Modulating carrier confinement in inorganic metal halide perovskites for enhanced efficiencies in light-emitting diodes

Ng, Yan Fong

2019

Ng, Y. F. (2019). Modulating carrier confinement in inorganic metal halide perovskites for enhanced efficiencies in light-emitting diodes. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/136972>

<https://doi.org/10.32657/10356/136972>

This work is licensed under a Creative Commons Attribution-NonCommercial 4.0 International License (CC BY-NC 4.0).

Downloaded on 26 Apr 2023 22:54:34 SGT

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**MODULATING CARRIER CONFINEMENT IN INORGANIC
METAL HALIDE PEROVSKITES FOR ENHANCED
EFFICIENCIES IN LIGHT-EMITTING DIODES**

NG YAN FONG

**Interdisciplinary Graduate School
Energy Research Institute @ NTU**

2019

**MODULATING CARRIER CONFINEMENT IN INORGANIC
METAL HALIDE PEROVSKITES FOR ENHANCED
EFFICIENCIES IN LIGHT-EMITTING DIODES**

NG YAN FONG

INTERDISCIPLINARY GRADUATE SCHOOL
ENERGY RESEARCH INSTITUTE @ NTU

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

2019

Statement of Originality

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

31st July 2019

.....
Date

A handwritten signature in black ink, consisting of stylized, overlapping strokes that form the name 'Ng Yan Fong'.

.....
Ng Yan Fong

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

31st July 2019

.....
Date

.....
Assoc Prof Nripan Mathews

Authorship Attribution Statement

This thesis contains material from papers published in the following peer-reviewed journals where I was the first author.

Chapter 4 is published as Y.F. Ng, N.F. Jamaludin, N. Yantara, M. Li, V.K.R. Irukuvarjula, H.V. Demir, T.C. Sum, S. Mhaisalkar, and N. Mathews. Rapid Crystallization of All-Inorganic CsPbBr₃ Perovskite for High-Brightness Light-Emitting Diodes. *ACS Omega* **2** (6), 2757-2764 (2017). DOI: 10.1021/acsomega.7b00360.

The contributions of the co-authors are as follows:

- Dr N. Yantara and Prof N. Mathews suggested the research direction.
- I co-designed the experiments with N.F. Jamaludin and both of us contributed equally in all laboratory works at the Energy Research Institute @ NTU (ERI@N) as well as the School of Physical and Mathematical Sciences (SPMS), Physics and Applied Physics (PAP) department, including preparation of thin film samples, various characterization such as X-ray diffraction, scanning electron microscopy, absorption and photoluminescence measurements, as well as fabrication and testing of devices.
- Dr M. Li performed time-resolved photoluminescence study with input from Prof T.C. Sum
- V.K.R. Irukuvarjula assisted with tooling and optimization of the electron transport layer.
- I carried out photoluminescence quantum yield measurements under the supervision of Prof H.V. Demir.
- I co-prepared the manuscript drafts with N.F. Jamaludin. The manuscript was revised together with Dr N. Yantara, Prof H.V. Demir, Prof T.C. Sum, Prof S. Mhaisalkar and Prof N. Mathews.

Chapter 5 is published as Y.F. Ng, W.J. Neo, N.F. Jamaludin, N. Yantara, S. Mhaisalkar, and N. Mathews. Enhanced Coverage of All-Inorganic Perovskite CsPbBr₃ through

Sequential Deposition for Green Light-Emitting Diodes. *Energy Technology* **5** (10), 1859-1865 (2017). DOI: 10.1002/ente.201700475.

The contributions of the co-authors are as follows:

- I conceived the idea with guidance from Prof N. Mathews and performed all laboratory work and analysis at ERI@N.
- W.J. Neo helped with sample preparation and optical measurements including absorption and photoluminescence.
- N.F. Jamaludin assisted with scanning electron microscopy and device fabrication.
- Dr N. Yantara contributed to the data analysis.
- I prepared the manuscript drafts. The manuscript was revised together with Dr N. Yantara, Prof S. Mhaisalkar and Prof N. Mathews.

Chapter 6 is published as Y.F. Ng, S.A. Kulkarni, S. Parida, N.F. Jamaludin, N. Yantara, A. Bruno, C. Soci, S. Mhaisalkar, and N. Mathews. Highly Efficient Cs-based Perovskite Light-Emitting Diodes Enabled by Energy Funnelling. *Chemical Communications* **53** (88), 12004-12007 (2017). DOI: 10.1039/C7CC06615E.

The contributions of the co-authors are as follows:

- I conceived the idea with guidance from Dr S.A. Kulkarni and Prof N. Mathews.
- I performed all laboratory work at ERI@N, with the help of S. Parida in sample preparation and optical measurements including absorption and photoluminescence.
- I fabricated, tested and analyzed the devices with input from Dr S.A. Kulkarni.
- N.F. Jamaludin and Dr A. Bruno performed the time-resolved photoluminescence spectroscopy measurements under the supervision of Prof C. Soci.
- I prepared the manuscript drafts. The manuscript was revised together with Dr S.A. Kulkarni, Dr N. Yantara, Prof C. Soci, Prof S. Mhaisalkar and Prof N. Mathews.

Chapter 7 is currently being prepared as a manuscript: Y.F. Ng, B. Febriansyah, N.F. Jamaludin, D. Giovanni, N. Yantara, T.C. Sum, S. Mhaisalkar, and N. Mathews. Rational

Design of Ligand Molecules for Mixed-Dimensional CsPbBr₃ Perovskite Light-Emitting Diodes.

The contributions of the co-authors are as follows:

- I conceived the idea with B. Febriansyah, with guidance from Prof N. Mathews.
- B. Febriansyah performed the chemical synthesis of all requisite organic compounds as well as growing of single crystals.
- I performed all laboratory work and analysis at ERI@N, including sample preparation and characterization.
- N.F. Jamaludin assisted with device fabrication and testing.
- D. Giovanni performed transient absorption spectroscopy measurements under the supervision of Prof T.C. Sum.
- Dr N. Yantara and B. Febriansyah contributed to the analysis of the data.
- I prepared the manuscript drafts. The manuscript was revised together with B. Febriansyah, Dr N. Yantara, Prof T.C. Sum, Prof S. Mhaisalkar and Prof N. Mathews.

31st July 2019

.....
Date

.....
Ng Yan Fong

Abstract

Lead halide perovskites have revolutionized the field of optoelectronic research in recent years owing to the excellent semiconductor properties offered by this class of materials. Thin films of these materials possess superior electronic qualities despite being low-cost and solution-processed, with exceptional characteristics such as defect tolerance, band gap tunability, high absorption coefficient and long-range balanced charge transport. Many of such traits are not even found in well-established silicon and gallium arsenide semiconductor technologies. The past decade has seen an unprecedented rise in perovskite photovoltaic research, with power conversion efficiencies reaching 25.2%, surpassing the best-in-class thin-film photovoltaic technologies and almost catching up with silicon. While most of the research work are focused on solar cells, these remarkable properties have made halide perovskites promising semiconductor materials for various other applications, especially light emission. Inorganic and organic light-emitting diodes (LEDs) have transcended the field of artificial lighting and display, bringing significant benefits such as high brightness and efficiencies. Despite this, the high material and processing costs along with inherent limitations have hampered their widespread use. Halide perovskites, leveraging on their extraordinary optical and electronic properties, have manifested strong and efficient electroluminescence. Extremely high colour purity, along with band gap tunability that allows emission colours across the full visible spectrum, has made perovskites strong contenders for display emitters. Within two years since their first incorporation in LEDs, research has led to high luminosities and efficiencies that organic LEDs only managed to achieve after two decades. Recently, external quantum efficiencies (EQEs) have exceeded 20% with various employed strategies such as additive engineering, passivation, and dimensional modulation. Additional waveguide and outcoupling techniques have achieved a record EQE of 28.2%. While more studies have been focused on the organic-inorganic hybrid perovskites (e.g. $\text{CH}_3\text{NH}_3\text{PbX}_3$ where X represents a halide), fully inorganic compounds like CsPbBr_3 are more thermally stable, although poor intrinsic properties such as low exciton binding energy and defective morphology have resulted in lower photoluminescence quantum yield and EQE. The main limitation of this material can be generalized as a carrier confinement problem, and thus the objective of this

thesis is aimed at overcoming this. Strategies to enhance the confinement effect can be classified into two approaches, a geometrical approach which involves physical and spatial confinement of charge carriers, and a dimensional approach which entails electronically confining the charge carriers through an energy cascade phenomenon. The geometrical approach was explored using two different methods: first, a rapid crystallization process was executed which showed that the stronger spatial confinement imparted by smaller grain sizes is essential; and second, a sequential deposition process was carried out to significantly improve the film coverage in order to confine the charge carriers within the perovskite emitter layer and reduce leakage pathways. Both studies firmly show the importance of morphological tuning in the geometrical confinement of charge carriers, confirming that the ideal morphology required is a compact film with small grain size. In the dimensional approach, a mixture of two- and three-dimensional phases, obtained through the excess addition of a large ligand molecule, phenylethylammonium bromide, has shown outstanding photo- and electroluminescence. The multiphase existence provides a cascading energy landscape where the energy or carriers funnel from the high band gap domains to the lowest band gap state, thereby electronically confining the charge carriers and significantly augmenting the carrier density within the emitter phase. In addition, the ligand molecules are found to restrict the growth of the perovskite grains, forming a smooth and compact layer of nano-sized grains. The combination of both geometrical and electronic confinement in the case of the mixed-dimensional perovskite has achieved more than fifty-fold enhancement in LED performances as compared to the pristine CsPbBr₃. Its exceptional results thus spurred the last study, where multiple mixed-dimensional systems are explored with the aim of uncovering the desired characteristics of the ligand molecule. Based on a series of rigorous characterization and comparison, a list of some general guidelines for an effective ligand molecule is established, which is likely applicable to any mixed-dimensional perovskite system. Importantly, these studies lay down the various concepts governing the confinement of charge carriers in CsPbBr₃ and demonstrate their significance in attaining efficient light emission. The knowledge gained will be useful in designing the next generation of perovskite emitters for light-emitting applications, while the ease of scaling up these deposition processes make commercialization of halide perovskite LEDs highly anticipated in the near future.

Lay Summary

The invention of light-emitting diodes (LEDs) have brought better light sources that are brighter, more efficient and reliable than traditional technologies. Over the years, LEDs have evolved from the inorganic material-based, e.g. gallium nitride, to organic (OLED) and quantum dot LEDs, while the applications have also expanded from general lighting to displays such as television and mobile phone screens. Despite their advantages, several manufacturing drawbacks such as the need for difficult and costly fabrication processes have consequentially made LED appliances highly expensive. Halide perovskites, on the other hand, are inexpensive materials that can be solution-processed, for instance, by printing. Despite its low cost and simple deposition process, halide perovskites possess remarkable optical and electronic properties along with bright emission that make them excellent semiconductor materials, especially for light-emitting applications. By simply tuning its chemical composition, the colour of the emitted light can be easily adjusted, which makes it perfect for display applications. This thesis focuses on a specific perovskite compound, cesium lead bromide (CsPbBr_3), for LEDs. Due to the lack of charge confinement, the positive and negative charges do not recombine efficiently, which limits its light emission. Using a simple analogy, if two blind mice are placed in a large, open hall, the chances of them colliding into each other will be extremely low. However, if the hall is modified into a small enclosed room, the probability of collision will be significantly higher. The collision between charge carriers is necessary for light emission. Here, two different strategies were explored to overcome this limitation: first through a geometrical approach, analogous to the blind mice in the large hall and small room scenario; and second through a dimensional approach, which can be described using the following analogy: two randomly moving balls on a level ground will be unlikely to hit each other, but if one modifies the ground into a terrain with multiple slopes (dimensions) and a common valley, one can control the motion of the two balls and force them to roll down towards the valley where they are more likely to collide. The second approach of dimensional confinement proves to be more superior, explained by the energetics of the different dimensions (slopes) that directs the charge carriers towards a common point (valley) and confining them in this specific region, allowing the LED performance to increase more than fifty times.

Eventually, a set of guidelines is established for the future design of such perovskite systems. Importantly, these studies lay down the various concepts governing the confinement of charge carriers in CsPbBr₃ and demonstrate their significance in achieving more efficient light emission. The knowledge gained from this work will be useful in designing the next generation of perovskite light emitters, paving a luminous and cheap way towards commercialization of high-performance perovskite LEDs that may in time, possibly replace the conventional technologies.

Acknowledgements

I would like to take this opportunity to express my deepest gratitude to the following people, without whom I would never have made it to the end.

First and foremost, I would like to show my utmost gratitude to my thesis advisory committee, the best that any student could ever wish for. I would like to thank my super supervisor, Assoc Prof Nripan Mathews, for his invaluable guidance these four years, and for his awesomeness. I am extremely grateful to Prof Sum Tze Chien for his strong support as an innovative co-supervisor. And I would like to show my heartfelt appreciation to my inspirational mentor, Prof Subodh Mhaisalkar, whose encouraging supervision during my undergraduate time has inspired me to take on this journey.

Next, I would like to express my deepest gratitude to Dr Natalia Yantara, for patiently guiding me and for always being the teacher I could count on in times of desperation. I would also like to extend my appreciation to Dr Sjoerd Veldhuis and Dr Chin Xin Yu, both of whom have led our PeLED team to greater heights, and for all their useful advices and suggestions that allowed me to progress further. In addition, I would like to express my thanks to the whole PeLED team who have contributed to my work in one way or another, to all researchers in ERI@N who have been fantastic colleagues, and not forgetting all fellow PhD students who are always there to support one another. Especially, I would like to thank Ms Guo Xintong for helping with last-minute characterizations, as well as Mr Benny Febriansyah who helped synthesize countless molecules for my study as if he owns a chemical plant.

Furthermore, I would like to thank my collaborators for their help in various characterizations, including researchers from the Femtosecond Dynamics Lab, Dr Li Mingjie, Dr Wu Bo, Mr Fu Jianhui, Mr Eugene Tay Yong Kang and Dr David Giovanni; as well as Prof Volkan Demir from Luminous! and Prof Cesare Soci from the Centre for Disruptive Photonic Technologies. Also, I would like to specially thank Prof Henk Bolink

and Prof Christoph Brabec for the eye-opening and delightful lab visits in Spain and Germany respectively.

I would like to further show my sincere gratitude to all administrative staffs from ERI@N and IGS for facilitating the admin procedures and making them smooth sailing, in particular Ms Huang Minying. I would also like to acknowledge IGS, MSE and NTU in general for providing me this scholarship and opportunity to take on this journey, as well as the National Research Foundation Singapore for the funding support through the Competitive Research Programme.

Last but definitely not least, I would like to wholeheartedly thank my family and friends for the encouraging support in stressful and depressing times, without which I would certainly have turned into a zombie by now. And I am extremely thankful to have Ms Nur Fadilah on this adventure with me from the start till the very end, keeping my sanity in check, otherwise part of my mind and soul would have very likely obliterated somewhere along the journey. No matter how little light my LED gives, I know that I always have the brightest one of them all.

