensity as a function of wavelength (350, 400, 450, 500, and 525 nm). (b) Theoretical biexcitonic ASE threshold (extracted from (a)) as a function of excitation wavelength.

wavelength < 350 nm may be more suitable due to higher absorption coefficient (Figure 4.2). However, given PEPI is very susceptible to UV degradation (< 350 nm) [15], the use of such excitation wavelength is avoided.

4.2.8 Exciton-Phonon Interaction in PEPI

The effect of exciton-phonon interaction on optical gain properties in PEPI should also be investigated. Specifically the interaction could lead to scattering of excitons away from the metastable state (Figure 1.2 and 4.18). Consequently, a higher excitation fluence (or ASE threshold) is required for population inversion.

However, the effect of exciton-phonon interaction in PEPI is expected to be low, given its small exciton-phonon coupling strength [4]. In particular, the coupling strength in PEPI is ~ 2 to 3 times smaller compared to ZnO quantum well [16], white emitting (EDBE)PbBr₄ 2D-OMHP [17], and samples from Chapter 5 and 6. Notably, optical gain phenomenon has also been observed in ZnO quantum

Figure 4.18: Schematic of exciton-phonon scattering process. The scattering of excitons with phonons (with energy $\hbar\omega_{LO}$) are denoted by arrows. Figure adapted from Reference [16].

well systems with large exciton-phonon interaction [18–20]. This suggests that exciton-phonon interaction may not be a determining factor that limits optical gain.

4.2.9 Proposed Methods to overcome the gain problem

While semiconductors such as AlInGaP and GaN have contributed to the realization of electrically pumped red and blue lasers, a suitable lasing medium for green lasers is currently still elusive [21]. As such, overcoming the “green gap” with identifying a more efficient and directly generated green laser still remains an important area of research, and is attractive for high quality red, green and blue laser-based displays [22].

Solution processed 2D-OMHP, which is exhibiting strong optically and electrically pumped spontaneous green emission, could be one of the candidates for

electrically pumped green laser. However, achieving optical gain in this system has proven challenging (Section 4.2.4). Based on the experimental results and literature findings, several solutions (Figure 4.19) that could help overcome the optical gain problem in 2D-OMHP are proposed.

Managing excitonic recombination losses is an important step to promote optical gain in 2D-OMHP. In this study, significant surface trapping was found to be responsible for formation of bound excitons (from free excitons) and bound biexcitons (from bound excitons) - Figure 4.13. However, this surface trapping also leads to significant biexcitonic losses in PEPI. These competing relaxation channels could explain the high theoretical biexcitonic threshold of $\sim 1.4 \text{ mJ/cm}^2$. A possible solution to reduce these losses (and lowering ASE threshold) would be to introduce ultrahigh quality laser cavities, such as those shown in Figure 4.19(a). The function of these cavities would be to induce net optical gain by increasing gain and reducing losses.

Another viable solution for inducing optical gain would be to employ 2D-OMHP nanocrystals. Two excitons, more specifically biexcitons, are typically responsible for optical gain in these nanocrystals. Unfortunately, the formation of biexcitons at high excitation fluence would promote Auger recombination, and further increase ASE threshold. Auger recombination is a non-radiative process in which energy from electron-hole/exciton recombination is used in excited state absorption of another electron, hole, and/or excitons. It can be reduced by employing a type II core/shell configuration to promote carrier-induced Stark effect. This effect will also discourage and induce biexciton and single exciton gain respectively [23]. A type II configuration allows electrons and holes to be spatially separate between the core and shell. This creates a strong local electric field which shifts the absorption level (carrier-induced Stark effect) and breaks the symmetry between absorption and emission. The result of using this configuration is a lower single exciton ASE threshold. Building on this idea, a suitable semiconductor

Figure 4.19: Proposed strategies that could promote optical gain in 2D-OMHP. (a) Inserting 2D-OMHP in an optical cavity, such as distributed Bragg reflector and distributed feedback cavity. Promoting single exciton gain with a type II electronic configuration by (b) surrounding 2D-OMHP nanocrystals with suitable semiconductor shell, or (c) selecting a suitable small band gap organic constituent. (d) Employing a (H₃N-R-NH₃)PbI₄ structure to improve film morphology and possibility reduce trapping.

shell surrounding 2D-OMHP nanocrystals (core) can be used (Figure 4.19(b)). Similarly, with a careful choice of organic precursor, 2D-OMHP thin film with type II electronic configuration [24] could also be fabricated (Figure 4.19(c)) to realize single exciton gain.

As shown from the XPS elemental composition ratio in Table 4.1, surface defects in PEPI were found to originate from C and N deficiencies, and could be due to C–N bond breakage in the organic layer. This suggests that an organic constituent with larger C–N bond dissociation energy would be helpful to reduce these defects. An example would to employ covalently bonded ammonium units with a formula of $(\text{NH}_3\text{--R--NH}_3)\text{PbI}_4$ [24]. In the case of PEPI $((\text{R--NH}_3)\text{PbI}_4$ structure), the two ammonium units are bonded by weaker van der Waals forces. A stronger covalently bonded constituents could lead to better film morphology [25], which can further reduce traps caused by organic deficiencies.

4.3 Conclusions

In conclusion, PL measurements revealed the challenges in obtaining ASE from PEPI thin film at both low (~ 10 K) and room temperature. These challenges are mainly due to competing excitonic relaxation pathways, and low damage threshold. Ultrafast spectroscopy measurements revealed relationship between formation and relaxation of free excitons, bound excitons and biexcitons. These competing channels limit biexcitonic population inversion, and increase ASE threshold. The theoretical threshold was found to be $\sim 1.4 \text{ mJ/cm}^2$, which is one order of magnitude larger than the damage threshold. Lastly, several recommendations have been proposed based on experimental data and literatures, which could help overcome optical gain problem in 2D-OMHP.

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Chapter 5

Self-Trapped Excitons in PEPC Perovskites

In this chapter, the mechanism of white emission from PEPC perovskite will be investigated. Firstly, white emission from PEPC is confirmed with CIE 1931 coordinates. Next, the intrinsic nature of white emission due to recombination of self-trapped excitons (bound excitons) will be discussed. The presence of exciton self-trapping at the organic framework will also be highlighted. Lastly, the photostability of PEPC thin film will be presented.

5.1 Introduction

PEPC is a 2D-OMHP that is structurally similar to PEPI. However, it possesses a larger band gap than PEPI, with excitonic absorption peak in UV region. Correspondingly, free excitonic emission from PEPC also lies in UV region, and is consistent with several literature reports [1, 2]. Despite these reports, optical phenomenon of PEPC in visible region (400 nm to 700 nm) have not been explored. Surprisingly, PEPC emits broadly in visible region, and is first reported in this study. This phenomenon also demonstrates the white emitting capability of PEPC. Concurrently, there is also an increasing number of white emission reports from selected 2D-OMHP in these few years [3–7]. Many studies have

been devoted to understanding photophysical properties, in particular the origins of white emission, of these novel white emitters. The origins of white emission is especially important since they provide insights to fabricating 2D-OMHP with optimized white emitting functionalities. Till date, exciton self-trapping at inorganic framework has been commonly attributed to origins of white emission in 2D-OMHP [5, 7]. However, there is no reason to rule out the role of organic framework, given white emission is also observed upon changing of organic framework, *e.g.* from PEPB [8] to (EDBE)PbBr₄ [4].

Herein, PEPC white emitter is employed to investigate the effects of organic framework on broad emission. Room temperature PL studies on PEPC nanoparticles solution, powders, thin films, and single crystals showed an intrinsic origin to the broad emission. TRPL studies have also confirmed the emission to be from a single excitonic state. Temperature dependent PL studies revealed strong exciton-phonon coupling strength, which arises from exciton self-trapping at the organic framework. The presence of self-trapped states is also consistent with photo-induced absorption region from transient absorption measurements. These findings highlight that organic framework in PEPC is important for white emission, and does not only acts as an inert spacer. Lastly, the photostability of PEPC is demonstrated to highlight its potential as a white emitter.