Table of Contents

Abstract.....	i
Lay Summary	iii
Acknowledgements	v
Table of Contents	vii
Table Captions.....	xii
Figure Captions.....	xiii
Abbreviations	xxv
 Chapter 1 Introduction.....	 1
1.1 Background and Motivation	2
1.2 Problem Statement.....	5
1.3 Objectives and Scope.....	6
1.4 Dissertation Overview	8
1.5 Findings and Outcomes/Originality.....	9
References	11
 Chapter 2 Literature Review	 13
2.1 Lighting and Display Technologies.....	14
2.2 Evolution of Light-Emitting Diodes (LEDs).....	16
2.3 Emergence of Halide Perovskites.....	20

2.3.1	Halide Perovskite Structure	20
2.3.2	Perovskite Solar Cells (PSCs).....	21
2.3.3	Unique Advantages and Properties of Halide Perovskites	27
2.4	Perovskites in LEDs (PeLEDs)	30
2.4.1	Device Architecture and Working Principle.....	31
2.4.2	Interfacial Layers	32
2.4.3	Factors Affecting PeLED Performance	37
2.4.4	Lower Dimensional Perovskites	39
2.5	Summary of Literature Status, Gaps, and This Thesis in Perspective.....	43
	References	45
Chapter 3 Experimental Methodology.....		67
3.1	Material Synthesis	68
3.1.1	Chemicals.....	68
3.1.2	Synthesis of Naphthyl-based Ligand Molecules.....	69
3.1.3	Characterization of Synthesized Products	71
3.1.4	Perovskite Solution Preparation.....	72
3.2	Perovskite Thin Film Deposition.....	73
3.2.1	N ₂ -Facilitated Spin-Coating.....	74
3.2.2	Sequential Deposition	74
3.3	PeLED Device Fabrication	75
3.4	Characterization.....	77
3.4.1	Crystal Structure and Phase Identification.....	77
3.4.2	Morphological.....	78
3.4.3	Optical.....	78
3.4.4	Electrical	81

References	83
Chapter 4 Charge Carrier Confinement through Grain Size Modulation.....	87
4.1 Introduction	88
4.2 Results and Discussions.....	89
4.2.1 Morphological Control with Gas-Facilitated Process.....	89
4.2.2 Crystal Structure and Phase Analysis	90
4.2.3 Optical Properties.....	92
4.2.4 Verifying Absence of Cs ₄ PbBr ₆ Impure Phase in Deposited CsPbBr ₃ Films..	93
4.2.5 Charge Dynamics Comparison	94
4.2.6 PeLED Device Performance	95
4.2.7 Electroluminescence Spectra Comparison.....	100
4.2.8 Eliminating Thickness Effect.....	101
4.2.9 Effect of N ₂ Gas Pressure and Introduction Time	103
4.3 Conclusion	105
References	106
Chapter 5 Controlling Film Morphology through Sequential Deposition.....	109
5.1 Introduction	110
5.2 Results and Discussions.....	111
5.2.1 Crystal Structure and Phase Analysis	111
5.2.2 Morphological Tuning via Deposition Conditions	114
5.2.3 Optical Properties and Band Gap Determination.....	118
5.2.4 Device Performance with respect to Dipping Time.....	122
5.3 Conclusion	124
References	125

Chapter 6 Elucidating the Energy Cascade Phenomena in CsPbBr₃ Mixed-Dimensional Perovskites..... 129

6.1	Introduction	130
6.2	Results and Discussions.....	130
6.2.1	Optical Properties of Mixed-Dimensional PEABr–CsPbBr ₃ Perovskite.....	130
6.2.2	Energy Funnelling Observed through PL Excitation Spectra and Transient Spectroscopy	133
6.2.3	Morphological Enhancement with Mixed-Dimensional System.....	137
6.2.4	Crystal Structure and Phase Analysis	139
6.2.5	Device Comparison.....	141
6.2.6	Electroluminescence Shift and Analysis.....	143
6.3	Conclusion	144
	References	145

Chapter 7 Ligand Design for Modulation of Mixed-Dimensional Perovskites for Enhanced LED Performance 149

7.1	Introduction	150
7.2	Results and Discussions.....	151
7.2.1	Preliminary Study with Octylammonium Spacer Groups	151
7.2.2	Electroluminescence of Mixed-dimensional CsPbBr ₃ with OABr Spacer Groups.....	154
7.2.3	Mixed-dimensional CsPbBr ₃ with Phenyl Alkyl Spacer Groups	156
7.2.4	Optical Properties of Mixed-dimensional CsPbBr ₃ with Phenyl Alkyl Spacer Groups.....	157
7.2.5	Device Electroluminescence of Mixed-dimensional CsPbBr ₃ with Phenyl Alkyl Spacer Groups.....	164

7.2.6	Towards Naphthyl-based Systems	169
7.2.7	Characterization of 2D Naphthyl-based Lead Bromide Perovskites	170
7.2.8	Morphological and Optical Characterization of Mixed-Dimensional CsPbBr ₃ Perovskites using Naphthyl-based Ligand Molecules	173
7.2.9	Electroluminescence Characteristics of Naphthyl-based Mixed-Dimensional PeLEDs.	184
7.3	Conclusion	192
	References	194
Chapter 8 Conclusion and Outlook.....		199
8.1	Summary of Thesis	200
8.1.1	Geometrical Confinement	200
8.1.2	Electronic Confinement	202
8.2	Overall Contributions and Implications	204
8.3	Outlook and Future Directions	206
8.3.1	Exploration into Functional Molecular Design.....	206
8.3.2	Assessment of Charge Injection Balance.....	208
8.3.3	Towards Large-Area PeLEDs.....	210
8.3.3	Unveiling the Contributions from Energy and Carrier Funnelling.....	211
	References	213
Appendix.....		219

Table Captions

Table 2.1	Projected solid state lighting (SSL) LED lamp targets as compared to conventional incandescent and fluorescent sources. ¹	14
Table 2.2	Examples of LED applications requiring certain wavelengths of light. ²	15
Table 4.1	Optical and photophysical properties of conventional and N ₂ -facilitated CsPbBr ₃ films.....	93
Table 4.2	Comparison of device performance of conventional and N ₂ -facilitated CsPbBr ₃ PeLEDs.	100
Table 4.3	Comparison of device performance of CsPbBr ₃ PeLEDs spin-coated using conventional and N ₂ -facilitated method with N ₂ flow introduced at various timings and pressures.....	103
Table 5.1	Comparison of device performance for sequentially-deposited CsPbBr ₃ PeLEDs with different dipping durations.	124
Table 6.1	TRPL lifetimes and decay parameters of CsPbBr ₃ perovskite films prepared with different mole ratio of PEABr:CsPbBr ₃ (0:1, 0.3:1 and 0.8:1) at different wavelengths.....	136
Table 6.2	Summary of device performance of CsPbBr ₃ light-emitting diodes (PeLEDs) with different mole ratio of PEABr:CsPbBr ₃	143
Table 7.1	Summary of device performance of mixed-dimensional CsPbBr ₃ -based PeLEDs comparing PEABr and OABr as ligand molecules.	155
Table 7.2	Summary of device performance of mixed-dimensional CsPbBr ₃ -based PeLEDs with PhABr, PMABr, PEABr, PPABr and PBABr as ligand molecules.	167
Table 7.3	Summary of device performance of mixed-dimensional CsPbBr ₃ -based PeLEDs with 1-NMA, 2-NMA, 1-NEA, and 2-NEA as ligand molecules.	187

Figure Captions

Figure 1.1 Schematic illustration of (a) the crystal structure of a typical metal halide perovskite compound, (b) solution processing method used to deposit perovskite films,¹⁸ and (c) the device architecture of a standard perovskite light-emitting diode (where HTM, EML and ETL stand for hole transport material, emissive layer, and electron transport layer respectively). (d) Major trend of different display technologies showing comparison between OLED, QDLED and PeLED. The narrow full width at half maximum (FWHM) of the perovskite emission spectrum makes it a superior emitter material in terms of colour purity and saturation.¹⁹ Figure (b) is reprinted with permission from Jung, H. S.; Park, N. G., Perovskite solar cells: from materials to devices. *Small* **2015**, *11* (1), 10-25. Copyright © 2019 American Chemical Society. Figure (d) is reprinted with permission from Kim, Y.-H.; Cho, H.; Lee, T.-W., Metal halide perovskite light emitters. *Proceedings of the National Academy of Sciences* **2016**, *113* (42), 11694-11702. Copyright © 2019 National Academy of Sciences..... 4

Figure 1.2 Schematic illustration of different approaches to enhance exciton confinement in halide perovskites. (Top to down) Geometrical confinement achieved through control of morphology and thickness, (left to right) structural confinement achieved through reduction in dimensionality of the intrinsic lattice structure (3-dimensional bulk to 0-dimensional quantum dots).¹⁷ Reprinted with permission from Colella, S.; Mazzeo, M.; Rizzo, A.; Gigli, G.; Listorti, A., The Bright Side of Perovskites. *The Journal of Physical Chemistry Letters* **2016**, 4322-4334. Copyright © 2019 American Chemical Society. 6

Figure 2.1 (a) Schematic illustration of the working mechanism of a typical LED. (b) Radiative and (c) non-radiative recombination events occurring in LEDs.⁸ Reprinted with permission from Bender, V. C.; Marchesan, T. B.; Alonso, J. M., Solid-State Lighting: A Concise Review of the State of the Art on LED and OLED Modeling. *IEEE Industrial Electronics Magazine* **2015**, *9* (2), 6-16. Copyright © 2019 IEEE..... 17

Figure 2.2 Evolution of OLEDs from single layer to multilayer structure. ETL, EL and HTL refer to the electron transport, emitter and hole transport layers respectively.¹⁰

Reprinted with permission from Thejo Kalyani, N.; Dhoble, S. J., Organic light emitting diodes: Energy saving lighting technology—A review. <i>Renewable and Sustainable Energy Reviews</i> 2012 , 16 (5), 2696-2723. Copyright © 2019 Elsevier.	18
Figure 2.3 Schematic illustration of processes involved in an OLED operation. ¹¹ Reprinted with permission from Brütting, W.; Frischeisen, J.; Schmidt, T. D.; Scholz, B. J.; Mayr, C., Device efficiency of organic light-emitting diodes: Progress by improved light outcoupling. <i>physica status solidi (a)</i> 2013 , 210 (1), 44-65. Copyright © 2019 John Wiley and Sons.....	19
Figure 2.4 Schematic of a typical ABX ₃ perovskite structure.	21
Figure 2.5 NREL chart of best research solar cell efficiencies of various PV technologies over the years. ³¹	23
Figure 2.6 Schematic illustration showing the cross-section architecture of a conventional mesoscopic PSC. ³⁵ The perovskite material is used as the sensitizer layer that is responsible for light absorption and charge generation. TCO and HTM stands for transparent conductive oxide and hole transport material respectively. Reprinted with permission from Grätzel, M., The light and shade of perovskite solar cells. <i>Nature Materials</i> 2014 , 13 (9), 838-842. Copyright © 2019 Springer Nature.	24
Figure 2.7 Evolution of the PSC architecture from mesoscopic (a – b) to planar heterojunction structures (c). ³⁵ Reprinted with permission from Grätzel, M., The light and shade of perovskite solar cells. <i>Nature Materials</i> 2014 , 13 (9), 838-842. Copyright © 2019 Springer Nature.....	25
Figure 2.8 (a) Comparison of the absorption coefficient of MAPbI ₃ perovskite with various other PV technologies such as silicon, GaAs and thin-film systems. ⁸¹ Reprinted with permission from De Wolf, S.; Holovsky, J.; Moon, S.-J.; Löper, P.; Niesen, B.; Ledinsky, M.; Haug, F.-J.; Yum, J.-H.; Ballif, C., Organometallic Halide Perovskites: Sharp Optical Absorption Edge and Its Relation to Photovoltaic Performance. <i>The Journal of Physical Chemistry Letters</i> 2014 , 5 (6), 1035-1039. Copyright © 2019 American Chemical Society. (b) UV-vis absorption spectra of MAPb(I _{1-x} Br _x) ₃ films with different halide composition, showing increase in band gap with higher Br content (from 1 to 7). ⁸⁷ Reprinted with permission from Kulkarni, S. A.; Baikie, T.; Boix, P. P.; Yantara, N.; Mathews, N.; Mhaisalkar, S., Band-gap tuning of lead halide perovskites using a sequential	

deposition process. <i>Journal of Materials Chemistry A</i> 2014 , 2 (24), 9221-9225. Copyright © 2019 Royal Society of Chemistry.	29
Figure 2.9 Evolution of (left) EQE and (right) luminance of PeLEDs over the years as compared to OLEDs and QDLEDs. ¹⁰⁹ Reprinted with permission from Veldhuis, S. A.; Boix, P. P.; Yantara, N.; Li, M.; Sum, T. C.; Mathews, N.; Mhaisalkar, S. G., Perovskite Materials for Light-Emitting Diodes and Lasers. <i>Advanced Materials</i> 2016 , 28 (32), 6804-6834. Copyright © 2019 John Wiley and Sons.	31
Figure 2.10 Schematic of a PeLED device architecture showing the direction of charge carrier flow and radiative recombination in the emissive layer (EML).	32
Figure 2.11 Examples of common ETL and HTM with their respective energy levels graphed alongside the perovskite EML. ¹⁰⁹ Reprinted with permission from Veldhuis, S. A.; Boix, P. P.; Yantara, N.; Li, M.; Sum, T. C.; Mathews, N.; Mhaisalkar, S. G., Perovskite Materials for Light-Emitting Diodes and Lasers. <i>Advanced Materials</i> 2016 , 28 (32), 6804-6834. Copyright © 2019 John Wiley and Sons.	34
Figure 2.12 Ideal energy band alignment of a PeLED device for efficient charge confinement, showing carrier injection and blocking capabilities of the transport layers sandwiching the emitter.	36
Figure 2.13 Schematic illustration of (a) reduced dimensionality of halide perovskites through intercalation of the inorganic PbX_6 octahedra using large organic spacer cations, and (b) a multi quantum well structure of layered perovskites. ¹⁰⁹ Reprinted with permission from Veldhuis, S. A.; Boix, P. P.; Yantara, N.; Li, M.; Sum, T. C.; Mathews, N.; Mhaisalkar, S. G., Perovskite Materials for Light-Emitting Diodes and Lasers. <i>Advanced Materials</i> 2016 , 28 (32), 6804-6834. Copyright © 2019 John Wiley and Sons.	40
Figure 2.14 Crystal structure of 2D perovskites (left) $(2\text{-NMA})_2\text{PbBr}_4$ and (right) $(2\text{-NEA})_2\text{PbBr}_4$ visualized using VESTA. Crystallographic Information Files from the single crystal XRD are obtained from reference [186].	41
Figure 3.1 Molecular structure of various transport materials used: (left) PEDOT:PSS, (middle) Bphen, and (right) TPBi.	68
Figure 3.2 Synthesis route of various naphthyl alkyl amine ligand molecules used in this work.	69

Figure 3.3	Schematic illustration of the preparation of mixed-dimensional CsPbBr ₃ perovskite solution.	73
Figure 3.4	Schematic illustration of the N ₂ -facilitated film formation during the spin-coating process.	74
Figure 3.5	Schematic illustration of the sequential deposition process for CsPbBr ₃	75
Figure 3.6	Schematic illustration of (a) CsPbBr ₃ device architecture and (b) energy band level diagram for each layer.	76
Figure 3.7	Experimental setup for EL characterization of PeLED devices. ³⁰ Reprinted with permission from Chin, X. Y.; Perumal, A.; Bruno, A.; Yantara, N.; Veldhuis, S. A.; Martínez-Sarti, L.; Chandran, B.; Chirvony, V.; Lo, A. S.-Z.; So, J.; Soci, C.; Grätzel, M.; Bolink, H. J.; Mathews, N.; Mhaisalkar, S. G., Self-assembled hierarchical nanostructured perovskites enable highly efficient LEDs via an energy cascade. <i>Energy & Environmental Science</i> 2018 , 11 (7), 1770-1778. Copyright © 2019 Royal Society of Chemistry.	81
Figure 4.1	Surface (top row) and cross-sectional (bottom row) FESEM images of CsPbBr ₃ films deposited on ITO/PEDOT:PSS substrates using (a,c) conventional and (b,d) N ₂ -facilitated process.	89
Figure 4.2	XRD spectra of conventional (black) and N ₂ -facilitated (red) CsPbBr ₃ films (* corresponds to ITO peaks).	91
Figure 4.3	Absorption and PL spectra of the conventional (black) and N ₂ -facilitated (red) CsPbBr ₃ films.	92
Figure 4.4	PL spectra as a function of excitation wavelengths for (a) conventional and (b) N ₂ -facilitated CsPbBr ₃ films.	94
Figure 4.5	Time-resolved photoluminescence (TRPL) decay curves (solid lines are fitted curves) of conventional (black) and N ₂ -facilitated (red) CsPbBr ₃ films.	95
Figure 4.6	3D schematic illustration of the device architecture, carrier movement and corresponding energy levels of various layers in the CsPbBr ₃ PeLEDs used in this work.	97
Figure 4.7	(a) Current density (J) and luminance (L) versus driving voltage (V), and (b) Log J vs log V plot of conventional (black) and N ₂ -facilitated (red) PeLEDs showing various regions of conduction regimes.	98

- Figure 4.8** (a) Current efficiency versus current density, and (b) EQE versus luminance curves of both devices..... 100
- Figure 4.9** EL spectra of both devices at different driving voltages. Pictures in inset show the respective devices under applied bias. 101
- Figure 4.10** (a) Surface and (b) cross-sectional FESEM of conventionally spin-coated CsPbBr₃ films with increased spin speed at 5000 rpm. 102
- Figure 4.11** Surface (top row) and cross sectional (bottom row) FESEM images of N₂-facilitated CsPbBr₃ films deposited on ITO/PEDOT:PSS substrates using (a,c) 1-bar and (b,d) 2-bar pressure. 104
- Figure 4.12** Surface FESEM images of CsPbBr₃ films deposited on ITO/PEDOT:PSS substrates with N₂ flow introduced at (a) 1 s, (b) 3 s, and (c) 5 s from initiation of spin coating..... 105
- Figure 5.1** Photograph of sequentially-deposited CsPbBr₃ films with different PbBr₂ concentration and exposure time in a 10 mg ml⁻¹ CsBr solution..... 111
- Figure 5.2** XRD patterns of all CsPbBr₃ samples made via the sequential deposition technique with different initial PbBr₂ concentration and dipping duration in the CsBr solution. The bottom diffractogram corresponds to the Pnma orthorhombic structure of pristine CsPbBr₃ thin film..... 112
- Figure 5.3** Match! analysis of CsPbBr₃ sample with 1.0 M initial PbBr₂ dipped 5 min in CsBr, showing presence of CsPbBr₃ (PDF#18-0364, green lines), CsPb₂Br₅ (PDF#25-0211, olive lines) and PbBr₂ (PDF#01-0623, brown lines)..... 114
- Figure 5.4** Surface FESEM images of initial PbBr₂ films (top row), followed by converted CsPbBr₃ films upon dipping in CsBr solution for 5, 10 and 20 min (2nd, 3rd and 4th row respectively). The 3 columns represent the different starting PbBr₂ concentration increasing from 0.2, 0.5, to 1.0 M from left to right. Brackets in the bottom left corner of each image specifies the coverage of each converted perovskite film. All samples were deposited on ITO/PEDOT:PSS substrates. Scale bar represents 1 μm..... 115
- Figure 5.5** Cross-sectional FESEM images of converted CsPbBr₃ films. Columns from left to right show increasing initial PbBr₂ concentration (0.2 to 0.5 to 1.0 M) while rows from top to bottom show increasing dipping duration in CsBr solution (5 to 10 to 20 mins).

Brackets in the bottom left corner of each image specifies the average thickness of each film. Scale bar represents 100 nm.....	117
Figure 5.6 Plot of thickness against coverage based on FESEM results for all sequentially-deposited CsPbBr ₃ films.....	118
Figure 5.7 (a) UV-vis absorption for all sequentially-deposited CsPbBr ₃ samples. The absorption spectra of 0.5 M PbBr ₂ samples with different CsBr exposure time of (b) 5 min, (c) 10 min, and (d) 20 min are refitted using Elliot's theory for deconvolution of Wannier exciton (red dashed lines) and band-to-band (blue dashed lines) contributions. The electronic band gap is finally determined in each graph.....	119
Figure 5.8 (a) PL spectra and (b) PL peak wavelength versus thickness trend for all sequentially-deposited CsPbBr ₃ samples.....	120
Figure 5.9 PL redshift with (a) increasing initial PbBr ₂ concentration from 0.2 M (black), 0.5 M (red) to 1.0 M (blue) and (b-d) increasing dipping duration in CsBr solution.	121
Figure 5.10 Plot of energy shift (from calculated band gap energy of 2.46 eV) of PL peak with respect to optical density (obtained from absorbance data).....	122
Figure 5.11 Energy band levels of PeLED device architecture used in this work.	123
Figure 5.12 (a) Current density and luminance against voltage (<i>J-V-L</i>) and (b) current efficiency against luminance curves of sequential CsPbBr ₃ PeLEDs fabricated using 0.5 M initial PbBr ₂ concentration with different dipping durations.....	123
Figure 5.13 EL spectra of all devices at maximum luminance. Inset is a photograph of a 12 mm ² device showing homogeneous green light emission.	124
Figure 6.1 (a) UV-vis absorption (plotted with a constant offset, arrow indicates the absorption peak due to quasi-2D / 2D perovskite formation), (b) PL (absorbance-corrected), and (c) normalized PL spectra of CsPbBr ₃ perovskite films prepared with different molar excess addition of PEABr.	131
Figure 6.2 Photographs of CsPbBr ₃ perovskite films formed with different PEABr:CsPbBr ₃ mole ratios under UV illumination.....	132
Figure 6.3 PL excitation spectra (plotted with a constant offset) of CsPbBr ₃ perovskite films prepared with different molar excess addition of PEABr.....	134

- Figure 6.4** TRPL spectra for (a) pristine CsPbBr₃, (b) PEABr:CsPbBr₃ = 0.3:1, and (c) PEABr:CsPbBr₃ = 0.8:1 perovskite films. The colour of the curves (a-c) corresponds to the specific wavelengths measured as shown in each graph. 135
- Figure 6.5** Field emission scanning electron microscopic (FESEM) top-view images of CsPbBr₃ perovskite films prepared using different mole ratio of PEABr:CsPbBr₃, showing reduction in grain size with increasing compactness and smoothness of the film with increasing PEABr content. 138
- Figure 6.6** FESEM cross-section images of CsPbBr₃ perovskite films prepared using different mole ratio of PEABr:CsPbBr₃, showing smoother and flatter films with increasing PEABr content. Thicknesses of all films are closely similar (~ 85 nm). 139
- Figure 6.7** Superimposed XRD patterns of perovskite films prepared using different mole ratio of PEABr:CsPbBr₃: (a) As prepared films after vacuum drying and (b) thicker films prepared using drop-casting and subsequent annealing at 100 °C for 20 mins. 140
- Figure 6.8** (a) Energy level alignment of the device architecture used in this work. (b) J-V-L of PeLEDs fabricated with CsPbBr₃ perovskites prepared using different PEABr:CsPbBr₃ molar ratios. 142
- Figure 6.9** (a) Current efficiency, and (b) EQE curves of PeLEDs fabricated with CsPbBr₃ perovskites prepared using different PEABr:CsPbBr₃ molar ratios. 142
- Figure 6.10** Normalized EL spectra of all devices (in (a) linear scale and (b) log scale) under an applied bias of 6 V, showing single emission for all PEABr:CsPbBr₃ compositions. 144
- Figure 6.11** EL spectra of 0.8:1 PeLED device under different applied biases from 3 – 7 V, showing only a single emission peak even at high voltages. Inset shows an image of the device under an applied bias of 4 V. 144
- Figure 7.1** (Left) Molecular structure of octylammonium bromide (OABr). (Right) Photograph of a spin-coated mixed-dimensional CsPbBr₃ film with OABr as the spacer ligand. 152
- Figure 7.2** Absorption and PL spectra of (a, b) PEABr-CsPbBr₃ and (c, d) OABr-CsPbBr₃ films with different excess concentration (mol%) of ligand additives. 153
- Figure 7.3** (a) J-V-L and (b) current efficiency curves of mixed-dimensional PeLEDs fabricated with 80% PEABr (black), 80% OABr (green), and 100% OABr (orange). .. 155

Figure 7.4	Molecular structure of (a) phenylammonium bromide (PhABr), (b) phenylmethyammonium bromide (PMABr), (c) phenylethylammonium bromide (PEABr), (d) phenylpropylammonium bromide (PPABr), and (e) phenylbutylammonium bromide (PBABr).....	156
Figure 7.5	(a) UV-vis absorption and (b) PL spectra of PhABr-CsPbBr ₃ samples.	158
Figure 7.6	UV-vis absorption spectra of (a) PMABr-CsPbBr ₃ , (b) PEABr-CsPbBr ₃ , (c) PPABr-CsPbBr ₃ , and (d) PBABr-CsPbBr ₃ mixed-dimensional perovskite films.	159
Figure 7.7	Absorbance spectra (plots stacked with a constant offset of 0.1) of (a) 75% and (b) 100% excess ligand additives showing a diminution of the quasi-2D phases with increasing length of the spacer molecule. (c) Overlapped absorbance spectra of the 75% excess ligand additives (zoomed in to the 3D CsPbBr ₃ absorption region).	160
Figure 7.8	PL spectra of (a) PMABr-CsPbBr ₃ and (c) PEABr-CsPbBr ₃ mixed-dimensional perovskite films. (b) and (d) show the corresponding graphs plotted in logarithmic scale.	161
Figure 7.9	PL spectra of (a) PPABr-CsPbBr ₃ and (c) PBABr-CsPbBr ₃ mixed-dimensional perovskite films. (b) and (d) show the corresponding graphs plotted in logarithmic scale.	162
Figure 7.10	PL spectra of (a) 75% and (b) 100% excess ligand additives. Graphs on the right show the magnified logarithmic plot of the region of interest (boxed in green)....	163
Figure 7.11	J-V-L graphs of (a) PhABr, (b) PMABr, (c) PEABr, (d) PPABr, and (e) PBABr mixed-dimensional CsPbBr ₃ PeLEDs.....	165
Figure 7.12	Current efficiency graphs of (a) PhABr, (b) PMABr, (c) PEABr, (d) PPABr, and (e) PBABr mixed-dimensional CsPbBr ₃ PeLEDs.....	166
Figure 7.13	Comparison of (a) current efficiency and (b) luminance of mixed-dimensional CsPbBr ₃ PeLEDs with the five different ligand molecules.....	168
Figure 7.14	Molecular structures of the naphthyl-based 1-NMA, 2-NMA, 1-NEA and 2-NEA ligand molecules used for making mixed-dimensional CsPbBr ₃ perovskites.	170
Figure 7.15	XRD patterns of 2D naphthyl-based perovskites: (1-NMA) ₂ PbBr ₄ (black), (2-NMA) ₂ PbBr ₄ (red), (1-NEA) ₂ PbBr ₄ (blue), and (2-NEA) ₂ PbBr ₄ (magenta).....	171
Figure 7.16	(a) UV-vis absorption and (b) PL spectra of 2D naphthyl-based perovskites.....	172

- Figure 7.17** UV-vis absorption and PL spectra of (a) (1-NMA)₂PbBr₄, (b) (2-NMA)₂PbBr₄, (c) (1-NEA)₂PbBr₄, and (d) (2-NEA)₂PbBr₄ 2D perovskites..... 173
- Figure 7.18** Comparison of photoemission under UV light between 3D CsPbBr₃ (left) and mixed-dimensional CsPbBr₃ perovskites using naphthyl-based ligand molecules.. 174
- Figure 7.19** Top-view FESEM images of CsPbBr₃ perovskite films prepared using different concentration of NMA ligand molecules: (a) 40 mol% and (b) 60 mol% 1-NMA; (c) 40 mol% and (d) 60 mol% 2-NMA. The pristine CsPbBr₃ is shown in (e) for comparison. Scale bars (bottom right) represents 100 nm. 175
- Figure 7.20** Top-view FESEM images of CsPbBr₃ perovskite films prepared using different concentration of NEA ligand molecules: (a) 40 mol% and (b) 60 mol% 1-NEA; (c) 40 mol% and (d) 60 mol% 2-NEA. Scale bars (bottom right) represents 100 nm.... 176
- Figure 7.21** UV-vis absorption spectra of mixed-dimensional CsPbBr₃ perovskite films with different mol% excess concentration of (a) 1-NMA, (b) 2-NMA, (c) 1-NEA, and (d) 2-NEA ligand molecules..... 177
- Figure 7.22** UV-vis absorption spectra of mixed-dimensional CsPbBr₃ perovskites with (a) 40 mol%, (b) 60 mol%, and (c) 100 mol% excess naphthyl ligand molecules. 179
- Figure 7.23** Transient absorption (TA) spectra of mixed-dimensional CsPbBr₃ perovskite films with 100 mol% excess of (a) 1-NMA, (b) 2-NMA, (c) 1-NEA, and (d) 2-NEA at different delay times. 180
- Figure 7.24** Normalized PL spectra of mixed-dimensional CsPbBr₃ perovskite films with different mol% excess concentration of (a) 1-NMA, (b) 2-NMA, (c) 1-NEA, and (d) 2-NEA ligand molecules..... 181
- Figure 7.25** Normalized PL spectra of mixed-dimensional CsPbBr₃ perovskites with (a) 40 mol%, (b) 60 mol%, and (c) 100 mol% excess naphthyl ligand molecules. Graph on the right of (c) shows the magnified logarithmic plot of the region of interest (boxed in green), showing absence of quasi-2D emission. 182
- Figure 7.26** Full width at half maximum (FWHM) of the PL spectrum of each naphthyl-based mixed-dimensional CsPbBr₃ perovskite sample plotted against the concentration of ligand molecule (in excess mol%). 183

Figure 7.27 J-V-L graphs of mixed-dimensional CsPbBr ₃ PeLEDs fabricated with different concentration of naphthyl ligand molecules: (a) 1-NMA, (b) 2-NMA, (c) 1-NEA, and (d) 2-NEA.....	184
Figure 7.28 Current efficiency versus luminance graphs of mixed-dimensional CsPbBr ₃ PeLEDs fabricated with different concentration of naphthyl ligand molecules: (a) 1-NMA, (b) 2-NMA, (c) 1-NEA, and (d) 2-NEA.	185
Figure 7.29 EQE versus current density graphs of mixed-dimensional CsPbBr ₃ PeLEDs fabricated with different concentration of naphthyl ligand molecules: (a) 1-NMA, (b) 2-NMA, (c) 1-NEA, and (d) 2-NEA.	186
Figure 7.30 Comparison of (a) current efficiency and (b) EQE of mixed-dimensional CsPbBr ₃ PeLEDs with the different naphthyl ligand molecules against concentration.	189
Figure 7.31 EL spectra of mixed-dimensional CsPbBr ₃ PeLEDs with 40 and 60 mol% excess of naphthyl ligand molecules: (a) 1-NMA, (b) 2-NMA, (c) 1-NEA, and (d) 2-NEA.....	190
Figure 7.32 Full width at half maximum (FWHM) of the EL spectrum of each naphthyl-based mixed-dimensional CsPbBr ₃ PeLED plotted against the concentration of ligand molecule (in excess mol%).	191
Figure 7.33 Corresponding CIE coordinate based on EL spectra for (a) 40 mol% and (b) 60 mol% excess ligand additive.....	192
Figure 7.34 Plot of EL peak position versus voltage, showing negligible change in emission wavelength with increasing bias.....	192
Figure 8.1 Molecular structures of various proposed PAHs.	207
Figure 8.2 Schematic illustrating balanced injection of electrons and holes in a PeLED device, resulting in an almost flat EQE curve with current density from 0.1 to 200 mA cm ⁻² . ¹¹ Reprinted with permission from Fakharuddin, A.; Qiu, W.; Croes, G.; Devižis, A.; Gegevičius, R.; Vakhnin, A.; Rolin, C.; Genoe, J.; Gehlhaar, R.; Kadashchuk, A., Reduced Efficiency Roll-Off and Improved Stability of Mixed 2D/3D Perovskite Light Emitting Diodes by Balancing Charge Injection. <i>Advanced Functional Materials</i> 2019 , 1904101. Copyright © 2019 John Wiley and Sons.	209
Figure 8.3 Schematic illustrations showing various large-scale solution deposition technologies. ¹⁸ Reprinted with permission from Pasquarelli, R. M.; Ginley, D. S.; O'Hayre,	

R., Solution processing of transparent conductors: from flask to film. *Chemical Society Reviews* **2011**, 40 (11), 5406-5441. Copyright © 2019 Royal Society of Chemistry..... 211

Figure 8.4 Schematic illustrating the different possible funnelling mechanisms (charge transfer or energy transfer) in a quasi-2D perovskite.¹⁹ Reprinted with permission from Chen, P.; Meng, Y.; Ahmadi, M.; Peng, Q.; Gao, C.; Xu, L.; Shao, M.; Xiong, Z.; Hu, B., Charge-transfer versus energy-transfer in quasi-2D perovskite light-emitting diodes. *Nano energy* **2018**, 50, 615-622. Copyright © 2019 Elsevier. 212

Abbreviations

2D	Two-Dimensional
3D	Three-Dimensional
CB	Conduction Band
DSSC	Dye-Sensitized Solar Cell
EL	Electroluminescence
EML	Emissive Layer
EQE	External Quantum Efficiency
ETL	Electron Transport Layer
FESEM	Field Emission Scanning Electron Microscopy
FWHM	Full Width at Half Maximum
HOMO	Highest Occupied Molecular Orbital
HTL	Hole Transport Layer
IQE	Internal Quantum Efficiency
ITO	Indium-doped Tin Oxide
J-V-L	Current Density-Voltage-Luminance
LED	Light-Emitting Diode
LCD	Liquid Crystal Display
$L_{\max}$	Maximum Luminance
LUMO	Lowest Unoccupied Molecular Orbital
NP	Nanoparticle
OD	Optical Density
OLED	Organic Light-Emitting Diode
OPV	Organic Photovoltaic
PAH	Polycyclic Aromatic Hydrocarbon
PCE	Power Conversion Efficiency
PeLED	Perovskite Light-Emitting Diode
PESA	Photoelectron Spectroscopy in Air
PL	Photoluminescence
PLQY	Photoluminescence Quantum Yield

PSC	Perovskite Solar Cell
PV	Photovoltaic
QDLED	Quantum Dot Light-Emitting Diode
RP	Ruddlesden-Popper
RT	Room Temperature
SEM	Scanning Electron Microscopy
TA	Transient Absorption
TEM	Transmission Electron Microscopy
TRPL	Time-Resolved Photoluminescence
UPS	Ultraviolet Photoelectron Spectroscopy
UV-Vis	Ultra-Violet-Visible
VB	Valence Band
V_{th}	Threshold (Turn-on) Voltage
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

Chapter 1

Introduction

This chapter introduces halide perovskites in the field of lighting and display applications, focusing on the limitations and challenges of conventional technologies and how the extraordinary properties of perovskites make them highly promising candidates for light emitters. The scope of materials research in this thesis is narrowed down to the inorganic class of halide perovskite, more specifically CsPbBr₃, due to its high thermal stability, although this material has several intrinsic flaws. The weakness of this compound can be generalized as a lack of carrier confinement, overcoming of which then forms the research gap that contextualizes this thesis. Herein, the objectives are described with the main direction aimed at improving the carrier confinement in order to achieve higher efficiency light-emitting devices, while several strategies are proposed and discussed in the scope section. By accomplishing these studies, possible implications to the scientific community are aspired to be achieved. In the last section of this chapter, an overview of the flow of this thesis is addressed, followed by a summary of the major findings and outcomes.