5.2 Results and Discussion

5.2.1 Excitonic Absorption

The absorption spectrum of PEPC thin film and nanoparticles solution in toluene are shown in Figure 5.1. A sharp absorption peak is observed at 340 nm, which can be assigned to free excitonic absorption and is a result of strong excitonic confinement in PEPC. This peak is also blue-shift from that of PEPI (Figure 4.2).

Figure 5.1: Room temperature steady-state absorption spectrum of PEPC thin film and nanoparticles.

5.2.2 2D Layered Structure

The XRD pattern for spin coated thin film and drop casted nanoparticles of PEPC are shown in Figure 5.2. There exists a prominent diffraction peak at $2\theta \approx 5.2^\circ$, which is similar to PEPI. In addition, periodic diffraction peaks from inner (00n) planes are also observed from PEPC. These XRD features confirm the formation of layered PEPC samples for this study.

5.2.3 Intrinsic Broad Emission

Broad PL spectrum spanning from ~ 400 to 900 nm can be observed for PEPC nanoparticles solution, powders, thin film, and single crystal samples after 340 nm excitonic resonant excitation (Figure 5.3(a)). These near invariant spectra suggest an intrinsic origin to the emission. In addition, their PL kinetics measured at ~ 545 nm exhibit a single exponential decay with lifetime of 3.0 ± 0.4 ns (Figure 5.3(b)). These near invariant kinetics are also consistent with assignment of intrinsic origin behind the broad emission. Due to such **intrinsic** behavior,

Figure 5.2: XRD pattern of spin coated and drop casted nanoparticles PEPC samples. The periodic features are indicative of layered structure, and are characteristic of 2D-OMHP [9].

further studies will be conducted on PEPC single crystals in this chapter.

The PL kinetics is also investigated across the broad emission band for PEPC single crystal (Figure 5.4). The lifetimes measured at ~ 480 , 545, and 610 nm were found to be similar with a value of 4.2 ± 0.9 ns. The invariant mono-exponential decays suggest that a **single** species is responsible for the broad emission.

Therefore, these PL measurements conclude that the broad emission originates from a **single intrinsic** species. As such, there is a need to identify the exact electronic species behind this broad emission.

5.2.4 Excitonic Decay Dynamics

The nature of this species can be identified by investigating the change in TRPL peak intensity as a function of excitation fluence. Specifically, the TRPL peak intensity is largely contributed by recombination of dominant charge carriers species in the system. The PL decay profiles of PEPC single crystal measured

Figure 5.3: (a) PL spectrum of four different PEPC samples (nanoparticles (NP) solution, powder, thin film, and single crystal) spanning across visible spectrum. (b) TRPL kinetics of the four samples measured at emission peak (~ 545 nm) showing similar decay behaviour. The PL experiments were conducted using 340 nm excitation laser pulses (50 fs, 1 kHz) with a fluence of $7 \mu\text{J}/\text{cm}^2$ for steady-state PL measurements and $15 \mu\text{J}/\text{cm}^2$ for TRPL measurements.

Figure 5.4: TRPL kinetics of PEPC single crystal measured at selected wavelengths across the broad emission showing similar decay behaviour. Inset shows a photograph of PEPC single crystal with dimensions of $\sim 3 \text{ mm} \times 3 \text{ mm}$. The TRPL experiments were conducted using 340 nm excitation laser pulses (50 fs, 1 kHz) with a fluence of $15 \mu\text{J}/\text{cm}^2$.

Figure 5.5: (a) Excitation fluence-dependent PL kinetics of PEPC single crystal measured at peak emission (~ 545 nm), with fluence ranging from 15 to 210 $\mu\text{J}/\text{cm}^2$. (b) Peak TRPL intensities as a function of excitation fluence measured at 480, 545, and 610 nm emission wavelengths. These TRPL experiments were conducted using 340 nm excitation laser pulses (50 fs, 1 kHz).

at ~ 545 nm as a function of excitation fluence is shown in Figure 5.5(a). A linear dependence between TRPL peak intensity and excitation fluence can be observed (Figure 5.5 (b)), which suggests occurrence of monomolecular excitonic, and not bimolecular free-carriers ($\propto I^2$) recombination [10]. This linear behavior is also observed for measurements at ~ 480 and 610 nm (Figure 5.5 (b)). The similar behaviour at these measurement wavelengths concurs with the assignment of radiative recombination from a single species. In addition, the possibility of trap-related emission can be eliminated since PL saturation is not observed at higher fluences (Figure 5.6). In addition, the lack of PL saturation is also consistent with previous 2D-OMHP white emission reports [4, 7]. Contrastingly, trap saturation is responsible for white emission from 3D-OMHP nanoclusters [11].

Figure 5.6: Steady-state PL peak intensity of PEPC single crystal measured at various fluences. There is no PL saturation observed up to fluence of $\sim 180 \mu\text{J}/\text{cm}^2$. The PL experiment was conducted using 340 nm laser pulses (50 fs, 1 kHz).

5.2.5 Continuous Wave versus Pulsed Excitation

The PL spectrum of PEPC thin film excited using a xeon lamp is shown in Figure 5.7. Interestingly, there are several features in this spectrum that are different or not observed in Figure 5.3(a) (fs laser excited spectrum). Firstly, there is an emission peak at ~ 340 nm, which is not observed in fs laser excited spectrum. This peak can be attributed to free excitonic emission given its close wavelength proximity to free excitonic absorption peak in Figure 5.1. The absence of this emission peak in fs laser excited spectrum is very likely due to broad spectral overlap from intense fs laser peak, which is removed by a long pass excitation laser filter. Secondly, there is an apparent blue-shift in the broad emission peak, from ~ 585 nm using fs excitation to ~ 560 nm using continuous wave (CW) excitation (Figure 5.7(b)). This is also reflected in the CIE 1931 color plot (Figure 5.7(c)), where fs laser excitation gives rise to yellow-orange emission while CW excitation gives

rise to white emission with CIE coordinates and CCT of (0.37, 0.42) and 4426 K respectively. The shift in peak position can be attributed to larger degree of lattice heating caused by CW excitation. This subsequently leads to more phonon absorption and higher exciton energy. The influence of phonon absorption to PL spectrum will be discussed in greater detail in the next section.

The differences in PL profile, depending on choice of excitation sources, can demonstrate the versatile nature of PEPC for broad emitting applications. Specifically, PEPC can be optically excited using UV LEDs (closer to CW-excitation conditions) to obtain natural white emission, or electrically excited in the form of PEPC LEDs (closer to fs-excitation conditions) to obtain warmer light color.

5.2.6 Evidence of Self-trapped Excitons

Figure 5.8(a) shows the temperature dependent PL spectrum of PEPC single crystal. The decrease in temperature leads to slight FWHM narrowing (Figure 5.8(a) inset) and intensity enhancement. Nonetheless, these changes do not introduce significant changes to the CIE 1931 coordinates (Figure 5.9). The changes in spectral features as a function of temperature are summarized in Figure 5.8(b). Biexponential Arrhenius fitting of the black data set in Figure 5.8(b) using Equation 4.1 yields two activation energies: 12 ± 1 and 120 ± 10 meV. Therefore, the increase in PL intensity at lower temperature can be attributed to two processes.

The smaller activation energy of 12 ± 1 meV, which has been similarly observed in PEPI (Chapter 4.2.5 and Reference [13]), is likely related to bound exciton de-trapping process. At low temperature, these bound excitons do not have sufficient energy to overcome the trapping barrier, and this leads to a low probability of bound to free excitons conversion. As such, more intense PL emission from bound excitonic recombination can be observed at lower temperature. The larger

Figure 5.7: (a) PL spectrum of PEPC thin film excited using 300 (with 320 nm long pass emission filter) and 340 nm (with 380 nm long pass emission filter) CW source. (b) Comparison of PEPC thin film PL spectrum excited with either 340 nm CW source or fs pulses. (c) CIE 1931 color plot of samples excited with either 340 nm CW source (for PEPC thin film) or fs pulses (for PEPC nanoparticles, powders, thin film, and single crystal). The CIE 1931 chromaticity diagram template is obtained from OriginLab Technical Support [12].