1.1 Background and Motivation

The invention of lighting has revolutionized the world and transformed our way of life. Lighting technologies have evolved a long way, from gas lighting in the eighteenth century, to the famous invention of the incandescent lamp in the nineteenth century, and now to the ubiquitous fluorescent lamp and the up-and-coming light-emitting diodes (LEDs) of the twentieth century. The most commonly used types of artificial lighting technology nowadays include incandescent, fluorescent as well as gas discharge lamps. The main problem with these technologies is the low energy efficiency, leading to high energy consumption. From the electricity perspective, artificial lighting accounts for the highest proportion of world electricity generation ($\sim 20\%$),¹ ensuing an estimated 1,900 megaton of carbon dioxide emission per year. There is then a serious need to switch to alternative lighting technologies that are more energy efficient but at the same time able to provide bright light emission comparable to conventional light sources.

The LED is the newest and most promising technology in the field of lighting and displays. It was invented as early as 1927 by a Soviet inventor named Oleg Losev.² As compared to conventional lighting technologies such as incandescent, halogen and fluorescent lamps, LEDs have way more advantages, including high brightness and efficiency, long lifetime, high reliability, low voltage operation, low maintenance cost, and compact size.³⁻⁴ It has been estimated that up to half the total energy consumed for lighting could be saved if conventional lighting switches to the more efficient LED technology.¹ However, problems pertaining to conventional LEDs have hindered their widespread use. Even though inorganic LEDs have largely improved the standard of artificial lighting and afforded substantial energy savings, costly fabrication processes considering the need for high temperature and vacuum as well as epitaxial growth techniques have rendered them more expensive and less marketable.

The invention of organic LEDs (OLEDs), made of a thin film of organic light-emitting material, have not only led to possibility of having flexible and large area lighting panels, but also colour-tunability. This means that OLED lighting can offer different variants of

white light, from warm to cold, and is the light source with the closest capability to simulate natural light.⁵ Even more important is the fact that OLEDs can be designed to emit light of a specific colour, paving the way to beautiful and efficient display applications that transcend the most widely used liquid crystal displays (LCDs). OLEDs have been commercialized in various display applications such as smart phones and televisions by various companies such as Philips, Osram and LG.⁶ However, the need for vacuum-based sublimation processing results in high costs and low yield. The fundamental limitation of forbidden states in these organic compounds also restricts their emission capabilities.⁷⁻⁸ Quantum-dot LEDs (QDLEDs) are found to be highly luminescent but the high surface area has brought about significant non-radiative recombination in these surface defect sites.⁹ These problems of LEDs will need to be addressed before widespread implementation is possible. For new light-emitting technologies to rival the current ones, the tangible traits required are:¹⁰

- i) High efficiency, colour purity and tunability, and
- ii) Solution processability at low temperatures which will reduce the energy costs of production.

Challenging aims demand tuning of the emissive material, optimizing balanced carrier injection into the emitter, enhancing light extraction from the device, and minimizing losses that could arise from non-radiative recombination pathways.¹⁰ One promising candidate is the halide perovskite compound (Figure 1.1a), which has attracted a lot of attention in recent years due to the outstanding photovoltaic (PV) performances when incorporated in solar cells. The excellent properties such as low defect densities,¹¹⁻¹³ direct band gap¹⁴ and facile fabrication processes¹⁵ (Figure 1.1b) have largely overcome the problems faced in conventional LED technologies. The unique opto-electronic properties such as high photoluminescence quantum yields (PLQY),¹⁶ narrow emission linewidth and ideal emission properties via electroluminescence even at high carrier densities¹⁷ make perovskites highly promising light emitters with colour of high purity (Figure 1.1c and d). Low material and processing costs along with the versatility of this material have also promised a new generation of highly efficient and low-cost LEDs.

Figure 1.1 Schematic illustration of (a) the crystal structure of a typical metal halide perovskite compound, (b) solution processing method used to deposit perovskite films,¹⁸ and (c) the device architecture of a standard perovskite light-emitting diode (where HTM, EML and ETL stand for hole transport material, emissive layer, and electron transport layer respectively). (d) Major trend of different display technologies showing comparison between OLED, QDLED and PeLED. The narrow full width at half maximum (FWHM) of the perovskite emission spectrum makes it a superior emitter material in terms of colour purity and saturation.¹⁹ Figure (b) is reprinted with permission from Jung, H. S.; Park, N. G., Perovskite solar cells: from materials to devices. *Small* **2015**, *11* (1), 10-25. Copyright © 2019 American Chemical Society. Figure (d) is reprinted with permission from Kim, Y.-H.; Cho, H.; Lee, T.-W., Metal halide perovskite light emitters. *Proceedings of the National Academy of Sciences* **2016**, *113* (42), 11694-11702. Copyright © 2019 National Academy of Sciences.

Perovskite light-emitting diodes (PeLEDs) are a rapidly emerging field in recent years, leveraging on the extensive research conducted in perovskite solar cells (PSCs) and OLEDs. With the outstanding potential evidenced by past literatures and studies (discussed in Chapter 2), perovskites promise a highly positive outlook in this field of lighting and

display. Device performances are distinguished according to several main goals including luminance, efficiency, lifetime, and colour purity.

1.2 Problem Statement

A large range of halide perovskite materials have been discovered and synthesized, including organic-inorganic hybrid halide perovskites and fully inorganic ones. While more studies have been focused on the organic-inorganic hybrid systems (e.g. methylammonium (MA) or formamidinium (FA) lead halides), fully inorganic perovskites eliminate the concern of material stability under heat during device operation. This thesis will thus focus only on the fully inorganic class of perovskite, with most attention directed at the perovskite compound cesium lead bromide (CsPbBr_3), which gives green emission from the visible light spectrum. Despite the thermal resistance of this material, poor intrinsic properties such as low exciton binding energy and poor morphology have found challenges in its usability in LEDs. Poor emissive properties fundamentally stem from a lack of carrier confinement in the resulting solution-processed film, which is the main drawback of this system, but which also offers opportunities to explore ideas and strategies to overcome it. Carrier confinement is an all-important attribute in order to achieve excellent luminescence properties for an emitter material, both in terms of photo-excited luminescence (photoluminescence) as well as luminescence from electrically injected charge carriers (electroluminescence). Without ample confinement, charge carriers (from either photoexcitation or electrical injection) can travel freely in random directions to anywhere. For instance, they can move to grain surfaces or defect sites and become trapped, accumulate at interfaces, or just exist as free carriers without undergoing any radiative recombination. All these contribute to the non-radiative losses in perovskite emitters. However, if the charge carriers are efficiently confined, the carrier density within the confinement region will be immensely augmented, leading to a significant enhancement in the radiative recombination probability, thus outweighing the non-radiative losses. While the strength of the confinement effect can be determined by intrinsic properties of the material itself, e.g. exciton binding energy, it does not mean that materials with poor

intrinsic properties will not be able to confine charges efficiently. The confinement effect can be largely influenced by extrinsic factors, such as through geometrical control or structural modulation (Figure 1.2).

Figure 1.2 Schematic illustration of different approaches to enhance exciton confinement in halide perovskites. (Top to down) Geometrical confinement achieved through control of morphology and thickness, (left to right) structural confinement achieved through reduction in dimensionality of the intrinsic lattice structure (3-dimensional bulk to 0-dimensional quantum dots).¹⁷ Reprinted with permission from Colella, S.; Mazzeo, M.; Rizzo, A.; Gigli, G.; Listorti, A., *The Bright Side of Perovskites. The Journal of Physical Chemistry Letters* **2016**, 4322-4334. Copyright © 2019 American Chemical Society.

1.3 Objectives and Scope

Based on the motivation and problem statement, this thesis hereby aims to address the

challenges of the all-inorganic CsPbBr₃ perovskite material for light emission by understanding the confinement problem and exploring the geometrical and electronic approaches to overcome it, eventually validated by improvement in film properties as well as in LED device performances.

The scope of this thesis entails the following work:

- 1) To study the geometrical confinement effect on the photo- and electroluminescence properties of CsPbBr₃ perovskite emitter. The geometric effect is predominantly associated with the morphology of the deposited film, microstructure, coverage and grain size, which can be controlled by judicious engineering of the deposition process.
- 2) To explore the effect of reduced dimensionality and the use of a multidimensional perovskite achieved through incorporation of large organic cations into the inorganic CsPbBr₃ perovskite framework. In this study, confinement is achieved not through a physical phenomenon but rather through an electronic energy cascade formed from the different dimensions. The energetics involved need to be investigated further through optical and time-resolved spectroscopy techniques. In addition, the criteria of selecting an effective ligand molecule need to be deeply investigated and finally, a guideline should be established for future design and screening of ligand molecules for mixed-dimensional perovskites.

The material of interest in this thesis is focused on the all-inorganic CsPbBr₃ due to its well-known thermal stability, while its weakness provides the gap and motivation for in-depth research and improvement. The characterization methods employed in the understanding of these experiments include optical spectroscopy techniques using photoexcitation (both steady-state and ultrafast time-resolved measurements), electron microscopy, and electroluminescence measurement (for PeLED devices).

Through this study, the importance of carrier confinement in CsPbBr₃ perovskite emitters and strategies to strengthen it will enable the realization of better performance and higher efficiency PeLEDs. The knowledge gained will not only be applicable to the inorganic perovskites but also to any halide perovskites including the organic-inorganic hybrid

systems. Eventually, it is aspired that this work will open up the pave for cheaper and better LEDs using this extraordinary perovskite material, with a highly anticipated potential of replacing OLEDs and QDLEDs for display applications in the future.

1.4 Dissertation Overview

This thesis addresses each chapter as described below:

Chapter 1 starts off with the background and issues concerning the current lighting and display technologies, introduces the metal halide perovskite class of materials as a viable candidate, and discusses the underlying problems and gaps which then brings about the main motivation and rationale behind this research work in designing a new generation of light-emitting devices. The objectives and scope of this work are also outlined in this section, and finally the important findings are highlighted and summarized.

Chapter 2 gives a brief timeline of the evolution of lighting technologies from conventional sources to OLEDs before describing the structure and properties of the perovskite compound (the material of interest) and why it serves as a promising candidate to replace the light emissive layer in OLEDs. It goes on to review relevant literatures concerning the use of perovskites in LEDs and discuss various problems and issues with current state-of-the-art PeLEDs, thereby identifying gaps and unanswered questions which set the scene for this research work.

Chapter 3 elaborates in further details the experimental techniques used in this work and discusses the principles underlying the material synthesis, film deposition, device fabrication and various characterization tools employed for the study.

Chapter 4 presents the first part of the geometrical confinement study, discussing the effect of nanostructuring of the CsPbBr₃ film on the spatial confinement of charge carriers. The engineering of film deposition through rapid supersaturation of the precursor solution is

further elaborated.

Chapter 5 presents the second part of the morphological study, this time focusing on the coverage and thickness aspects of the CsPbBr₃ film modulated through a two-step sequential deposition technique. Critical parameters governing the phase conversion and morphological evolution through this process are also highlighted.

Chapter 6 moves on to show the electronic confinement study using a multidimensional system centred on the CsPbBr₃ three-dimensional framework. This chapter introduces a new concept of energy funnelling which will be discussed in details its highly favourable effects on the photo- and electroluminescence properties.

Chapter 7, the last result chapter, finally showcases a systematic yet comprehensive study of various ligand molecules for mixed-dimensional perovskite systems, making use of knowledge gained from the previous chapters. This chapter unveils several important criteria and guidelines for choosing and screening of promising ligand molecules for any mixed-dimensional halide perovskite systems, which will be helpful in designing such light-emitting materials in the future.

Chapter 8 lastly gives a conclusion of this thesis based on all the work accomplished, connecting the important findings of each chapter to the initial objectives of this thesis. The implications of this research are reviewed while several strategies to further advance this in future work are suggested based on the knowledge and insights gained.

1.5 Findings and Outcomes/Originality

This research work has methodically explored the various confinement strategies of the inorganic CsPbBr₃ perovskite for light-emitting applications. The novel outcomes and contributions to the research field is listed as follows:

1. The importance of geometrical confinement through reduction in grain size has

been demonstrated using a modified gas-facilitated spin-coating process, without the need for any additives. This unique technique that exploits the supersaturation rate of the perovskite precursor accelerates the crystallization of the perovskite crystals to achieve smaller grains. By eliminating all other factors, it is firmly proven that the spatial confinement imparted by smaller grains is essential to achieve more efficient light emission.

2. The morphological coverage limitation of the CsPbBr₃ film derived from the conventional one-step spin-coating method has been overcome by decoupling the deposition of each precursor through a sequential process. The intrinsic poor solubility of the CsBr precursor material is offset by separately depositing the PbBr₂ layer and then allowing it to convert to the final perovskite phase by dipping in a dilute solution of CsBr for an optimum duration, thereby achieving more than 90% film coverage, as compared to the one-step method which usually only managed less than 70%. The critical parameters controlling the phase conversion and morphology have also been identified and emphasized from the findings in this work.
3. A mixed-dimensional CsPbBr₃ perovskite has been shown for the first time for inorganic PeLEDs, synthesized using a large ligand molecule, phenylethylammonium (PEA) as the spacer structure. The electronic confinement effect occurs through an energy funnelling cascade process, proven using transient photoluminescence spectroscopy. By combining the effects of geometrical and electronic confinement, the mixed-dimensional PEA-CsPbBr₃ perovskite with an optimized compositional ratio achieved more than fifty-fold improvement in device performances, indicating the superiority of this approach and highlighting its potential for further research.
4. Finally, based on the inspiration from the mixed-dimensional work with PEA, a more comprehensive study involving ten different ligand molecules was conducted to unveil the ideal characteristics that should be looked out for in the quest to find better ligand molecules. Through rigorous comparison of each characterization substantiated by the corresponding device performance, a list of guideline has been established on how an effective ligand molecule should be designed and what

properties the resultant mixed-dimensional perovskite should hold. The findings are likely to be universal for all halide perovskite systems.

References

1. “*Light’s Labour’s Lost*” – *Policies for Energy-Efficient Lighting*; International Energy Agency: Paris, 29 Jun 2006.
2. Zheludev, N., The Life and Times of the LED - a 100-Year History. *Nature Photonics* **2007**, *1* (4), 189-192.
3. Li, J.; Zhang, G.-Q., *Light-Emitting Diodes: Materials, Processes, Devices and Applications*. Springer: 2018; Vol. 4.
4. Held, G., *Introduction to Light Emitting Diode Technology and Applications*. Auerbach Publications: 2016.
5. Müllen, K.; Scherf, U., *Organic Light Emitting Devices: Synthesis, Properties and Applications*. John Wiley & Sons: 2006.
6. Zissis, G.; Bertoldi, P., 2014 Status Report on Organic Light Emitting Diodes (OLED). *European Commission Joint Research Centre* **2014**.
7. Murawski, C.; Leo, K.; Gather, M. C., Efficiency Roll-Off in Organic Light-Emitting Diodes. *Advanced Materials* **2013**, *25* (47), 6801-6827.
8. Ogawa, S., *Organic Electronics Materials and Devices*. Springer: 2015.
9. Shirasaki, Y.; Supran, G. J.; Bawendi, M. G.; Bulović, V., Emergence of Colloidal Quantum-Dot Light-Emitting Technologies. *Nature Photonics* **2012**, *7*, 13.
10. Veldhuis, S. A.; Boix, P. P.; Yantara, N.; Li, M.; Sum, T. C.; Mathews, N.; Mhaisalkar, S. G., Perovskite Materials for Light-Emitting Diodes and Lasers. *Advanced Materials* **2016**, *28* (32), 6804-6834.
11. Stranks, S. D.; Eperon, G. E.; Grancini, G.; Menelaou, C.; Alcocer, M. J. P.; Leijtens, T.; Herz, L. M.; Petrozza, A.; Snaith, H. J., Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in an Organometal Trihalide Perovskite Absorber. *Science* **2013**, *342* (6156), 341-344.
12. Xing, G.; Mathews, N.; Lim, S. S.; Yantara, N.; Liu, X.; Sabba, D.; Grätzel, M.;

Mhaisalkar, S.; Sum, T. C., Low-Temperature Solution-Processed Wavelength-Tunable Perovskites for Lasing. *Nature Materials* **2014**, *13* (5), 476-480.

13. Xing, G.; Mathews, N.; Sun, S.; Lim, S. S.; Lam, Y. M.; Grätzel, M.; Mhaisalkar, S.; Sum, T. C., Long-Range Balanced Electron- and Hole-Transport Lengths in Organic-Inorganic $\text{CH}_3\text{NH}_3\text{PbI}_3$. *Science* **2013**, *342* (6156), 344-347.

14. Sarritzu, V.; Sestu, N.; Marongiu, D.; Chang, X.; Wang, Q.; Masi, S.; Colella, S.; Rizzo, A.; Gocalinska, A.; Pelucchi, E.; Mercuri, M. L.; Quochi, F.; Saba, M.; Mura, A.; Bongiovanni, G., Direct or Indirect Bandgap in Hybrid Lead Halide Perovskites? *Advanced Optical Materials* **2018**, *6* (10), 1701254.

15. Raj, V., Chapter 10 - Heterojunction Perovskite Solar Cells. In *Perovskite Photovoltaics*, Thomas, S.; Thankappan, A., Eds. Academic Press: 2018; pp 323-339.

16. Tan, Z.-K.; Moghaddam, R. S.; Lai, M. L.; Docampo, P.; Higler, R.; Deschler, F.; Price, M.; Sadhanala, A.; Pazos, L. M.; Credgington, D.; Hanusch, F.; Bein, T.; Snaith, H. J.; Friend, R. H., Bright Light-Emitting Diodes Based on Organometal Halide Perovskite. *Nature Nanotechnology* **2014**, *9* (9), 687-692.

17. Colella, S.; Mazzeo, M.; Rizzo, A.; Gigli, G.; Listorti, A., The Bright Side of Perovskites. *The Journal of Physical Chemistry Letters* **2016**, 4322-4334.

18. Jung, H. S.; Park, N. G., Perovskite Solar Cells: From Materials to Devices. *Small* **2015**, *11* (1), 10-25.

19. Kim, Y.-H.; Cho, H.; Lee, T.-W., Metal Halide Perovskite Light Emitters. *Proceedings of the National Academy of Sciences* **2016**, *113* (42), 11694-11702.

Chapter 2

Literature Review

Chapter 2 brings together various relevant studies presented in the literature and conducts a critical review to identify the research gaps that this thesis endeavors to fill. A brief overview of how lighting and display technologies have evolved over the years is first described, leading to the highly efficient light-emitting diodes in modern times. Concurrently, the rapid rise of halide perovskites in the field of photovoltaics has attracted appreciable attention in recent years. The sharp rise in solar cell efficiencies along with detailed studies to understand this cheap yet remarkable material has placed it at the forefront of optoelectronic semiconductors, including devices for light emission. The knowledge attained through these literatures is compiled and evaluated, along with a detailed review of current state-of-the-art perovskite light-emitting diodes. The different approaches used in various studies are examined and analyzed, and finally the major scientific challenges that still need to be addressed are identified, which rationalize the motivation and objectives of this thesis work.

2.1 Lighting and Display Technologies

Lighting has become a necessity in human life, so much so that it is used anywhere and at any time of the day, from general illumination to display applications such as television, computer and mobile phone screens. The majority of lighting systems nowadays still consist of conventional incandescent and fluorescent lamps, which are well established but inefficient technologies. Currently, LEDs are the most efficient source of lighting but are less commonly used due to high product costs. This is largely ascribed to the scarcity of the active materials used as well as the high temperature and strict control of the processing environment. Table 2.1 shows a comparison between solid-state LEDs and conventional incandescent and fluorescent lamps.¹ It is clearly shown that LEDs can achieve much higher efficiencies and lifetimes, but concomitantly, at higher costs.

Table 2.1 Projected solid state lighting (SSL) LED lamp targets as compared to conventional incandescent and fluorescent sources.¹

Technology	SSL-LED 2002	SSL-LED 2007	SSL-LED 2012	SSL-LED 2020	Incandescent	Fluorescent
Luminous efficacy (lm/W)	25	75	150	200	16	85
Lifetime (kh)	20	>20	>100	>100	1	10
Flux (lm/lamp)	25	200	1,000	1,500	1,200	3,400
Input power (W/lamp)	1	2.7	6.7	7.5	75	40
Lumens cost (\$/klm)	200	20	<5	<2	0.4	1.5
Lamp cost (\$/lamp)	5	4	<5	<3	0.5	5
Colour rendering index (CRI)	75	80	>80	>80	95	75
Lighting markets penetrated	Low-flux	Incandescent	Fluorescent	All		

Tungsten filament bulbs consume much more power than other types of lighting due to excessive heat and thermal radiation that come along with the incandescence. Fluorescent lamps are several times more efficient than incandescent lamps but most contain the hazardous element, mercury. Turning on the fluorescent light takes a longer time due to the ionization process and the lifetime is only in the order of a few thousands of hours. LEDs, on the other hand, show notable advancement from the conventional sources. Besides efficiency and lifetime of the devices, their colour purity are more superior over filtered lamps in monochromatic use.² Table 2.2 shows a list of available LED applications corresponding to the emission wavelength (colour).

Table 2.2 Examples of LED applications requiring certain wavelengths of light.²

LED Wavelength (Color)	LED Applications
410–420 nm (Violet)	Skin therapy
430–470 nm (Blue)	Dental curing instruments
470 nm (Blue)	White LEDs using phosphor, blue for RGB white lights
520–530 nm (Green)	Green traffic signal lights, green for RGB white lights
580–590 nm (Amber)	Amber traffic signal lights, amber for RGBA white lights
630–640 nm (Red)	Red signal lights, red for RGB white lights
660 nm (Deep Red)	Blood oximetry
680 nm (Deep Red)	Skin therapy
800–850 nm (Near-IR)	Night-vision illuminators and beacons for use with night-vision goggles or CCDs
850–940 nm (Near-IR)	Photoelectric controls
940 nm (Near-IR)	Covert illumination CCD-based systems

2.2 Evolution of Light-Emitting Diodes (LEDs)

LEDs operate based on the process termed electroluminescence (EL), defined as the emission of light from the radiative recombination of oppositely charged carriers in a material, usually a semiconductor, in response to an electric field or current. Upon recombination, energy is released in the form of photons with minimal heat loss as compared to incandescent and fluorescent lamps, where a large portion of electricity is wasted as heat.³ Conventional LEDs are built with doped semiconductor materials: an n-type doped with abundant negative charge carriers (electrons) and a p-type doped with abundant positive charge carriers (holes), much like a silicon solar cell. When a voltage is applied in the forward bias direction, the depletion region between the two doped layers is decreased until it completely disappears, thereafter charges can be injected across the junction and recombine to give light.⁴ The two main recombination events are namely radiative and non-radiative recombination. For a radiative recombination, the excess energy is converted into a photon with wavelength corresponding to the band gap of the active material. For a non-radiative recombination however, the excess energy is converted to lattice vibrations, also known as phonons. In other words, the electrical energy is converted into heat. The latter recombination case is often undesired as it leads to a lower efficiency and lifespan of the light-emitting device. The former process, however, can be highly efficient in the case of LEDs, with reports of internal quantum efficiency (IQE) close to 100%.⁴⁻⁷ The working mechanism of a typical LED is illustrated in Figure 2.1, showing charge recombination across a p-n junction as well as the radiative and non-radiative recombination events.

Figure 2.1 (a) Schematic illustration of the working mechanism of a typical LED. (b) Radiative and (c) non-radiative recombination events occurring in LEDs.⁸ Reprinted with permission from Bender, V. C.; Marchesan, T. B.; Alonso, J. M., *Solid-State Lighting: A Concise Review of the State of the Art on LED and OLED Modeling*. *IEEE Industrial Electronics Magazine* **2015**, 9 (2), 6-16. Copyright © 2019 IEEE.

While inorganic LEDs are more used in general lighting, organic ones (OLEDs) are more versatile and can be implemented in wide areas of lighting and even display applications. By substituting the inorganic emissive material with a light-emitting organic one, thinner, lighter and more flexible devices with higher colour purity can be achieved.⁹ Conventional display technologies such as cathode ray tubes (CRT), liquid crystal displays (LCD) and plasma displays suffer from limitations such as bulkiness and colour variation. OLEDs, however, possess all the desired traits of a good display, with high brightness and contrast, improved colour variation and resolution, higher operational efficiency, low voltage operation, and can be made thinner and lighter. They also have better viewing angle compared to other flat panel displays and consume less power than backlit LCD screens.¹⁰ A basic OLED architecture consist of an organic layer sandwiched between the cathode

and a transparent anode. Over the years, the structure has evolved to incorporate various charge transport and injection layers, forming a multilayer stack as shown in Figure 2.2.

Figure 2.2 Evolution of OLEDs from single layer to multilayer structure. ETL, EL and HTL refer to the electron transport, emitter and hole transport layers respectively.¹⁰ Reprinted with permission from Thejo Kalyani, N.; Dhoble, S. J., Organic light emitting diodes: Energy saving lighting technology—A review. *Renewable and Sustainable Energy Reviews* **2012**, 16 (5), 2696-2723. Copyright © 2019 Elsevier.

The operating principle of OLEDs are slightly different from inorganic LEDs. The working mechanism can be summarized into four main fundamental processes:¹¹

- (1) Injection of charges from electrodes (electrons from cathode and holes from anode).
- (2) Transport of charges across charge transport layers.
- (3) Formation of excitons (electron-hole pairs) in the emissive layer.

- (4) Radiative recombination leading to light emission.

These processes are schematically illustrated in Figure 2.3.

Figure 2.3 Schematic illustration of processes involved in an OLED operation.¹¹ Reprinted with permission from Brütting, W.; Frischeisen, J.; Schmidt, T. D.; Scholz, B. J.; Mayr, C., Device efficiency of organic light-emitting diodes: Progress by improved light outcoupling. *physica status solidi (a)* **2013**, 210 (1), 44-65. Copyright © 2019 John Wiley and Sons.

From an energetics point of view in Figure 2.3, positive charges (holes) from the anode are transferred into the highest occupied molecular orbital (HOMO) of the hole transport layer (HTL) while electrons from the cathode are transferred into the lowest unoccupied molecular orbital (LUMO) of the electron transport layer (ETL). A higher bias has to be applied to overcome the energy barrier between the work functions of the electrodes and the energy levels of the transport layers. If the energy levels are aligned properly, electrons and holes are injected into the emissive layer (EML) and confined within this region. In such a case, recombination can be maximised without any flow of excess carriers out of

this boundary (leakage current).¹¹ In order to fabricate high efficiency OLEDs, several approaches have been reported mainly through careful design and optimization of device architecture. These factors include having a thin device thickness, low carrier injection barrier, high carrier mobility, balanced injection, as well as effective exciton generation, confinement and recombination zone.¹² There are however, many drawbacks concerning vacuum-deposited OLEDs that have hampered their marketability, including high material and processing costs and low production yields. This has called for research into viable alternatives that are less costly and easier to process, and one promising candidate is halide perovskites.

2.3 Emergence of Halide Perovskites

2.3.1 Halide Perovskite Structure

Perovskites have gained a great deal of attention from the scientific community in the last decade, creating waves particularly in the field of PVs.¹³⁻¹⁶ Traditionally, this term refers to a classification of materials adopting the ABX_3 structure similar to that of calcium titanate,¹⁷ which is a mineral first discovered in 1839 and named after the Russian mineralogist, L. A. Perovski. In more recent years, studies have been focused on the organic-inorganic hybrid metal halide perovskite system, which comprises an organic-inorganic hybrid cation (e.g. $A = CH_3NH_3^+$), a divalent metal cation (e.g. $B = Pb^{2+}$), and a monovalent halide anion (e.g. $X = I^-$), arranged in a three-dimensional (3D) network of corner-sharing PbI_6 octahedra surrounding the central A-cation as shown in Figure 2.4.

Figure 2.4 Schematic of a typical ABX_3 perovskite structure.

The size of the central cation A is critical in order to form a perfectly close packed, undistorted configuration as this cation must fit into the confined cuboctahedral space formed by the eight octahedra connected through common corners.¹³ For this to happen, the following condition must be satisfied: $(R_A + R_X) = t\sqrt{2} (R_B + R_X)$ where R_A , R_B and R_X are ionic radii for A, B and X respectively and t is the Goldschmidt tolerance factor, ideally close to 1 but empirically found to be between 0.8 – 0.9 for most perovskite materials.¹⁸⁻¹⁹ Based on the radii of B and X, the central cation A must be sufficiently small enough to fit into the structure but at the same time maintaining a close packed arrangement. For organic-inorganic hybrid perovskites, the central cation A is usually limited to small organic molecules with only two or three atoms (excluding hydrogen atoms). Suitable examples are methylammonium (MA), ethylammonium (EA), or formamidinium (FA). Inorganic-based perovskites have also been researched into where the A site is occupied by a Cs^+ cation. Divalent metal cations such as Pb^{2+} and Sn^{2+} (Group 14) are commonly used for metal cation B while monovalent halide anions such as I^- , Br^- and Cl^- (Group 17) are typically used for anion X.¹³

2.3.2 Perovskite Solar Cells (PSCs)

Organic-inorganic hybrid metal halide perovskites have been studied as early as several decades ago,²⁰⁻²⁴ but not until recently have they been discovered as superb light absorbers. The first incorporation of the perovskite material in a solar cell was demonstrated by Tsutomu Miyasaka et al. in 2009.²⁵ By using a dye-sensitized solar cell (DSSC) device architecture, a power conversion efficiency (PCE) of 3.8% was achieved. However, the instability of the devices due to the dissolution of halides in the corrosive liquid electrolyte was a major stumbling block for further progress. In 2012, a breakthrough was achieved by Park et al. and Snaith et al. where the replacement of the liquid electrolyte with a solid-state hole conductor has led to stable PCEs up to and exceeding 10%.²⁶⁻²⁷ Following this breakthrough, a rapid surge in research in this field ensued, partially due to the low cost and solution processability of this material,²⁸ as compared to most other technologies that require high costs, stringent environments and long processes.²⁹⁻³⁰ Within a decade, PCEs of PSCs have seen an unprecedented rise from 3.8% in 2009 to 25.2% in 2019 as shown in the chart of best solar cell efficiencies in Figure 2.5,³¹ outperforming the best-in-class thin-film PV technologies³² and making PSCs the fastest advancing PV technology to date. Monolithic tandem solar cells combining perovskite and silicon in single-junction architectures have reached 28% PCE, exceeding the best efficiencies of the single-junction silicon technologies.

Figure 2.5 NREL chart of best research solar cell efficiencies of various PV technologies over the years.³¹

(This plot is courtesy of the National Renewable Energy Laboratory, Golden, CO.)

The expeditious rise of PSC along with extremely low production costs have made them highly commercially appealing. Leveraging on the knowledge and processing techniques of DSSCs and organic PVs (OPVs),³³⁻³⁴ different device architectures, material combinations and deposition engineering approaches have been studied.³⁵⁻³⁸ Figure 2.6 shows a schematic illustration of the typical and most commonly used mesoscopic PSC. The perovskite functions as a sensitizer which absorbs light and generate charges, which are then extracted via the ETL, TiO_2 in this case, and the HTL, usually spiro-MeOTAD.³⁵

Figure 2.6 Schematic illustration showing the cross-section architecture of a conventional mesoscopic PSC.³⁵ The perovskite material is used as the sensitizer layer that is responsible for light absorption and charge generation. TCO and HTM stands for transparent conductive oxide and hole transport material respectively. Reprinted with permission from Grätzel, M., The light and shade of perovskite solar cells. *Nature Materials* **2014**, 13 (9), 838-842. Copyright © 2019 Springer Nature.

Over the years, the architecture has developed from a mesoscopic structure to a planar heterojunction stack as shown in Figure 2.7.³⁵ This is possible due to the ambipolar nature of the MAPbI_3 perovskite semiconductor compound that allows both electron and hole transport in the same material,^{27, 39} thereby eliminating the need for a mesoporous TiO_2 scaffold.

Figure 2.7 Evolution of the PSC architecture from mesoscopic (a – b) to planar heterojunction structures (c).³⁵ Reprinted with permission from Grätzel, M., The light and shade of perovskite solar cells. *Nature Materials* **2014**, 13 (9), 838-842. Copyright © 2019 Springer Nature.

The solution processability of halide perovskites does not only offer a low-cost deposition route, but also versatility. For instance, the wet chemical film formation can either be a one-step spin-coating process⁴⁰ or a two-step sequential deposition process.⁴¹ The single-step method uses a premixed solution containing both MAI and PbI_2 precursors in a polar organic solvent such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), or gamma-Butyrolactone (GBL). The solution is dropped on the substrate and spin-coated to form a thin film upon crystallization. The sequential method, on the other hand, separates

the deposition of the two precursors. The PbI_2 precursor is first deposited on a substrate before being exposed to either an MAI solution^{37, 41-42} or vapour.⁴³ Initially, the two-step method is shown to achieve better control of the film morphology and higher device efficiencies.^{41-42, 44-45} However, in 2014, a solvent engineering technique was introduced to achieve PSCs with largely improved morphologies and device performances.⁴⁶⁻⁴⁸ This is performed by flushing a small volume of an anti-solvent on the substrate during the single-step spinning process. The anti-solvent is usually a non-polar solvent such as toluene, chlorobenzene, or diethyl ether. The purpose of this step is to facilitate the film crystallization process resulting in a highly uniform and dense film with large grains.⁴⁹ Further works also show that by changing the solvent to a mixture of DMF and DMSO as compared to only DMF, the film morphologies and grain size can be improved.⁵⁰ This is ascribed to the formation of a Lewis-base adduct, where the PbI_3^- and PbI_4^{2-} intermediate complexes bind to DMSO, before forming the final perovskite phase when annealed.^{37, 51-52} A similar process has also been shown by Dong Yang et al., albeit through a different approach, by forming a chelated intermediate with the help of a dimethyl sulfide additive to control the crystallization rate, thereby forming large crystalline grains with low trap density.⁵³ The crystallization dynamics is also manipulated by Grätzel et al., using a vacuum-flash assisted technique to achieve highly smooth and crystalline solar cells with PCEs exceeding 20%;⁵⁴ while the use of poly(methyl methacrylate) (PMMA) polymer as a templating agent to modulate the nucleation rate and growth process has realized stable PCEs of up to 21.6%.⁵⁵ Many of these work demonstrate the importance of the crystallization dynamics and the consequential morphology of the deposited film in determining the performance of the PSC device.