Figure 5.8: (a) Temperature dependent PL spectrum of PEPC single crystal taken from 20 and 300 K. Inset shows the overlaid normalized PL spectrum of the crystal at 20 and 300 K. (b) Integrated PL intensity (black) and FWHM (blue) of PEPC single crystal as a function of temperature. These plots are extracted from (a). The black and blue data points are fitted with Equation 4.1 and 5.2 respectively. The PL experiment was conducted using 340 nm excitation laser pulses (50 fs, 1 kHz) with a fluence of $3.5 \mu\text{J}/\text{cm}^2$.

Figure 5.9: CIE 1931 coordinates of PEPC single crystal as a function of temperature. There is no significant change in coordinates when the temperature is varied from 80 K to 300 K. The CIE 1931 chromaticity diagram template originates from OriginLab Technical Support [12].

activation energy of 120 ± 10 meV can be interpreted to be: (i) energy difference between free excitonic level and conduction band minimum, or (ii) energy difference between bound excitonic level and conduction band minimum, or (iii) energy of phonons (E_{LO}) behind non-radiative recombination. Interpretation (i) and (ii) could lead to PL increase at lower temperature due to decreased bound excitons de-trapping. However, these interpretations are incorrect since PEPC exciton binding energy is typically very large (~ 430 meV [14]). Interpretation (iii) is more probable due good correspondence of 120 ± 10 meV with the energy of an organic mode in PEPC (Figure 5.10 - 994 cm^{-1} or 124 meV). The relationship between phonon population (N_{phonon}) and temperature can be described using Bose–Einstein distribution:

$$N_{phonon} = \frac{1}{e^{\frac{E_{LO}}{k_B T}} + 1}. \quad (5.1)$$

Importantly, the decrease in N_{phonon} at low temperature can lead to reduced non-radiative recombination assisted by phonon absorption. This could explain the PL enhancement at low temperature. The reduced non-radiative recombination can also be seen from PL lifetime lengthening at lower temperature (Figure 5.11). The FWHM broadening at higher temperature can be attributed to carrier-scattering processes, and can be expressed using the equation:

$$\Gamma(T) = \Gamma_0 + \Gamma_{LO}(e^{\frac{E_{LO}}{k_B T}} - 1)^{-1} + \Gamma_{Inh}e^{-\frac{E_A}{k_B T}}, \quad (5.2)$$

where Γ_0 represents FWHM (in meV) at 0 K, Γ_{LO} represents exciton-LO phonon coupling coefficient, E_{LO} represents LO phonon energy, and Γ_{Inh} represents inhomogeneous broadening coefficient. This equation (or similar variant) has been employed previously to extracted electron or exciton-phonon coupling strength [4, 16–30]. The first term in Equation 5.2 is also known as natural linewidth. The second term in Equation 5.2 is a result of exciton-phonon coupling, and is derived using Fermi's golden rule [18]. The perovskite lattice can act as a scatterer

Figure 5.10: Room temperature Raman spectrum of PEPC single crystal. Peaks corresponding to reported Raman modes of phenethylammonium chloride [15] are also labeled with arrows in the spectrum.

Figure 5.11: Temperature dependent PL kinetics of PEPC single crystal. The TRPL experiment was conducted using 340 nm excitation laser pulses (50 fs, 1 kHz) with a fluence of $3.5 \mu\text{J}/\text{cm}^2$.

for excitons, such that creation and annihilation of phonons take place [31]. The creation ($a^\dagger$) and annihilation (a) phonon operators are described by:

$$a^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle, \quad (5.3)$$

$$a |n\rangle = \sqrt{n} |n-1\rangle, \quad (5.4)$$

where $|n\rangle$ represents the phonon state with energy:

$$E_n = (n + \frac{1}{2})\hbar\omega. \quad (5.5)$$

It is the process of phonon absorption and emission that broadens and red-shifts the emission peak. In return to being scattered by the lattice, excitons also create lattice deformation in an attempt to stabilize themselves from scattering processes. Consequently, the lattice deformation creates a potential well that leads to exciton self-trapping. The third term in Equation 5.2 is a phenomenological expression and can be used to account for inhomogeneous broadening due to exciton self-trapping.

A good fit, with an adjusted R-squared value of 0.995, can be obtained by fitting the blue data points in Figure 5.8(b) with Equation 5.2. The fitted parameters are $\Gamma_0 = 581$ meV, $\Gamma_{LO} = 265 \pm 80$ meV, $E_{LO} = 54 \pm 6$ meV, $\Gamma_{Inh} = 90$ meV, and $E_A = 12$ meV. Three conclusions can be derived from these fitted parameters. The first conclusion is the presence of strong exciton-phonon coupling in PEPC. The value of Γ_{LO} is approximately twice larger compared to that obtained from previous white emitting 2D-OMHP [4]. It is also comparable to that obtained from ZnO quantum well [22], which is a well-known system with strong exciton-phonon coupling strength. As such, these findings strongly indicate the presence of self-trapped excitons. The Γ_{LO} values for various semiconductors are also listed in Table 5.1.

The second conclusion is the presence of a 54 ± 6 meV phonon mode that allows exciton self-trapping to take place. This fitted value agrees well with a 60 meV

Table 5.1: Exciton-phonon coupling strength for various excitonic systems.

Material	Γ_{LO} (meV)
PEPC (this work)	265 ± 80
β -GaN Epilayer [23]	706
ZnO Bulk [22]	~ 400
α -GaN Epilayer [23]	371
ZnO Quantum Well [22]	~ 200
(EBDE)[PbBr ₄] Powders [4]	130 ± 7
PEPI Thin Film[17]	~ 70
ZnSe Bulk [21]	60
PbSe Nanocrystals [19]	27
CdSe/ZnS Core/Shell Quantum Dots [20]	21 ± 7
CdSe/CdS Core/Shell Dot-in-Rod[16]	20
GaAs quantum Well [18]	4

organic mode in PEPC (Figure 5.10). Importantly, this mode is a pre-requisite for exciton-phonon coupling to take place.

The last conclusion is the presence of a 12 meV energy barrier. This value corresponds well to that obtained from biexponential Arrhenius fitting of Figure 5.8(b). Therefore, it can be assigned to bound exciton de-trapping barrier. Specifically, it can be taken as self-trapping barrier since self-trapped excitons can also be treated as bound excitons. This barrier must be overcome before self-trapping can take place [32].

Importantly, this is the first reported observation of strong exciton-phonon coupling to **organic framework**, leading to white emission. This could explain the lack of broad emission in fully inorganic CsPbCl₃ perovskite [33, 34]. This is also unlike the conclusion by Hu *et al.* [5], where self-trapped excitons are situated in the inorganic framework.

Nonetheless, both assignments are consistent with literature reports demonstrating that changing either organic (*e.g.* from PEPB to (C₆H₁₁NH₃)₂PbBr₄ or (N-MPDA)[PbBr₄] to (N-MEDA)[PbBr₄]) or inorganic framework (*e.g.* from EDBE[PbI₄] to EDBE[PbCl₄] or PEPB to PEPC (this work - section 5.2.8) is crucial for white emission. The PL spectra of these materials are shown in Figure 5.12

TAS is another technique that can be used to ascertain the presence of self-trapped excitons in PEPC. Figure 5.13(a) shows the pseudocolor TA plot of PEPC single crystal as a function of probe delay time and wavelength. There exists a broad and featureless photo-induced absorption (PIA) signal across visible probe wavelength (Figure 5.13(b) inset), which is consistent with previous white emitting 2D-OMHP report [5]. In addition, the TA kinetics probed at selected wavelengths (500, 600, and 700 nm) across the PIA plateau ($\Delta A > 0$) showed invariant lifetimes, which is consistent with PL findings in Figure 5.4. The absence of photobleaching signal ($\Delta A < 0$) also suggests that the probed state cannot be directly

Figure 5.12: White emission from 2D-OMHP by changing either organic (a [8], b [7], c [4], and d [4]) or inorganic (e [3], and f [3]) framework. The emission spectrum are marked with red asterisks (*).