In addition, various studies using additives and compositional tuning have also shown enhancement in PCEs beyond 20%. Seok et al. have shown that the addition of triiodide ions to the precursor solution using a two-step deposition method is able to suppress the concentration of deep-level defects, thereby obtaining a PCE of 22.1%.⁵⁶ The use of multi-cation perovskite has also been proven to attain better performing solar cells. For instance, composition engineering of the MA and FA ratio improves the phase stability of the FAPbI_3 perovskite, thus enhancing the PCE to over 18%;⁵⁷ while a triple cation system consisting

of MA, FA and Cs further enhances the PCE to $\sim 21\%$ along with better cell stability.⁵⁸ A quadruple cation cascade system with Rb shows even better material properties and suppressed growth of PbI_2 impurities, leading to stabilized PCEs of more than 21% ;⁵⁹⁻⁶⁰ while substituting Rb with K also reveals reduction in defect density at the interface, resulting in a PCE of more than 20% with no hysteresis.⁶¹

Apart from the perovskite layer, various studies have also been performed on the interfacial transport layers (ETL and HTL). For instance, replacing TiO_2 with ZnO nanoparticles (NPs) eliminates the need for high temperature sintering and thus allows fabrication of PSCs on flexible substrates.⁶² Another strategy using an inverted architecture employing PEDOT:PSS and PCBM as the HTL and ETL respectively has also been shown to achieve flexible PSCs fabricated on a polyethylene terephthalate (PET) substrate.⁶³ Recently, various modified SnO_2 ETLs have become popular substitutes for TiO_2 due to better transport properties and work function, resulting in PCEs of more than 21% .⁶⁴⁻⁶⁵ Deposited perovskite films on SnO_2 also show better crystallinity and coverage along with lower trap densities.⁶⁶⁻⁶⁹ The high cost and low stability of the commonly used spiro-MeOTAD HTL has also called for more research into possible replacements. Various low-cost organic HTLs have been synthesized and tested in PSCs showing comparable or even higher PCEs than spiro-MeOTAD-based devices,⁷⁰⁻⁷² with poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) and poly(3-hexylthiophene) (P3HT) showing the best PCEs of more than 22% .^{56, 73}

2.3.3 Unique Advantages and Properties of Halide Perovskites

This relatively new generation of PV technology has managed to claim a spot in the list of *Science's* Top 10 Breakthroughs in 2013.⁷⁴ The reason is not just because of the rapid rise in efficiencies, but also due to the unique properties of the halide perovskite that make it an exceptional semiconductor material of high electronic quality.⁷⁵

Organic-inorganic hybrid perovskites are the most widely studied class of perovskite compounds, combining the flexibility and versatility of the organic component as well as the structural order and thermal stability of the inorganic part which leads to interesting properties and useful functionalities.⁷⁶ In the context of solar cells, the active material plays a critical role in light absorption and charge generation, which implies the need for reasonable optical and electronic properties. Perovskites possess extraordinarily high extinction and optical absorption coefficient ($\sim 10^4 - 10^5 \text{ cm}^{-1}$ at 550 nm),^{13, 77} which means that an ultrathin film thickness of $< 1 \text{ }\mu\text{m}$ is sufficient to absorb the full visible light spectrum. This explains its outstanding external quantum efficiency (EQE) with films as thin as 300 – 600 nm,⁷⁸ which is almost 3 orders of magnitude smaller than silicon solar cells.⁷⁹ The implication of this is the realization of highly efficient solar cells that can be concomitantly flexible and light. The lower thickness of the absorber layer also means shorter pathways for photogenerated charge carriers to travel and lower probability of recombination, leading to lower energetic losses and higher open-circuit voltages (V_{OC}).⁸⁰

Besides the high absorption coefficient of MAPbI_3 , the steep absorption edge with Urbach energy as low as 15 meV implies the absence of deep level states and energetic losses (Figure 2.8a),⁸¹ which also explains the high V_{OC} values reported for PSCs.⁸² The direct band gap of MAPbI_3 is measured to be 1.5 – 1.55 eV^{26, 40}, which allows a wide spectral response of up to 800 nm of the electromagnetic spectrum. The band gap is easily tunable through compositional engineering by varying the ratio of different halide anions,⁸³⁻⁸⁶ which is a unique trait rarely seen in other PV technologies. For instance, the band gap can be gradually increased by increasing the ratio of bromide to iodide in the precursor composition (Figure 2.8b).⁸⁷ This unique flexibility is extremely useful when a certain band gap is required, for example a higher band gap top cell is desired in tandem PV applications.⁸⁸⁻⁸⁹

Figure 2.8 (a) Comparison of the absorption coefficient of MAPbI₃ perovskite with various other PV technologies such as silicon, GaAs and thin-film systems.⁸¹ Reprinted with permission from De Wolf, S.; Holovsky, J.; Moon, S.-J.; Löper, P.; Niesen, B.; Ledinsky, M.; Haug, F.-J.; Yum, J.-H.; Ballif, C., Organometallic Halide Perovskites: Sharp Optical Absorption Edge and Its Relation to Photovoltaic Performance. *The Journal of Physical Chemistry Letters* **2014**, 5 (6), 1035-1039. Copyright © 2019 American Chemical Society. (b) UV-vis absorption spectra of MAPb(I_{1-x}Br_x)₃ films with different halide composition, showing increase in band gap with higher Br content (from 1 to 7).⁸⁷ Reprinted with permission from Kulkarni, S. A.; Baikie, T.; Boix, P. P.; Yantara, N.; Mathews, N.; Mhaisalkar, S., Band-gap tuning of lead halide perovskites using a sequential deposition process. *Journal of Materials Chemistry A* **2014**, 2 (24), 9221-9225. Copyright © 2019 Royal Society of Chemistry.

A few important studies have shown long-range balanced charge transport properties with carrier diffusion lengths exceeding 1 μm for halide perovskites,^{18, 76, 90-92} which means that majority of the charge carriers can be extracted before they recombine since the thickness of the layer is much smaller than the diffusion length. These long diffusion distances are associated with low recombination rates, long carrier lifetimes⁹²⁻⁹³ and balanced charge mobilities ($\sim 25 \text{ cm}^2/\text{Vs}$),⁹⁴⁻⁹⁵ which could be related to the three-dimensional, corner-connected, octahedral structure of PbX₆.⁹⁰ Weak exciton binding energies ($\sim 30 - 50 \text{ meV}$)⁹⁶ have also been reported for MAPbI₃, leading to enhanced light harvesting and photogeneration of charge carriers at room temperature.⁹⁷ Several reports have also shown crystalline films with extremely low levels of defects present in its electronic structure for

halide perovskites.^{78, 98-104} These defects are found to at the shallow transition levels, which are benign and do not affect the electronic properties of the material, giving it a defect tolerant property.¹⁰⁵⁻¹⁰⁶ This is important as the crystallinity will define the distribution of energetic states and disorder.¹³

All of these excellent optoelectronic properties along with versatility to tune its properties, low material cost and solution processability explain the superior performance of PSCs and highlight the potential use in various optoelectronic applications such as light-emitting diodes (LEDs), lasers, transistors and photodetectors etc.¹⁰⁷ A good solar cell material is likewise a good light emitter based on the fact that a solar cell needs to have an external luminescence efficiency of $\sim 100\%$ in order to reach the Shockley-Queisser efficiency limit of 33% .¹⁰⁸⁻¹⁰⁹ Various optoelectronic properties possessed by the halide perovskites are highly desirable for light emission as well. The band gap tunability is especially attractive in the field of display applications, allowing any emission colour in the full visible spectrum to be easily achieved.¹¹⁰⁻¹¹¹ Its narrow emission bandwidth also means that the colour obtained from the thin film and corresponding PeLED devices can be extremely pure.¹¹²

2.4 Perovskites in LEDs (PeLEDs)

With the highly promising optoelectronic properties of halide perovskites, PeLEDs have become a rapidly emerging field in recent years, leveraging on the knowledge gained from established OLED and PSC technologies. The first demonstration of light emission from perovskites was shown through an amplified spontaneous emission by Xing et al., showing electrically driven lasing.¹¹³ Thereafter, Tan et al. and Chin et al. fabricated and demonstrated the first PeLED¹¹⁴ and perovskite light-emitting field-effect transistor¹¹⁵ respectively. Following the steep rise in performance of PSCs in the field of PVs, PeLEDs have also seen a similar trend in the field of light emission as well. Figure 2.9 shows the remarkable rise in both brightness and external quantum efficiency (EQE) of PeLEDs within just a few years as compared to OLEDs and quantum dot LEDs (QDLEDs).¹⁰⁹

Figure 2.9 Evolution of (left) EQE and (right) luminance of PeLEDs over the years as compared to OLEDs and QDLEDs.¹⁰⁹ Reprinted with permission from Veldhuis, S. A.; Boix, P. P.; Yantara, N.; Li, M.; Sum, T. C.; Mathews, N.; Mhaisalkar, S. G., *Perovskite Materials for Light-Emitting Diodes and Lasers. Advanced Materials* **2016**, 28 (32), 6804-6834. Copyright © 2019 John Wiley and Sons.

2.4.1 Device Architecture and Working Principle

The most common device architecture of PeLEDs follows that of the triple layer OLED,¹⁰⁹ where the perovskite emissive layer (EML) is sandwiched between an ETL and a HTL as shown in Figure 2.10. The working mechanism of a PeLED is similar to that of the PSC, although the process is reversed. Electrons and holes are injected through the cathode and anode respectively, transported across the ETL and HTL charge transport layers, and recombined within the perovskite EML. Since most halide perovskites possess direct band gaps, the wavelength of the emitted light is then equivalent to the band gap of the perovskite EML.¹¹⁶

Figure 2.10 Schematic of a PeLED device architecture showing the direction of charge carrier flow and radiative recombination in the emissive layer (EML).

Research into PeLEDs is swiftly gaining momentum since the first report in 2014, whereby the organic-inorganic hybrid perovskite EML ($\text{CH}_3\text{NH}_3\text{PbBr}_3$) is sandwiched between a HTL (PEDOT:PSS) and an ETL (poly(9,9-di-n-octylfluorenyl-2,7-diyl), also known as F8), reaching a maximum luminance (L_{max}) of 364 cd m^{-2} and a current efficiency of 0.3 cd A^{-1} .¹¹⁴ The high colour purity, coupled with low costs associated with the ease of material synthesis and device fabrication, makes PeLEDs an attractive candidate for display applications. Within a short span of two years, works carried out to further enhance device performance (such as by tailoring the interfacial charge transport layers,¹¹⁷⁻¹¹⁸ employing a polymer-perovskite blend,¹¹⁸⁻¹¹⁹ and using solvent engineering techniques to enhance film formation¹²⁰) have given rise to improvements in the current efficiency of up to 42.9 cd A^{-1} .¹²⁰ On the other hand, research in OLEDs took almost two decades to reach similar levels of efficiencies (Figure 2.9).^{109, 121}

2.4.2 Interfacial Layers

The device functions only as efficiently as how well the charges are injected from the interfacial layers.¹⁰⁹ Without these interfacial layers, charges will simply travel to the opposite electrodes, resulting in large amounts of leakage current. These interfacial materials can be termed as the charge transport layer, charge injection layer, or blocking layer due to the three functions that they serve. In order to achieve balanced charge injection into the perovskite emitter, the charge transport layers sandwiching the perovskite emitter, *i.e.* the HTL and ETL, must be cautiously selected.¹²²⁻¹²³ This selection is governed by a few criteria. Firstly, the charge transport layers have to carry their respective charges efficiently (charge transport). In other words, the HTL should possess high hole mobility while the ETL should have high electron mobility. Based on this criteria, many compounds have been identified and classified as good HTLs or ETLs. Various lists of transport materials have been made available in journals and even in commercial websites. They may range from organic compounds (more common) to inorganic ones (usually oxides). Some examples of common ETLs and HTMs are shown in Figure 2.11 along with their respective HOMO and LUMO levels.

Figure 2.11 Examples of common ETL and HTM with their respective energy levels graphed alongside the perovskite EML.¹⁰⁹ Reprinted with permission from Veldhuis, S. A.; Boix, P. P.; Yantara, N.; Li, M.; Sum, T. C.; Mathews, N.; Mhaisalkar, S. G., *Perovskite Materials for Light-Emitting Diodes and Lasers. Advanced Materials* **2016**, 28 (32), 6804-6834. Copyright © 2019 John Wiley and Sons.

However, not every one of the listed materials are suitable for a given device architecture. The second criterion is more specific to the system of interest. Efficient injection of charges requires matching of energy levels between the charge transport layers and the sandwiched emitter.¹²⁴ The electronic band structure describes the range of energy states which electrons can occupy and is derived through quantum mechanical calculations. From an energetics point of view, it is more energetically favourable for an electron to jump from a higher energy state to a lower unoccupied level, whereas the opposite is true for holes. Henceforth, it is best recommended that the conduction bands (CB) and valence bands (VB) of the ETL align with the LUMO and HOMO of the transport layers such that $\text{LUMO}_{\text{ETL}} > \text{CB}_{\text{EML}}$ (for electron injection) and $\text{HOMO}_{\text{HTL}} < \text{VB}_{\text{EML}}$ (for hole injection). Ideally, the respective charge injection layers should also act as blocking layers for the opposite charges,

which brings across the third criterion. This means that the energy band levels of the charge injection or transport layers should also present a barrier to the opposite charges so as not to allow any current to escape from the EML. The HTM should possess low electron affinity while the ETL should have deep HOMO levels, *i.e.* $\text{HOMO}_{\text{ETL}} \ll \text{VB}_{\text{EML}}$ (for hole blocking) and $\text{LUMO}_{\text{HTM}} \gg \text{CB}_{\text{EML}}$ (for electron blocking). Combining the second and third criteria, this eventually results in the formation of a quantum well that efficiently confines electrons and holes within the EML, thereby increasing the carrier concentration (n) and enhancing the probability of radiative recombination ($\propto n^2$), ultimately leading to an increase in both the luminance and efficiency of the device.¹⁰⁹ Figure 2.12 illustrates an ideal alignment of energy levels between the charge transport layers and the EML, showing both the charge injection and blocking mechanisms. In order to identify the VB positions of semiconductor materials, characterization techniques such as X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and particle elastic scattering analysis (PESA) may be employed.¹²⁵ By coupling the band gap information obtained using ultraviolet-visible (UV-vis) spectroscopy and the corresponding Tauc plots, the conduction band of the material can be determined. Knowledge of the energy band levels will enable more effective selection of HTLs and ETLs for better charge transfer across the band edges. It is however worth noting that processing conditions and techniques may also alter the band positions.¹²⁶⁻¹²⁸

Figure 2.12 Ideal energy band alignment of a PeLED device for efficient charge confinement, showing carrier injection and blocking capabilities of the transport layers sandwiching the emitter.