Figure 5.13: (a) Pseudocolor TA plot of PEPC single crystal showing the pump-induced probe absorption change (ΔA) as a function of probe delay time and probe wavelength. (b) TA kinetics of PEPC single crystal probed across the positive ΔA region at 500, 600, and 700 nm. Inset shows the TA spectrum as a function of visible probe wavelength at selected delay time from -1 ps to 5 ns. The TA experiment was conducted using 340 nm excitation laser pulses (150 fs, 1 kHz) with a fluence of $25 \mu\text{J}/\text{cm}^2$.

excited. In addition, the presence of PIA signal is consistent with assignment of self-trapped excitons since these excitons are formed via transfer from an intermediate state and cannot be directly excited. Furthermore, the rise time of TA kinetics in Figure 5.13(b) were fitted to be ~ 100 fs (limited by the laser pulse width). This is in good agreement with self-trapped excitons formation time, which can be estimated using the vibration period of 60 meV mode involved in the coupling. The formation time was calculated to be ~ 69 fs.

5.2.7 Summary of PL and TAS findings

The processes occurring in PEPC single crystal can be summarized in Figure 5.14. Firstly, excitonic resonant excitation with 340 nm fs laser populates the free excitonic state (black arrow). Subsequently, some of these excitons undergo

Figure 5.14: Schematic of excitonic processes in PEPC. Broadband emission arises from recombination of self-trapped excitons.

self-trapping after overcoming a barrier of ~ 10 meV (red arrow). These excitons, which are responsible for broad emission, then relax to the bottom of self-trapped excitonic band (purple arrow). The increase in PL at low temperature is due to reduction of non-radiative recombination (green arrow) and exciton de-trapping.

These processes could also explain various observations in this chapter:

Little change in PL spectrum with temperature.

There may be a perception that the broad PL spectrum of PEPC will change considerably at lower temperature due to significant freezing of phonon mode. The freezing process could lead to modification of exciton-phonon interactions, which changes the spectrum. However, the PL spectrum of PEPC in this study did not undergo significant changes with temperature (Figure 5.8(a)). This observation can be explained using the non-symmetrical behaviour between phonon absorption and emission. The phonon population (N_{phonon}) can be described by Equation 5.1, which indicates that N_{phonon} will be lesser at lower temperature.

Consequently, exciton-phonon coupling will be affected since there will be fewer thermally generated phonons for absorption at low temperature. On the other hand, phonons can also be generated via phonon emission; phonons can be released as excitons relax towards the bottom of self-trapped excitonic band (purple arrow in Figure 5.14). As such, the phonons released could still play a part in exciton self-trapping process at low temperature, leading to a broad emission. These could account for the less drastic change in PL spectrum at low temperature.

Blue-shifting of PL peak for CW excitation.

The effect of blue-shifting as a result of different excitation sources is shown in Figure 5.7(b) (Section 5.2.5). Self-trapping involves simultaneous absorption and emission of phonon, with spectrum blue-shifting much affected by the former. The excitation duration of a CW source is much longer than a fs pulse. As such, more energy is deposited on the sample with CW excitation, which causes more lattice heating. This means that there would be more phonon scattering events, particularly more phonon absorption. This could lead to a blue-shift in emission spectrum since more phonon absorption can lead to population of higher self-trapped excitonic energy states (orange arrow in Figure 5.14).

Self-trapping does not involve every phonon mode.

While there are numerous phonon modes in the Raman spectrum of PEPC (Figure 5.10), not all of them will be involved in self-trapping process. The presence of phonon mode is only a pre-requisite for self-trapping and it is the strength of exciton-phonon coupling that determines the occurrence of self-trapping. This could explain why certain perovskites are non-white emitters despite possessing numerous Raman modes. Nonetheless, the occurrence of strong exciton-phonon coupling cannot be easily predicted and more studies should be carried out to account for the existence of broad emission in certain perovskites.

5.2.8 Stable Broad Emission

An ideal white emitting material should be solution processible, inexpensive to fabricate, and relatively stable. PEPC is a white emitting material that can be easily fabricated in various forms (single crystals, thin films, powders, and nanoparticles solution) using solution-processed techniques. However, its air, moisture, and photo-stability have not been reported. Even though some perovskites were found to be unstable in air and moisture, these instabilities can be mitigated using proper device encapsulation or surface passivation. On the other hand, photostability is an intrinsic property which cannot be easily mitigated, and should be investigated to determine its suitability for devices. The photostability of PEPC thin film was examined by observing the change in broad PL peak intensity under continuous fs laser excitation. The excitation source is a 340 nm fs laser with repetition rate of 1 kHz with fluence of $2.1 \mu\text{J}/\text{cm}^2$. After ~ 14 hours of excitation ($\sim 10^5$ laser shots), the thin film exhibit negligible reduction of normalized PL peak intensity at ~ 545 nm (Figure 5.15) with a mean and standard deviation of 0.98 and 0.05 respectively. This measurement demonstrates good UV stability of PEPC thin film.

A comparison was also done on its bromide counterpart (PEPB), which emits at ~ 410 nm (Figure 5.15 inset). In contrast to PEPC, PEPB demonstrates poor photostability with a significant 80 % reduction in PL peak intensity after 6 hours. This measurement is also consistent with previous report of poor UV stability of PEPB [35].

5.3 Summary

PEPC is a photostable 2D-OMHP exhibiting white emission with good correlated color temperature and CIE 1931 coordinates, desired for white emitting LEDs applications. PL and TAS measurements revealed that self-trapped excitons are

Figure 5.15: Photostability of PEPC and PEPB thin film. Inset shows the normalized PL spectrum of PEPC and PEPB thin film at initial time ($t = 0$ hour). The photostability measurement was conducted using 340 nm excitation laser pulses (50 fs, 1 kHz) with a fluence of $\sim 2.1 \mu\text{J}/\text{cm}^2$. The excitation laser was incident on PEPC and PEPB thin film for ~ 14 and 6 hours continuously in an inert N_2 environment.

responsible for broadband emission from PEPC. In addition, these measurements revealed that the excitons undergo self-trapping at the organic framework. This is unlike conventional assignment of exciton self-trapping at the inorganic framework. Therefore, our results highlight the importance of organic framework. A judicious selection of both organic and inorganic precursors is essential for tuning the white emission from 2D-OMHP.

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Chapter 6

Self-Trapped Excitons in *m*-XDLB Perovskites

*In this chapter, the mechanism of white emission from *m*-XDLB thin film with excess lead bromide will be covered. Firstly, white emission from excess leaded *m*-XDLB perovskite will be confirmed with CIE 1931 coordinates. Next, the role of excess lead in *m*-XDLB perovskite in influencing white emission will be investigated. Lastly, the importance of both organic (Chapter 5) and inorganic frameworks (this chapter) for white light emission will be re-emphasized.*

6.1 Introduction

Perovskites possess low formation energy and can be fabricated easily using solution-processed methods. These methods include solution-growth and spin-coating of perovskite single crystals and thin films respectively [1]. Single crystals growth, which often takes hours or even weeks, allows slow assembly of perovskites with less defects [2, 3]. On the other hand, spin-coating, which is a facile and rapid fabrication method, may introduce defects or structural deviations during perovskite formation even with solution prepared using stoichiometric precursors ratio. One example can be seen from the spin coating of CsSnI_3 thin films, where excess SnF_2 is required to prepare films with lesser traps and

better optical gain properties [4]. In this study, *m*-XDLB thin films prepared with stoichiometric amount of precursors were found to self-assemble differently and possess structure which is different from their single crystal form. These structural differences could be minimized with the addition of excess PbBr_2 to precursor solution. In addition, white emission is only observed from *m*-XDLB thin films prepared with excess ($\sim 50\%$) PbBr_2 precursors. Even so, the emission spectrum and XRD pattern showed no contribution from pristine PbBr_2 . Those films that are been fabricated with less than 50 % excess PbBr_2 exhibit only a narrow excitonic emission. These results highlight that excess inorganic precursors is important for obtaining white emission from perovskites films. In addition, white emission was also similarly observed from *m*-XDLB single crystals, with the formula $(\text{NH}_3\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3)\text{PbBr}_6$. This is consistent with XRD findings that using excess PbBr_2 precursors actually minimizes structural difference and give rise to desired optical properties.