Not only do the charge transport and injection depend on the band alignment, the interface too plays an equally important role. This includes the interface between the emissive and charge transport layers as well as between the charge transport layers and electrodes. Even if the materials exhibit favourable band alignment, without good interfacial contact, charge transport can be affected. The ideal interface should be smooth, homogeneous, uniform,

defect-free and have good adhesion with the adjacent layer.¹⁰⁹ This can be affected by intrinsic factors such as bonding between two different material surfaces and difference in lattice parameters. Extrinsically, processing conditions can also influence the interfacial quality such as surface treatment and deposition techniques.¹²⁹⁻¹³³

2.4.3 Factors Affecting PeLED Performance

Despite the outstanding potential of PeLEDs, the long-term stability has been one of the major concerns hindering its widespread use. Moisture exposure could induce degradation of the material due to the affinity of organic cations to water molecules.¹³⁴ Moreover, its thermal stability is also governed by the low-temperature sublimation of the organic cations. Fully inorganic perovskite materials have been reported by substituting the organic cation with Cs^+ , giving the material higher resistance to thermal degradation.¹³⁵⁻¹³⁸ However, initial research into this material has been little as compared to their organic-inorganic counterparts. The first CsPbBr_3 PeLED paper showed reduced trap density with excess CsBr in the precursor solution which achieved L_{max} of 407 cd m^{-2} and a current efficiency level of 0.035 cd A^{-1} .¹³⁵ The passivation of atomic Pb defects with the excess CsBr was key to reducing non-radiative decay pathways, as supported by Cho's group.¹²⁰ Zhang et al. have also demonstrated PeLEDs employing CsPbBr_3 nanocrystals achieving improved L_{max} of $1,377 \text{ cd m}^{-2}$ and current efficiency of 0.19 cd A^{-1} through interface engineering.¹³⁹ A synthetic approach of PEO-assisted CsPbBr_3 films has also been demonstrated, yielding a smoother and pinhole-free morphology with smaller crystals, leading to highly luminescent and efficient PeLEDs.¹⁴⁰ Morphology is therefore shown to be a critical factor in determining the performance of the final devices, which can affect the resultant charge dynamics in the film, similar to the earlier discussion on PSCs.⁹³ A major factor influencing it is the crystallization rate. Padture et al. have reported a comprehensive study to understand solution-processed perovskite film formation, with particular emphasis on the nucleation, growth, coarsening and evolution aspects.¹⁴¹ The slow evaporation of commonly used solvents (*e.g.* DMF and DMSO) due to their high boiling points has somewhat hindered the perovskite crystallization during the spin-coating process. As a

result, low nuclei density has led to acicular structures and incomplete coverage from conventional spin-coating process.¹⁴² A commonly used method to circumvent this problem and achieve highly efficient perovskite solar cells and PeLEDs is by using a solvent engineering method, whereby an antisolvent such as toluene or chloroform is introduced to supersaturate the perovskite precursor solution and induce precipitation.^{46, 143-145} Using this method, the nucleation rate is greatly enhanced while the growth rate is suppressed simultaneously,¹⁴⁶ resulting in a smooth and fine-grained film with good coverage, although scale-up production of such devices remains hampered by low reproducibility arising from propensity for radial and inhomogeneous growth gradient as well as the toxic nature of commonly used antisolvents.^{54, 147}

In both organic-inorganic hybrid ($\text{CH}_3\text{NH}_3\text{PbBr}_3$) and fully inorganic (CsPbBr_3) systems, smaller grain size and thus increased grain boundary area are expected to be beneficial for PeLEDs due to the spatial confinement of excitons and charge carriers within the restricted nanoscale geometries which consequently blocks their diffusion and thereby increases the radiative recombination.¹¹² This has been demonstrated in several early reports where processing has been modified in various ways to modulate grain size such as through nanocrystal pinning,¹²⁰ quick annealing process,¹⁴⁸ and incorporation in polymer matrix.¹⁴⁹

Recently, various strategies have been shown to produce highly efficient PeLEDs. For instance, using different interfacial layers have shown better energy band alignment and better perovskite morphology, leading to significant enhancements to device performances, similar to the interfacial engineering previously discussed for PSCs.¹⁵⁰⁻¹⁵² Light extraction efficiency has been improved using light out-coupling methods such as special substrates with nanophotonic structures, increasing EQE of these devices to more than 20%.¹⁵³⁻¹⁵⁴ Core-shell structures utilizing MABr to passivate the perovskite emitter have also been shown to reduce non-radiative defects, thereby greatly improving the PLQY and EQE of the device.^{148, 155} Passivation has been found to be an important strategy, and other studies have also reported various passivating functional moieties such as amino acid additives to achieve EQEs of close to 21%.¹⁵⁶⁻¹⁵⁷ A combination of perovskite and polymer heterostructure has also been demonstrated to improve efficiencies and lifetime of

devices.^{118, 158-160} Balanced carrier injection is also found to be crucial for optimizing the radiative recombination efficiency within the perovskite EML, leading to better confinement and higher stability of devices.^{133, 161} In addition, an interesting approach using multidimensional perovskites have also shown improved light emission properties via a tailored energy cascade landscape within the perovskite emitter,^{133, 158, 162-167} which will be described in the next section.

2.4.4 Lower Dimensional Perovskites

In recent years, there has been increasing interests in lower and mixed-dimensional perovskites. Two-dimensional (2D) perovskites were first synthesized and characterized by S. N. Ruddlesden and P. Popper in 1957,¹⁶⁸⁻¹⁶⁹ thus these compounds are also known as Ruddlesden-Popper (RP) perovskites. As compared to the three-dimensional (3D) perovskites, RP perovskites have a layered structure consisting of individual planes of corner-sharing PbX_6 octahedra kept apart by bulky organic cations that are too large to fit inside the 3D lattice (Figure 2.13).¹⁷⁰⁻¹⁷¹ These compounds have a general formula of $\text{L}_2\text{A}_{n-1}\text{B}_n\text{X}_{3n+1}$, where L is usually a long, bulky ammonium cation. In this case, n represents the number of BX_6 layers that are dimensionally confined, with $n = 1$ representing a pure 2D perovskite, $n = \infty$ representing a pure 3D perovskite, and $1 < n < \infty$ representing a quasi-2D layered perovskite.¹⁷²

Figure 2.13 Schematic illustration of (a) reduced dimensionality of halide perovskites through intercalation of the inorganic PbX_6 octahedra using large organic spacer cations, and (b) a multi quantum well structure of layered perovskites.¹⁰⁹ Reprinted with permission from Veldhuis, S. A.; Boix, P. P.; Yantara, N.; Li, M.; Sum, T. C.; Mathews, N.; Mhaisalkar, S. G., Perovskite Materials for Light-Emitting Diodes and Lasers. *Advanced Materials* **2016**, 28 (32), 6804-6834. Copyright © 2019 John Wiley and Sons.

3D perovskites usually suffer from low photoluminescence quantum yield (PLQY) as a result of inherently low exciton binding energy that leads to a low radiative recombination rate.¹⁷³⁻¹⁷⁴ This is compounded by trap state densities which are prevalent at low injected carrier densities leading to higher non-radiative recombination rates.^{113, 175} As a result, the PLQY of 3D perovskites is usually low at low excitation intensity, thus limiting device efficiencies.¹⁷² Besides, it is often challenging to obtain solution-processed thin films with uniform and crystalline morphologies, which leads to leakage currents and non-radiative recombination related losses,^{120, 176} although various strategies have also been proven to overcome it.^{149-150, 156, 177} On the other hand, 2D layered perovskites show promising advantages over the 3D counterpart, such as high PLQY due to larger exciton binding energies,¹⁷⁸⁻¹⁸⁰ and highly crystalline thin films as well as smooth morphologies.¹⁸¹⁻¹⁸² The other advantage is that 2D perovskites possess better ambient stability than the 3D ones, with better resistance against moisture, heat and light-induced degradation.¹⁸³⁻¹⁸⁸ Various studies on 2D perovskites have been conducted.¹⁸⁹⁻¹⁹⁰ For example, single crystals of (2-

$(\text{NMA})_2\text{PbBr}_4$ and $(2\text{-NEA})_2\text{PbBr}_4$ have been grown and characterized using single crystal XRD and the crystal structures have been solved as depicted in Figure 2.14.¹⁹⁰

Figure 2.14 Crystal structure of 2D perovskites (left) $(2\text{-NMA})_2\text{PbBr}_4$ and (right) $(2\text{-NEA})_2\text{PbBr}_4$ visualized using VESTA. Crystallographic Information Files from the single crystal XRD are obtained from reference [186].

In this study, the distortion of 2D single crystal perovskites with different ligand molecules is compared based on a quantitative evaluation model developed by Robinson et al.,¹⁹¹ as described by the octahedral bond length elongation (λ_{oct}) and the octahedral bond angle variance (σ_{oct}^2):

$$\lambda_{oct} = \frac{1}{6} \sum_{i=1}^6 (d_i/d_0)^2$$

where d_i and d_0 are the Pb–X bond lengths for the studied system and an ideal regular polyhedron respectively, and

$$\sigma_{oct}^2 = \frac{1}{11} \sum_{i=1}^{12} (\alpha_i - 90)^2$$

where α_i represents the X–Pb–X bond angles within the octahedra.¹⁸⁹⁻¹⁹⁰

Based on the equations, the distortions can be quantitatively evaluated with the help of the VESTA software.¹⁹² The derived distortion index shows the quadratic elongation and bond angle variance to be 1.0040 and 13.57 deg² for (2-NMA)₂PbBr₄ and 1.0038 and 13.58 deg² for (2-NEA)₂PbBr₄. For an ideal regular octahedral, the elongation should be 1 and the bond angle variance should be 0.¹⁹³ The octahedra bond elongations for both materials appear to be very close to 1, while the bond angle variances of ~ 13.5 deg² show the presence of some distortion, which can also be visually observed from the top view of the crystal structure in Figure 2.14. The octahedral distortions have been used to explain various phenomena in 2D perovskites. For instance, higher distortions reduce the formation energy of interfacial defect states, resulting in broad-band emission of the butylammonium lead iodide 2D perovskite,¹⁸⁹ while the bond angle variance has also been shown to tune the band gap of the perovskite by up to 1 eV.¹⁹⁴

Despite the advantages of pure 2D perovskites over the 3D counterparts, the problem of poor charge transport due to its isolated octahedral layers has limited its applications in PSCs and LEDs.^{183, 195-196} By combining 3D and 2D perovskites to form a mixed phase of quasi-2D states (mixed/multidimensional perovskites with intermediate dimensionality), benefits of charge transport from the 3D portion and enhanced radiative recombination due to the higher exciton confinement from the 2D phase¹⁹⁷ can both be acquired, leading to a synergistic effect in these mixed systems.^{183, 198-199} In addition, the co-existence of multiphases in the film is found to exhibit an energy funnelling phenomenon as a result of the different band gaps of the different dimensions.¹⁶²⁻¹⁶⁴ This cascading energy landscape is particularly beneficial in LEDs due to the enhanced carrier confinement in the lowest band gap phase which brings about higher radiative recombination that largely outcompetes the non-radiative losses. Various studies utilizing different ligand molecules such as butylammonium (BA),^{173, 200} phenylethylammonium (PEA)^{166-167, 201} and phenylbutylammonium (PBA)²⁰² have all shown enhanced photo- and electroluminescence

properties of the mixed-dimensional perovskite as compared to the pristine 3D system, indicating a promising prospect for quasi-2D PeLEDs.

2.5 Summary of Literature Status, Gaps, and This Thesis in Perspective

Perovskite research has come a long way since its first incorporation into a DSSC electrified the whole PV community. Within a decade (2009 – 2018), more than ten thousand papers were published, with close to four hundred thousand citations.¹⁶ This figure means that more than two papers were published each day, with topics covering a wide range of aspects involving different branches of science and engineering. This includes studies with regard to the materials, devices, processing methods, various engineering techniques, as well as chemistry and photophysics analyses elucidating the scientific concepts and theories behind the remarkable performance of this material in solar cells and LEDs. While significant efforts have been invested in every area of perovskite optoelectronics, several unresolved gaps remain that still need to be filled to advance the field further, especially for the area of light emission and LEDs.

Firstly, although several earlier reports have shown that smaller grain sizes (< 100 nm) are required for spatial confinement of charge carriers and excitons,^{112, 120, 129, 173, 177, 203-205} many of these studies make use of additives in the film deposition procedure, which adds another variable which could have contributed to the rise in PLQY/EQE. The additional species such as polyethylene oxide polymer, TPBi small organic molecule, or incorporation in a matrix made of a different material could have given rise to other passivation or confinement effects, which need to be examined deeper to differentiate the contributions from multiple factors. Various recent studies have also shown that sub-micron sized grains were able to achieve high efficiencies in PeLEDs as well,^{156-157, 206} which contradict the claims from earlier reports, although the focuses of these papers are on other factors such as additive passivation and architecture designs. The role of grain size on the luminescence properties of perovskites is thus not patently established even though morphology plays a critical role in both film properties and device performances. There is then an urgent need

to unravel this correlation using deposition procedures that do not entail multiple factors which can lead to debatable conclusions.

Furthermore, quasi-2D/multidimensional perovskites have shown promising potential as light emitters, yielding high PLQYs and EQEs due to a tailored energy landscape,^{162-165, 167, 173} However, the proposed funnelling phenomenon still lacks thorough investigation and explanation, although a more recent study has revealed the kinetics of the mechanism by probing the transient response of mixed-dimensional FAPbBr₃ perovskites with changing the acceptor (3D) to donor (2D) ratio.¹⁶⁵ A deeper analysis of the energy cascade is still necessary in order to understand the mechanism and design more efficient quasi-2D perovskite systems. In addition, most literatures on multidimensional PeLEDs focus only on one single type of ligand molecule while varying its concentration/ratio or processing techniques. The effect of the molecular structure of this ligand molecule remains unknown, which presents a knowledge barrier when it comes to selecting the type of ligand molecules for a particular perovskite system. Although several literatures have investigated different ligand molecules for mixed-dimensional PSCs,²⁰⁷⁻²¹⁰ the findings are disparate since the working principle is opposite in PeLEDs. PSCs require minimum confinement in order to extract charge carriers, which means that the electronic confinement through an energy cascade is undesired, while PeLEDs operate more efficiently with stronger confinement due to the need for recombination. The different energy landscape created by changing the spacer molecule is expected to have an effect on both the film properties and device performances, and this missing information needs to be uncovered in order to design more efficient quasi-2D systems.

These scientific challenges that still remain to be addressed rationalize the motivation and objectives behind this thesis, as stated in Chapter 1. These gaps are filled by investigating the geometrical and electronic confinement in 3D and quasi-2D CsPbBr₃ perovskites. The grain size uncertainty is unraveled by controlling the crystallization rate of the perovskite without any additives so as to eliminate contribution from extra factors. A quasi-2D perovskite composition based on the all-inorganic CsPbBr₃ is also demonstrated for the first time in PeLEDs and used to investigate the energy transfer across the energetic

landscape. The same system is subsequently repeated using different ligand molecules to find out the ideal characteristics required of a ligand molecule and the corresponding mixed-dimensional phase, thereby establishing a guideline for future design of mixed-dimensional perovskites. Accomplishing these studies will allow a better understanding of the confinement effects in CsPbBr₃ PeLEDs, which are likely applicable to other perovskite material systems as well, eventually paving the way towards cheaper and better LEDs for display applications in the future.

References

1. Tsao, J. Y. *Light Emitting Diodes (LEDs) for General Illumination: An Oida Technology Roadmap Update 2002*; Nov 2002.
2. Light-Emitting Diodes: A Primer, Photonics Handbook. <http://www.photonics.com/EDU/Handbook.aspx> (accessed 10 Oct 2016).
3. Cassarly, W. J., High-Brightness LEDs. *Opt. Photon. News* **2008**, *19* (1), 18-23.
4. Ashdown, I., Solid-State Lighting: A Systems Engineering Approach. *Opt. Photon. News* **2007**, *18* (1), 24-30.
5. Li, J.; Zhang, G.-Q., *Light-Emitting Diodes: Materials, Processes, Devices and Applications*. Springer: 2018; Vol. 4.
6. Karpov, S. Y.; Makarov, Y. N., Dislocation Effect on Light Emission Efficiency in Gallium Nitride. *Applied Physics Letters* **2002**, *81* (25), 4721-4723.
7. Li, N.; Han, K.; Spratt, W.; Bedell, S.; Ott, J.; Hopstaken, M.; Libsch, F.; Li, Q.; Sadana, D., Ultra-Low-Power Sub-Photon-Voltage High-Efficiency Light-Emitting Diodes. *Nature Photonics* **2019**.
8. Bender, V. C.; Marchesan, T. B.; Alonso, J. M., Solid-State Lighting: A Concise Review of the State of the Art on LED and OLED Modeling. *IEEE Industrial Electronics Magazine* **2015**, *9* (2), 6-16.
9. Felton, M. J., Thinner, Lighter, Better, Brighter Organic Light-Emitting Diodes May Make Cathode Ray Tubes and Liquid Crystal Displays Obsolete. *TODAYS CHEMIST AT WORK* **2001**, *10* (11), 30-35.

10. Thejo Kalyani, N.; Dhoble, S. J., Organic Light Emitting Diodes: Energy Saving Lighting Technology—A Review. *Renewable and Sustainable Energy Reviews* **2012**, *16* (5), 2696-2723.
11. Brütting, W.; Frischeisen, J.; Schmidt, T. D.; Scholz, B. J.; Mayr, C., Device Efficiency of Organic Light-Emitting Diodes: Progress by Improved Light Outcoupling. *physica status solidi (a)* **2013**, *210* (1), 44-65.
12. Jou, J.-H.; Kumar, S.; Agrawal, A.; Li, T.-H.; Sahoo, S., Approaches for Fabricating High Efficiency Organic Light Emitting Diodes. *Journal of Materials Chemistry C* **2015**, *3* (13), 2974-3002.
13. Boix, P. P.; Nonomura, K.; Mathews, N.; Mhaisalkar, S. G., Current Progress and Future Perspectives for Organic/Inorganic Perovskite Solar Cells. *Materials Today* **2014**, *17* (1), 16-23.
14. Green, M. A.; Ho-Baillie, A.; Snaith, H. J., The Emergence of Perovskite Solar Cells. *Nature photonics* **2014**, *8* (7), 506.
15. Kamat, P. V., Acs Journals Celebrate 10 Years of Perovskite Photovoltaics. *ACS Energy Letters* **2019**, *4*, 1055-1056.
16. De Angelis, F., Celebrating 10 Years of Perovskite Photovoltaics. ACS Publications: 2019.
17. Cheng, Z.; Lin, J., Layered Organic-Inorganic Hybrid Perovskites: Structure, Optical Properties, Film Preparation, Patterning and Templating Engineering. *CrystEngComm* **2010**, *12* (10), 2646-2662.
18. Kim, H.-S.; Im, S. H.; Park, N.-G., Organolead Halide Perovskite: New Horizons in Solar Cell Research. *The Journal of Physical Chemistry C* **2014**, *118* (11), 5615-5625.
19. Mitzi, D. B., Synthesis, Structure, and Properties of Organic-Inorganic Perovskites and Related Materials. In *Progress in Inorganic Chemistry, Volume 48 (Ed K. D. Karlin)*, John Wiley & Sons, Inc.: Hoboken, NJ, USA, 1999; pp 1-121.
20. Møller, C. K., A Phase Transition in Cæsium Plumbochloride. *Nature* **1957**, *180* (4593), 981-982.
21. Møller, C. K., Crystal Structure and Photoconductivity of Cæsium Plumbohalides. *Nature* **1958**, *182* (4647), 1436-1436.
22. Wasylishen, R. E.; Knop, O.; Macdonald, J. B., Cation Rotation in

Methylammonium Lead Halides. *Solid State Communications* **1985**, 56 (7), 581-582.