In this study, self-trapped excitons were found to be responsible for broad emission from *m*-XDLB with 50 % excess PbBr_2 . Different from PEPC in Chapter 5, these excitons undergo self-trapping at the inorganic framework. Temperature dependent PL measurements revealed a self-trapping barrier and large exciton-phonon coupling strength. The self-trapping process appears as a short lifetime component in PL lifetime measurements, and was absent in non-white emitting samples. Consistently, this component was also observed in TAS measurements with ultrafast lifetime of (~ 170 fs). Lastly, spectral features from TAS measurements also concurs with the presence of self-trapped excitons.

6.2 Results and Discussion

6.2.1 Excess PbBr₂ precursor for White Emission

The absorption spectrum of *m*-XDLB perovskite thin films fabricated with various amount of excess PbBr₂ is shown in Figure 6.1(a). The spectra with 0 and 0.5 mole of excess PbBr₂ showed similar excitonic absorption at ~311 nm. Thin films fabricated without excess PbBr₂ (0 mole) employ organic and inorganic precursors with ratio of 2:1. On the other hand, the excitonic absorption red shifts to 381 nm with the addition of 1 mole of excess PbBr₂. Correspondingly, drastic changes to emission properties were also observed in these samples (Figure 6.1(b)). The addition of PbBr₂ in such large amount (1 mole) gives rise to broad emission with 310 nm excitation, which contrasts to only a narrow emission from the other two samples. Similar to PEPI (Chapter 4) and PEPC (Chapter 5), the narrow PL peaks at ~375 nm in Figure 6.1(b) can be assigned to free excitonic emission due to close wavelength proximity from free excitonic absorption peaks in Figure 6.1(a).

6.2.2 Excitonic White Emission

The species responsible for broad emission from *m*-XDLB thin films with 1 mole of excess PbBr₂ can be identified by changing the excitation wavelength to 360 nm. This wavelength is chosen to obtain near-resonant absorption of free excitons, and also to prevent overlapping of the laser tail with the emission spectrum. As shown in Figure 6.2(a), a similar broad emission is obtained with 360 nm excitation, which strongly suggests excitonic origins behind the broad emission. Calculations of CIE 1931 coordinates showed that the broad emission lies in the white region of the CIE 1931 color plot, with coordinates of (0.36, 0.40) (Figure 6.2(b)). The CCT was also calculated to be 4805 K, and resembles Sunlight

Figure 6.1: (a) Steady-state absorption and (b) PL spectrums of *m*-XDLB thin films prepared with different amount of excess PbBr_2 . The PL experiment was conducted using 310 nm excitation laser pulses (50 fs, 1 kHz) with a fluence of $5.7 \mu\text{J}/\text{cm}^2$.

(Figure 2.12). Similar to PEPC, PL lifetimes of these samples remain unchanged at 2.8 ± 0.1 ns when measured across the broad emission at 500, 550, and 600 nm. This suggests that the broad emission originates from a single excitonic state (Figure 6.2(c)).

Unlike PEPC (Chapter 5), power dependent measurements could not be conducted on *m*-XDLB thin films to verify the species responsible for broad emission, since samples photodegrade at higher laser fluences. Both emission peaks at ~ 400 and 550 nm suffers from a reduction in intensities at higher fluences (Figure 6.3(a) and (b)). In addition, measurements at high laser fluences could not be conducted for extended period of time due to UV-induced samples degradation (Figure 6.3(c)), where a 20 % decrease in PL intensity is observed after 30 minutes of continuous excitation. This UV-degradation phenomenon has also been observed in another low dimensional bromide perovskite [6], and has been attributed to degradation of organic framework. Compared to PEPC (Figure 5.15), this material is much unstable under UV photoexcitation.

Figure 6.2: (a) Steady-state PL spectrum, (b) CIE 1931 color plot, and (c) TRPL kinetics measured at 500, 550, 600 nm of *m*-XDLB thin film fabricated using 1 mole of excess PbBr_2 . The PL and TRPL experiments were conducted using 360 nm ($5.7 \mu\text{J}/\text{cm}^2$) and 310 nm ($8.5 \mu\text{J}/\text{cm}^2$) excitation laser pulses (50 fs, 1 kHz) respectively. The CIE 1931 chromaticity diagram template is obtained from OriginLab Technical Support [5].

Figure 6.3: (a) Excitation fluence-dependent PL spectrum, (b) PL peak intensity as a function of laser fluence, and (c) photostability measurements of *m*-XDLB thin film prepared using 1 mole of excess PbBr_2 . The PL and photostability experiments were conducted using 360 nm excitation laser pulses (50 fs, 1 KHz). The photostability measurement was conducted continuously for ~ 2 hours at fluence of $30 \mu\text{J}/\text{cm}^2$ in an N_2 environment.

Figure 6.4: (a) Steady-state absorption and (b) PL spectrum of pristine PbBr_2 and *m*-XDLB thin film prepared using 1 mole of excess PbBr_2 . The PL experiment was conducted using 310 nm excitation laser pulses (50 fs, 1 kHz) with a fluence of $4.2 \mu\text{J}/\text{cm}^2$.

6.2.3 Negligible Contributions from PbBr_2 Thin Film

The influence from unreacted PbBr_2 on white emission should also be investigated given the large amount used. PbBr_2 could potentially contribute to the white emission since it can be photoexcited at both 310 and 360 nm (Figure 6.4(a)). However, no emission could be observed from it in the visible region following 310 nm above-bandgap excitation (Figure 6.4(b)). This measurement demonstrates that large amount of excess PbBr_2 precursors has negligible influence on white emission.

6.2.4 *m*-XDA₂ PbBr_6 Single Crystals

Stoichiometric *m*-XDLB single crystals can be prepared using vapor-assisted crystallization. Compared to spin-coating, the long crystallization process allows slow assembly of stoichiometric perovskites with defect density expected to be low. Single crystal XRD revealed the chemical formula of these crystals to be $(\text{NH}_3\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3)_2\text{PbBr}_6$ (or *m*-XDA₂ PbBr_6). Theoretically, this formula

Figure 6.5: PL spectrum of *m*-XDA₂PbBr₆ single crystal showing broad emission across the visible spectrum. The PL experiment was conducted using 310 nm excitation laser pulses (50 fs, 1 kHz) with a fluence of 8.5 $\mu\text{J}/\text{cm}^2$.

can be obtained by using $\text{BrNH}_3\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3\text{Br}$ and PbBr_2 precursors in molar ratio of 2:1. Surprisingly, these single crystals also emit white light (Figure 6.5) with CIE 1931 coordinates of (0.35, 0.40). This phenomenon is different from narrow emitting *m*-XDLB thin film fabricated using 2:1 precursors ratio (or 0% excess PbBr_2) (Figure 6.1(b)). These results imply that *m*-XDLB formation is different during spin-coating and vapor-assisted crystallization. However, these observations are not universal since similar PL spectra are observed from $\text{CH}_3\text{NH}_3\text{PbI}_3$ 3D-OMHP fabricated using spin-coating and vapor-assisted crystallization [7].

Structural analysis was also carried out by Mr. Krishnamoorthy Thirumal using single crystal XRD data. These analysis revealed that there is no corner sharing of PbI_6^{4-} octahedra in *m*XDA₂PbBr₆ single crystals. As such, *m*XDA₂PbBr₆ possessed a “0D” perovskite structure, which is similar to Cs_4PbBr_6 perovskite (Figure 6.6). The XRD patterns of *m*-XDLB samples with various amount of

Figure 6.6: Structure of Cs_4PbBr_6 showing isolated PbI_6^{4-} octahedra [9].

excess PbBr_2 is shown in Figure 6.7. Significant changes in XRD features can be observed with addition of excess PbBr_2 . Notably, the XRD features of single crystal (black) and thin film without excess PbBr_2 (red) are significantly different, and is consistent with PL findings in Figure 6.1(b) and 6.5. In addition, no PbBr_2 peaks (typically at $\sim 10^\circ$ [8]) were observed in all patterns, which is consistent with the lack of PbBr_2 visible emission in Figure 6.4.

As such, the introduction of excess PbBr_2 favours the formation of stoichiometric white emitting perovskite, with pattern resembling that of single crystal as PbBr_2 amount increases. This can also be seen from the similarities between XRD peak at $\sim 8^\circ$ (Figure 6.7) and PL spectrums of single crystal (black) and *m*-XDLB thin film fabricated with 1 mole of excess PbBr_2 (Figure 6.1 and 6.5).

6.2.5 Evidence of Self-trapped Excitons

Figure 6.8(a) shows the temperature dependent PL spectrum of *m*-XDLB thin film prepared using 1 mole of excess PbBr_2 . Similar to PEPC, there is PL enhancement and FWHM narrowing when temperature is lowered. However, the emission deviates from white at low temperature, which is different from PEPC

Figure 6.7: XRD pattern of different *m*-XDLB samples. The simulated pattern is derived from single crystal XRD data of *m*-XDA₂PbBr₆ single crystal.

(Figure 6.9).

Similar analysis to temperature dependent integrated PL intensity and FWHM can be carried out using Equation 4.1 and 5.2. Firstly, two activation energies of 9.4 ± 0.7 and 57 ± 3 meV were found to be responsible for temperature dependent integrated PL intensity change (black data points - Figure 6.8 (b)). The smaller energy of 9.4 ± 0.7 meV is likely to be a self-trapping barrier, which can easily be overcome and lead to PL reduction at higher temperature. This barrier is also similarly observed in PEPC (Chapter 5.2.6). The larger energy of 57 ± 3 meV (or 460 ± 20 cm⁻¹) corresponds to a Raman mode in mXDA₂PbBr₆ single crystal (labelled in Figure 6.10 (a)). In addition, this mode corresponds well to a Raman mode in the organic precursors (Figure 6.10 (b) and Reference [10]), which suggests reduction in PL intensity at higher temperature is also due to increased non-radiative recombination assisted by organic phonon mode. The reduction of non-radiative recombination is also consistent with lifetime lengthening of the broad emission at lower temperature (Figure 6.11).

The fitting of temperature dependent FWHM plot with Equation 5.2 yields the

Figure 6.8: (a) Temperature dependent PL spectrum of *m*-XDLB thin film fabricated with 1 mole of excess PbBr_2 between 20 and 300 K. Inset shows the evolution of peak intensity at ~ 400 and 600 nm as a function of temperature. (b) Integrated PL intensity (black) and FWHM (blue) of the same sample as a function of temperature. These plots are extracted from (a). The black and blue data points are fitted with Equation 4.1 and 5.2 respectively. The PL experiment was conducted using 310 nm excitation laser pulses (50 fs, 1 kHz) with a fluence of $4.2 \mu\text{J}/\text{cm}^2$.

Figure 6.9: CIE 1931 coordinates of *m*-XDLB thin film prepared using 1 mole of excess PbBr_2 as a function of temperature. There is a shift in coordinates towards orange region as temperature is lowered. The experiment was conducted using 310 nm excitation laser pulses (50 fs, 1 kHz) with a fluence of $4.2 \mu\text{J}/\text{cm}^2$. The CIE 1931 chromaticity diagram template is obtained from OriginLab Technical Support [5].

Figure 6.10: Room temperature Raman spectrum of (a) *m*- $\text{XDA}_2\text{PbBr}_6$ single crystal, and (b) *m*- XDABr_2 organic precursor.

Figure 6.11: Temperature dependent PL kinetics of *m*-XDLB thin film fabricated with 1 mole of excess PbBr_2 . The TRPL experiment was conducted using 310 nm excitation laser pulses (50 fs, 1 kHz) with a fluence of $4.2 \mu\text{J}/\text{cm}^2$.

following parameters: $\Gamma_0 = 504 \text{ meV}$, $\Gamma_{LO} = 140 \pm 40 \text{ meV}$, $E_{LO} = 16 \pm 3 \text{ meV}$, $\Gamma_{Inh} = 150 \text{ meV}$, and $E_A = 9.0 \text{ meV}$. There is a small shift in LO phonon energy of $16 \pm 3 \text{ meV}$ (or $130 \pm 30 \text{ cm}^{-1}$) from single crystal Raman peak at 110 cm^{-1} (labelled in Figure 6.10). The mode at 110 cm^{-1} also agrees well with a reported mode in PbBr_2 [11, 12]. The slight deviation in Raman frequencies is also consistent with XRD measurements, where there is a 0.5° difference between peaks values (at $\sim 8^\circ$) for single crystal and thin film with 1 mole of excess PbBr_2 (Figure 6.7 - black and purple patterns).

The large value of Γ_{LO} ($140 \pm 40 \text{ meV}$), which is comparable to white emitting (EBDE)[PbBr_4] [13], also suggests strong exciton-phonon coupling. Therefore the species responsible for broad emission can be assigned to self-trapped excitons. The self-trapping process can also be inferred from Figure 6.8(a) inset since there is a reduction in free excitonic PL intensity at $\sim 400 \text{ nm}$ below 120 K (or 10 meV). Less self-trapped excitons can undergo detrapping to form free excitons

below 120 K.

6.2.6 Self-trapping Kinetics in White Emitting *m*-XDLB Thin Film

Unlike PEPC, the presence of both free and self-trapped excitonic features in the emission spectrum allows more self-trapping kinetics studies to be carried out. Figure 6.12(a) shows the short time-scale PL kinetics of free excitons (measured at 400 nm) in *m*-XDLB thin films fabricated with varying amount of excess PbBr₂ precursors. The white emitting sample with 1 mole of excess PbBr₂ exhibits a short decay component, which is absent in non-white emitting samples. This component has a lifetime of 5 ± 10 ps (limited by ~ 10 ps resolution of streak camera) and can be associated with self-trapping process. The intrinsic difference between these perovskites is also reflected in the long time-scale PL kinetics measured at 400 nm (Figure 6.12(b)), with significantly longer free excitonic lifetime observed for the white emitting perovskite. In addition, the short decay component is only observed for emission at 400 nm (free excitons) and not 550 nm (self-trapped excitons), which further suggests self-trapping of free excitons (Figure 6.12(c)).

Temperature dependent PL kinetics in Figure 6.12(d) also revealed an interplay between non-radiative recombination and self-trapping in the white emitter. The action of lowering temperature can reduce non-radiative recombination of free excitons due to phonon absorption. This leads to a higher free excitonic PL peak intensity at lower temperature (**Region A** in Figure 6.12(d)). Besides self-trapping of free excitons, de-trapping of self-trapped excitons can also occur simultaneously. The increase in temperature provides enough thermal energy to overcome self-trapping, converting self-trapped excitons back to free excitons. As such, more free excitons can undergo radiative recombination giving rise to higher PL intensity (**Region B** in Figure 6.12(d)). The increased conversion of self-trapped excitons back to free excitons also concur with a decrease of

self-trapped excitonic PL at higher temperature (Figure 6.8(a) inset). As such, the temperature dependent PL kinetics of *m*-XDLB provides evidence of self-trapping process.

TAS also revealed a broad and featureless PIA plateau from *m*-XDLB white emitter, which provides complementary evidence for the presence of self-trapped excitons (Figure 6.13(a) and (b) inset). This feature is also similarly observed from PEPC in Chapter 5.2.6. In addition, the PIA lifetimes probed across the broad plateau at 450, 500, 550, and 600 nm were found to be similar (Figure 6.13 (b)), and is consistent with the invariant PL lifetimes of self-trapped excitons in Figure 6.2(c).

Self-trapping lifetime in this white emitting material can be determined by probing away from the broad PIA plateau towards UV region. A short component, consistent with PL measurement in Figure 6.13(c), can be observed when probed away from the self-trapped excitonic state towards UV region where free excitonic absorption occurs. This component, which is limited by the laser FWHM, has a lifetime of 170 ± 150 fs. This also gives a better estimate of self-trapping time compared to PL measurements in Figure 6.12(c). This ultrafast lifetime is also consistent with extracted phonon period of 260 ± 40 fs or (16 ± 3) meV, and suggests efficient self-trapping. This efficient process is possible due to the presence of a small self-trapping barrier (~ 10 meV) in this material. The kinetics of free and self-trapped excitons are summarized in Figure 6.14.

6.2.7 Comparision between PEPC and *m*-XDLB Perovskites

Table 6.1 summarizes the similarities and differences of white emitting PEPC and *m*-XDLB perovskites from Chapter 5 and 6. Both white emitting materials are solution processable and shows strong excitonic properties. However, the key difference lies in the location where excitonic self-trapping occurs: organic

Figure 6.12: (a) Short and (b) long time scale PL kinetics of *m*-XDLB thin film fabricated with different amount of excess PbBr_2 measured at 400 nm (free excitonic emission). (c) PL kinetics of *m*-XDLB thin film fabricated with 1 mole of excess PbBr_2 measured at 400 (free excitonic emission) and 550 nm (self-trapped excitonic emission). (d) Temperature dependent PL kinetics of *m*-XDLB thin film fabricated with 1 mole of excess PbBr_2 measured at 400 nm (free excitonic emission). The TRPL experiment was conducted using 310 nm excitation laser pulses (50 fs, 1 kHz) with a fluence of 8.5 $\mu\text{J}/\text{cm}^2$.

Figure 6.13: (a) Pseudocolor TA plot and (b) PIA kinetics of *m*-XDLB thin film fabricated with 1 mole of excess PbBr_2 precursor. Inset shows the TA spectrum as a function of visible probe wavelength at selected delay time from -2 ps to 5 ns. (c) TA kinetics of *m*-XDLB thin film fabricated with 1 mole of excess PbBr_2 precursor probed away from self-trapped states. The TA experiment was conducted using 310 nm excitation laser pulses (50 fs, 1 kHz) with a fluence of 23.8 $\mu\text{J}/\text{cm}^2$.

Figure 6.14: Summary of excitonic processes and lifetimes in white emitting *m*-XDLB perovskite.

framework for PEPC and inorganic framework for white emitting *m*-XDLB. In addition, PEPC appears to be more suitable for both optically pumped and electrically gated devices given good UV photostability and lack of potential barriers in the parallel plane. On the contrary, the poor photostability and non-corner sharing PbBr_6^{4-} limits its applications for devices. Nonetheless, this work highlights the importance of both organic and inorganic precursors for the design of perovskite white emitters.

Table 6.1: Comparison between PEPC and *m*-XDLB white emitters.

Perovskites	PEPC	<i>m</i> -XDLB
Dimensionality	2D	0D
Excitonic Absorption Maximum (nm)	340	400
Solution Processible	Yes	Yes
Emissive Species	Excitons	Excitons
Nature of Broad Emission in Thin Films	Intrinsic	Dependent on excess PbBr ₂
Location of Excitonic Self-trapping	Organic framework	Inorganic framework
Exciton-phonon Coupling Strength (meV)	265 ± 80 (Large)	140 ± 40 (Large)
CIE 1931 Coordinates	White region	White region
Low Temperature CIE 1931 Coordinates	Nearly invariant	Shifts to orange region
Dominant Modes causing non-radiative recombination	Organic phonon mode	Inorganic phonon mode
Self-trapping time (fs)	-	170 ± 150
Photostability (UV)	Stable	Unstable

6.3 Summary

The addition of excess inorganic precursors was found to be crucial, especially during spin coating, for white emission from low dimensional perovskites. The broadband emission from excess leaded *m*-XDLB thin film was investigated using PL and TAS and was found to originate from self-trapped excitonic recombination, which occurs at ultrafast time scale (~ 170 fs) after laser excitation. It was also found that self-trapping occurs at the inorganic framework in this white emitter, and is consistent with conventional role of inorganic framework for white emission from perovskites. Together with findings in Chapter 5, our study affirms the importance of both organic and inorganic precursors for white emission from low dimensional perovskites.

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Chapter 7

Conclusion and Future Works

In this chapter, a summary of findings in this thesis will first be given. Next, the implications of these findings to the perovskite field will be discussed. The hypotheses in chapter 1 will also be revisited to reconcile with the findings. In addition, outstanding questions in this thesis will be discussed. Lastly, future works pertaining to this thesis will also be covered.

7.1 Conclusion

The roles of bound excitons in low dimensional light emitting perovskites are investigated in this thesis. Specifically two hypothesis in Chapter 1 on light emission properties of perovskites were tested.

The first hypothesis states the lack of biexcitonic optical gain in layered 2D-OMHP is due to influence from defects. Optical studies were carried out on PEPI thin film (**Chapter 4**) to test out this hypothesis. These studies revealed that the presence of defects is one of the reason that limits biexcitonic gain in this material. The presence of defects aids the formation of bound excitons, which subsequently allows the formation of bound biexcitons. It was found that the dominant defect species limiting optical gain are organic surface vacancies. The process of

biexcitons formation is also limited by free and bound excitonic recombination, which in turn greatly increases biexcitonic ASE threshold. Theoretical modelling based on these excitonic dynamics revealed that competing relaxation channels give rise to a large biexcitonic ASE threshold of $\sim 1.4 \text{ mJ/cm}^2$ in PEPI thin film. The second reason that limits biexcitonic optical gain in PEPI was due to its low damage threshold. No optical gain was observed below this threshold at both low (10 K) and room temperature. In addition, the damage threshold value was found to be ~ 1 order of magnitude smaller than calculated ASE threshold. Above this value, PL intensity of PEPI diminishes irreversibly and optical damage takes place. These findings highlight the role of defects in limiting optical gain for 2D-OMHP.

The second hypothesis states that obtaining white emission from low dimensional perovskites is highly dependent on sample preparation (type and amount of precursors). Till now, the effects of sample preparation have not been investigated thoroughly for these white emitting materials. The dependence on white emission on type of precursors is deduced from literature, where changing either organic or inorganic precursors leads to white emission. As of now, general consensus points to the role of inorganic precursors for white emission. Surprisingly, the role of organic framework is not reported. Optical studies on PEPC show that the organic framework do play a role in exciton-phonon coupling, leading to white emission (**Chapter 5**). The white emission is a result of excitons coupled to the organic framework. The exciton-phonon coupling strength was found to be large and comparable to ZnO quantum well, which is known for their strong exciton-phonon coupling strength. Scattering of excitons by phonons to higher energies is responsible for the broad emission. The dependence of precursors amount to white emission is also observed in **Chapter 6**, where excess precursor is needed for formation of stoichiometric *m*-XDLB thin film. PL studies show that excess inorganic precursors is important for white emission from *m*-XDLB thin film. In

addition, White emission is similarly observed for *m*-XDLB single crystals. The XRD pattern of *m*-XDLB thin film tends to that of single crystal as amount of PbBr₂ precursor increases. Similarly to PEPC, the species responsible for white emission in *m*-XDLB is self-trapped excitons. However, these excitons are coupled strongly to the inorganic framework. These findings also highlight the importance of sample preparation for white emission.

All in all, the two hypotheses are tested and validated to be true, with new findings generated in the process.

7.1.1 Significance and Novelty of Findings to Scientific Community

The new findings in this work have answered two important questions in the scientific community:

The first question is on the difficulty of obtaining optical gain from layered 2D-OMHP thin films, which has been unanswered over the past 20 years. The results in Chapter 4 lead to a few proposed solutions in overcoming the optical gain problems (Chapter 4.2.9), which might be useful in guiding the development of 2D-OMHP-based gain medium for laser applications.

The second question is on the influence of precursors on optical properties of low dimensional white emitting perovskites. It is currently accepted by the scientific community that inorganic framework is responsible for the broad emission. However, the findings from Chapter 5 and 6 suggest that both organic framework and excess inorganic precursors are equally important for obtaining white emission in these materials. Importantly, these factors may shed new light on the mechanism of white emission, and suggest additional versatility in tuning the white emission using the organic framework. These knowledge could assist the scientific community with fabrication of novel white emitting perovskites with better optical properties. These findings also suggest new candidates for white light

applications.

7.2 Outstanding Questions

Despite the findings in this thesis, there are still outstanding questions that needs to be addressed for future works:

The first question is based on the three proposed solutions in Chapter 4.2.9. These solutions have not been tested, even though they are proposed based on sound experimental findings. As such, this becomes the first outstanding question in this thesis and should be revisited as future work.

The second question is regarding the choice of precursors for white emission from low dimensional perovskites. It was found in Chapter 5 and 6 that both organic and inorganic precursors are important for white emission. Nonetheless, no one has been able to predict the correct organic and inorganic precursors combination that gives rise to white emission. This prediction, which is the second outstanding question, should be a part of future works.

The third question is regarding several unknown intrinsic parameters, such as charge carriers diffusion length, trap density, and recombination rate constants in white emitting perovskites. These parameters should be measured and analysed as they have direct correlation to device performance.

7.3 Future Works

The following sections discuss three works that addresses the outstanding questions in this thesis.

7.3.1 Type II Perovskites for ASE

The three proposed solutions in Chapter 4 involve employing (i) laser cavity, (ii) $(\text{H}_3\text{N}-\text{R}-\text{NH}_3)\text{PbI}_4$ structure, and (iii) type II electronic configuration. Solution (i) and (ii) could reduce lasing threshold by increasing optical feedback and reducing trap density respectively. They could be implemented during sample fabrication. On the other hand, the implementation of solution (iii) is not straight forward and requires the right organic precursors for a type II structure. A type II structure allows single excitonic gain to occur at a much lower threshold [1]. Till now, this type of electronic alignment has not been realized in 2D-OMHP.

In principle, one could modify the highest occupied molecular orbital (HOMO) and/or lowest unoccupied molecular orbital (LUMO) of the organic framework to yield a type II configuration. This can be carried by introducing more electron donating or withdrawing groups to the π -conjugated organic precursors. In general, electron donating groups will raise HOMO energy level while electron withdrawing groups will lower LUMO energy level [2, 3]. As such, a proposed strategy would be to introduce more electronegative nitrogen content in organic precursors to increase HOMO energy level (Figure 7.1). Consequently, this could result in a type II configuration to realize single excitonic gain, and could also drive the perovskite field towards lasing with a even lower threshold. In addition, computational screening with different organic frameworks could also be carried out to identify possible perovskites with a type II configuration.

7.3.2 Fingerprints of White Emitting Perovskites

It is currently challenging to predict the correct combinations of organic and inorganic precursors that give rise to white emission. As such, it is important to gather all white emitting 2D-OMHP in literature to carry out a systematic study to identify fingerprints that are unique to white emission.

Figure 7.1: Possible modification of organic framework to create a type II 2D-OMHP.

A plausible fingerprint that is unique to white emission would be the polarization of both organic and inorganic frameworks. This polarization could result in selective coupling of excitons to either organic or inorganic framework. The experimental findings could also be supplemented with computational studies that investigate the relationship between polarization and exciton-phonon coupling strength. These findings could lead to new perspective on the origins of white emission in these low dimensional perovskites.

7.3.3 Intrinsic Parameters of White Emitting Perovskites

As of now, most studies in literature are focusing on the origins of white emission in low dimensional perovskites. However, white emitting performance in devices are also dependent on other intrinsic parameters, such as charge carriers diffusion length, trap density, and recombination rate constants. Charge carriers diffusion length is proportional to probability of radiative recombination from injected charges. The amount of traps in the material can also limit this probability. Recombination rate constants provide information of monomolecular,

Figure 7.2: Typical recombination processes in semiconductors. Figure adapted from Reference [11].

bimolecular, and Auger recombination in the material (Figure 7.2). Auger recombination, which is a non-radiative trimolecular process, should be studied since it is significant at high carrier concentrations, and is typically found in working LEDs. These intrinsic parameters could be measured using ultrafast optical spectroscopic techniques such as TRPL and TAS, and should be pursued as future works. The importance of ultrafast optical measurements are reflected in the 3D-OMHP solar cell field, where numerous photophysical studies are carried out with aim to better understand and further improve the material [4–10].

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Appendix A

Correction of PL Spectrum

Instrument-related artifacts can arise during PL measurements due to the wavelength dependent response (quantum efficiency) of CCD, PMT, and monochromator. All fs laser excited PL spectrums are measured using CCD and monochromator while all CW excited PL spectrums are measured using PMT and monochromator. Different detection configurations are needed because different set-ups are used to measure fs and CW excited PL spectrum. The relationship between quantum efficiency and wavelength is also known as the response function ($R(\lambda)$). There is a need to perform spectral correction on the detected PL spectrum ($I_{det}(\lambda)$) to obtain the true PL spectrum ($I(\lambda)$). This is especially crucial for sample emission that has large overlap with the working wavelengths of CCD, PMT and monochromator, *e.g.* broad emission.

The steady state PL spectrum correction are performed using the following mathematical expression:

$$I(\lambda) = \frac{I_{det}(\lambda)}{\prod_i R_i(\lambda)}, \quad (\text{A.1})$$

where $R_i(\lambda)$ represents individual component in the detector setup that possesses wavelength dependent response. In addition, the overall response function function ($\prod_i R_i(\lambda)$) is assumed to be largely influenced by only the CCD, PMT, and monochromator response functions (R_{CCD} , R_{PMT} , and R_{mono}) in Figure 3.7 and

A.2. As such, Equation A.1 reduces to:

$$I(\lambda) = \frac{I_{det}(\lambda)}{R_{CCD}(\lambda)R_{mono}(\lambda)}, \quad (A.2)$$

which can be used for fs laser excited PL spectrum correction, and

$$I(\lambda) = \frac{I_{det}(\lambda)}{R_{PMT}(\lambda)R_{mono}(\lambda)}, \quad (A.3)$$

which can be used for CW excited PL spectrum correction.

Both $I_{det}(\lambda)$ and $I(\lambda)$ of PEPC thin film under 340 nm CW excitation are shown in Figure A.1. A red-shift in PL spectrum can be observed after spectral correction. This is particularly due to the low quantum efficiency of R928P photon counting PMT (Horiba Fluoromax-4 Spectrofluorometer) at red wavelengths (Figure A.2), which is consistent with a more intense PL emission at red wavelengths after correction in Figure A.1. Similar correction is also performed for the fs laser excited PL spectrum for all broad emitting samples in this thesis. The correction is also important for accurate comparison of spectral differences between CW and fs excited PL spectrum in Chapter 5.2.7. Notably, the uncorrected PL spectrum of PEPC thin film using CW excitation shows a large unphysical blue-shift from the corrected fs excited PL spectrum (Figure A.3).

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Figure A.1: PL spectrum of PEPC thin film before and after spectral correction.

Figure A.2: Typical spectral response of R928 PMT. Figure adapted from Reference [1].

Figure A.3: Comparison of (a) corrected and (b) uncorrected CW excited PL spectrum with corrected fs excited PL spectrum of PEPC thin film.