23. Poglitsch, A.; Weber, D., Dynamic Disorder in Methylammoniumtrihalogenoplumbates (II) Observed by Millimeter - Wave Spectroscopy. *The Journal of Chemical Physics* **1987**, 87 (11), 6373-6378.
24. Wyckoff, R., The Crystal Structures of Monomethyl Ammonium Chlorostannate and Chloroplatinate. *American Journal of Science* **1928**, (94), 349-359.
25. Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T., Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *Journal of the American Chemical Society* **2009**, 131 (17), 6050-6051.
26. Kim, H.-S.; Lee, C.-R.; Im, J.-H.; Lee, K.-B.; Moehl, T.; Marchioro, A.; Moon, S.-J.; Humphry-Baker, R.; Yum, J.-H.; Moser, J. E.; Grätzel, M.; Park, N.-G., Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%. *Scientific Reports* **2012**, 2, 591.
27. Lee, M. M.; Teuscher, J.; Miyasaka, T.; Murakami, T. N.; Snaith, H. J., Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites. *Science* **2012**, 338 (6107), 643-647.
28. Van Noorden, R., Cheap Solar Cells Tempt Businesses. *Nature News* **2014**, 513 (7519), 470.
29. Antonietta Loi, M.; Hummelen, J. C., Perovskites under the Sun. *Nature Materials* **2013**, 12, 1087.
30. Hodes, G., Perovskite-Based Solar Cells. *Science* **2013**, 342 (6156), 317-318.
31. NREL Best Research-Cell Efficiency Chart. <https://www.nrel.gov/pv/cell-efficiency.html> (accessed 30 July 2019).
32. Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W.; Dunlop, E. D., Solar Cell Efficiency Tables (Version 48). *Progress in Photovoltaics: Research and Applications* **2016**, 24 (7), 905-913.
33. Chung, I.; Lee, B.; He, J.; Chang, R. P. H.; Kanatzidis, M. G., All-Solid-State Dye-Sensitized Solar Cells with High Efficiency. *Nature* **2012**, 485, 486.
34. Razza, S.; Castro-Hermosa, S.; Carlo, A. D.; Brown, T. M., Research Update: Large-Area Deposition, Coating, Printing, and Processing Techniques for the Upscaling of Perovskite Solar Cell Technology. *APL Materials* **2016**, 4 (9), 091508.

35. Grätzel, M., The Light and Shade of Perovskite Solar Cells. *Nature Materials* **2014**, *13*, 838.
36. Salim, T.; Sun, S.; Abe, Y.; Krishna, A.; Grimsdale, A. C.; Lam, Y. M., Perovskite-Based Solar Cells: Impact of Morphology and Device Architecture on Device Performance. *Journal of Materials Chemistry A* **2015**, *3* (17), 8943-8969.
37. Correa-Baena, J.-P.; Abate, A.; Saliba, M.; Tress, W.; Jesper Jacobsson, T.; Grätzel, M.; Hagfeldt, A., The Rapid Evolution of Highly Efficient Perovskite Solar Cells. *Energy & Environmental Science* **2017**, *10* (3), 710-727.
38. Qiu, J.; Yang, S., Material and Interface Engineering for High-Performance Perovskite Solar Cells: A Personal Journey and Perspective. *The Chemical Record* **2019**. DOI:10.1002/tcr.201900028.
39. Etgar, L.; Gao, P.; Xue, Z.; Peng, Q.; Chandiran, A. K.; Liu, B.; Nazeeruddin, M. K.; Grätzel, M., Mesoscopic CH₃NH₃PbI₃/TiO₂ Heterojunction Solar Cells. *Journal of the American Chemical Society* **2012**, *134* (42), 17396-17399.
40. Jung, H. S.; Park, N. G., Perovskite Solar Cells: From Materials to Devices. *Small* **2015**, *11* (1), 10-25.
41. Burschka, J.; Pellet, N.; Moon, S.-J.; Humphry-Baker, R.; Gao, P.; Nazeeruddin, M. K.; Gratzel, M., Sequential Deposition as a Route to High-Performance Perovskite-Sensitized Solar Cells. *Nature* **2013**, *499* (7458), 316-319.
42. Luo, Y.; Meng, F.; Zhao, E.; Zheng, Y.-Z.; Zhou, Y.; Tao, X., Fine Control of Perovskite-Layered Morphology and Composition via Sequential Deposition Crystallization Process Towards Improved Perovskite Solar Cells. *Journal of Power Sources* **2016**, *311*, 130-136.
43. Chen, Q.; Zhou, H.; Hong, Z.; Luo, S.; Duan, H.-S.; Wang, H.-H.; Liu, Y.; Li, G.; Yang, Y., Planar Heterojunction Perovskite Solar Cells via Vapor-Assisted Solution Process. *Journal of the American Chemical Society* **2014**, *136* (2), 622-625.
44. Wu, Y.; Islam, A.; Yang, X.; Qin, C.; Liu, J.; Zhang, K.; Peng, W.; Han, L., Retarding the Crystallization of PbI₂ for Highly Reproducible Planar-Structured Perovskite Solar Cells via Sequential Deposition. *Energy & Environmental Science* **2014**, *7* (9), 2934-2938.
45. Zhang, T.; Yang, M.; Zhao, Y.; Zhu, K., Controllable Sequential Deposition of Planar CH₃NH₃PbI₃ Perovskite Films via Adjustable Volume Expansion. *Nano Letters* **2015**, *15*

(6), 3959-3963.

46. Jeon, N. J.; Noh, J. H.; Kim, Y. C.; Yang, W. S.; Ryu, S.; Seok, S. I., Solvent Engineering for High-Performance Inorganic–Organic Hybrid Perovskite Solar Cells. *Nature Materials* **2014**, *13* (9), 897-903.

47. Xiao, M.; Huang, F.; Huang, W.; Dkhissi, Y.; Zhu, Y.; Etheridge, J.; Gray-Weale, A.; Bach, U.; Cheng, Y.-B.; Spiccia, L., A Fast Deposition-Crystallization Procedure for Highly Efficient Lead Iodide Perovskite Thin-Film Solar Cells. *Angewandte Chemie* **2014**, *126* (37), 10056-10061.

48. Zhao, Y.; Zhu, K., Solution Chemistry Engineering toward High-Efficiency Perovskite Solar Cells. *The Journal of Physical Chemistry Letters* **2014**, *5* (23), 4175-4186.

49. Gao, L.; Yang, G., Organic-Inorganic Halide Perovskites: From Crystallization of Polycrystalline Films to Solar Cell Applications. *Solar RRL* **2020**. DOI:10.1002/solr.201900200.

50. Li, W.; Fan, J.; Li, J.; Mai, Y.; Wang, L., Controllable Grain Morphology of Perovskite Absorber Film by Molecular Self-Assembly toward Efficient Solar Cell Exceeding 17%. *Journal of the American Chemical Society* **2015**, *137* (32), 10399-10405.

51. Ahn, N.; Son, D.-Y.; Jang, I.-H.; Kang, S. M.; Choi, M.; Park, N.-G., Highly Reproducible Perovskite Solar Cells with Average Efficiency of 18.3% and Best Efficiency of 19.7% Fabricated via Lewis Base Adduct of Lead(II) Iodide. *Journal of the American Chemical Society* **2015**, *137* (27), 8696-8699.

52. Lee, J.-W.; Kim, H.-S.; Park, N.-G., Lewis Acid–Base Adduct Approach for High Efficiency Perovskite Solar Cells. *Accounts of Chemical Research* **2016**, *49* (2), 311-319.

53. Feng, J.; Zhu, X.; Yang, Z.; Zhang, X.; Niu, J.; Wang, Z.; Zuo, S.; Priya, S.; Liu, S.; Yang, D., Record Efficiency Stable Flexible Perovskite Solar Cell Using Effective Additive Assistant Strategy. *Advanced Materials* **2018**, *30* (35), 1801418.

54. Li, X.; Bi, D.; Yi, C.; Décoppet, J.-D.; Luo, J.; Zakeeruddin, S. M.; Hagfeldt, A.; Grätzel, M., A Vacuum Flash–Assisted Solution Process for High-Efficiency Large-Area Perovskite Solar Cells. *Science* **2016**, *353* (6294), 58-62.

55. Bi, D.; Yi, C.; Luo, J.; Décoppet, J.-D.; Zhang, F.; Zakeeruddin, Shaik M.; Li, X.; Hagfeldt, A.; Grätzel, M., Polymer-Templated Nucleation and Crystal Growth of Perovskite Films for Solar Cells with Efficiency Greater Than 21%. *Nature Energy* **2016**,

1, 16142.

56. Yang, W. S.; Park, B.-W.; Jung, E. H.; Jeon, N. J.; Kim, Y. C.; Lee, D. U.; Shin, S. S.; Seo, J.; Kim, E. K.; Noh, J. H.; Seok, S. I., Iodide Management in Formamidinium-Lead-Halide-Based Perovskite Layers for Efficient Solar Cells. *Science* **2017**, *356* (6345), 1376-1379.
57. Jeon, N. J.; Noh, J. H.; Yang, W. S.; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. I., Compositional Engineering of Perovskite Materials for High-Performance Solar Cells. *Nature* **2015**, *517*, 476.
58. Saliba, M.; Matsui, T.; Seo, J.-Y.; Domanski, K.; Correa-Baena, J.-P.; Nazeeruddin, M. K.; Zakeeruddin, S. M.; Tress, W.; Abate, A.; Hagfeldt, A.; Grätzel, M., Cesium-Containing Triple Cation Perovskite Solar Cells: Improved Stability, Reproducibility and High Efficiency. *Energy & Environmental Science* **2016**, *9* (6), 1989-1997.
59. Saliba, M.; Matsui, T.; Domanski, K.; Seo, J.-Y.; Ummadisingu, A.; Zakeeruddin, S. M.; Correa-Baena, J.-P.; Tress, W. R.; Abate, A.; Hagfeldt, A.; Grätzel, M., Incorporation of Rubidium Cations into Perovskite Solar Cells Improves Photovoltaic Performance. *Science* **2016**, *354* (6309), 206-209.
60. Matsui, T.; Yamamoto, T.; Nishihara, T.; Morisawa, R.; Yokoyama, T.; Sekiguchi, T.; Negami, T., Compositional Engineering for Thermally Stable, Highly Efficient Perovskite Solar Cells Exceeding 20% Power Conversion Efficiency with 85 °C/85% 1000 h Stability. *Advanced Materials* **2019**, *31* (10), 1806823.
61. Bu, T.; Liu, X.; Zhou, Y.; Yi, J.; Huang, X.; Luo, L.; Xiao, J.; Ku, Z.; Peng, Y.; Huang, F.; Cheng, Y.-B.; Zhong, J., A Novel Quadruple-Cation Absorber for Universal Hysteresis Elimination for High Efficiency and Stable Perovskite Solar Cells. *Energy & Environmental Science* **2017**, *10* (12), 2509-2515.
62. Liu, D.; Kelly, T. L., Perovskite Solar Cells with a Planar Heterojunction Structure Prepared Using Room-Temperature Solution Processing Techniques. *Nature Photonics* **2013**, *8*, 133.
63. You, J.; Hong, Z.; Yang, Y.; Chen, Q.; Cai, M.; Song, T.-B.; Chen, C.-C.; Lu, S.; Liu, Y.; Zhou, H.; Yang, Y., Low-Temperature Solution-Processed Perovskite Solar Cells with High Efficiency and Flexibility. *ACS Nano* **2014**, *8* (2), 1674-1680.
64. Yang, D.; Yang, R.; Wang, K.; Wu, C.; Zhu, X.; Feng, J.; Ren, X.; Fang, G.; Priya,

S.; Liu, S., High Efficiency Planar-Type Perovskite Solar Cells with Negligible Hysteresis Using EDTA-Complexed SnO₂. *Nature Communications* **2018**, *9* (1), 3239.

65. Liu, K.; Chen, S.; Wu, J.; Zhang, H.; Qin, M.; Lu, X.; Tu, Y.; Meng, Q.; Zhan, X., Fullerene Derivative Anchored SnO₂ for High-Performance Perovskite Solar Cells. *Energy & Environmental Science* **2018**, *11* (12), 3463-3471.

66. Rao, H.-S.; Chen, B.-X.; Li, W.-G.; Xu, Y.-F.; Chen, H.-Y.; Kuang, D.-B.; Su, C.-Y., Improving the Extraction of Photogenerated Electrons with SnO₂ Nanocolloids for Efficient Planar Perovskite Solar Cells. *Advanced Functional Materials* **2015**, *25* (46), 7200-7207.

67. Zhu, Z.; Bai, Y.; Liu, X.; Chueh, C.-C.; Yang, S.; Jen, A. K.-Y., Enhanced Efficiency and Stability of Inverted Perovskite Solar Cells Using Highly Crystalline SnO₂ Nanocrystals as the Robust Electron-Transporting Layer. *Advanced Materials* **2016**, *28* (30), 6478-6484.

68. Lee, H. B.; Jeon, M.-K.; Kumar, N.; Tyagi, B.; Kang, J.-W., Boosting the Efficiency of SnO₂-Triple Cation Perovskite System Beyond 20% Using Nonhalogenated Antisolvent. *Advanced Functional Materials* **2019**, *29* (32), 1903213.

69. Luan, Y.; Yi, X.; Mao, P.; Wei, Y.; Zhuang, J.; Chen, N.; Lin, T.; Li, C.; Wang, J., High-Performance Planar Perovskite Solar Cells with Negligible Hysteresis Using 2,2,2-Trifluoroethanol-Incorporated SnO₂. *iScience* **2019**, *16*, 433-441.

70. Krishna, A.; Grimsdale, A. C., Hole Transporting Materials for Mesoscopic Perovskite Solar Cells – Towards a Rational Design? *Journal of Materials Chemistry A* **2017**, *5* (32), 16446-16466.

71. Urieta-Mora, J.; García-Benito, I.; Molina-Ontoria, A.; Martín, N., Hole Transporting Materials for Perovskite Solar Cells: A Chemical Approach. *Chemical Society Reviews* **2018**, *47* (23), 8541-8571.

72. Connell, A.; Wang, Z.; Lin, Y.-H.; Greenwood, P. C.; Wiles, A. A.; Jones, E. W.; Furnell, L.; Anthony, R.; Kershaw, C. P.; Cooke, G.; Snaith, H. J.; Holliman, P. J., Low Cost Triazatruxene Hole Transporting Material for >20% Efficiency Perovskite Solar Cells. *Journal of Materials Chemistry C* **2019**, *7* (18), 5235-5243.

73. Jung, E. H.; Jeon, N. J.; Park, E. Y.; Moon, C. S.; Shin, T. J.; Yang, T.-Y.; Noh, J. H.; Seo, J., Efficient, Stable and Scalable Perovskite Solar Cells Using Poly(3-

Hexylthiophene). *Nature* **2019**, 567 (7749), 511-515.

74. Coontz, R. Science's Top 10 Breakthroughs of 2013. <http://www.sciencemag.org/news/2013/12/sciences-top-10-breakthroughs-2013> (accessed 5 Aug).

75. Yin, W.-J.; Chen, H.; Shi, T.; Wei, S.-H.; Yan, Y., Origin of High Electronic Quality in Structurally Disordered $\text{CH}_3\text{NH}_3\text{PbI}_3$ and the Passivation Effect of Cl and O at Grain Boundaries. *Advanced Electronic Materials* **2015**, 1 (6), 1500044.

76. Fan, J.; Jia, B.; Gu, M., Perovskite-Based Low-Cost and High-Efficiency Hybrid Halide Solar Cells. *Photonics Research* **2014**, 2 (5), 111-120.

77. Singh, S. P.; Nagarjuna, P., Organometal Halide Perovskites as Useful Materials in Sensitized Solar Cells. *Dalton Transactions, The Royal Society of Chemistry* **2014**, 43 (14), 5247-5251.

78. Yin, W.-J.; Shi, T.; Yan, Y., Unique Properties of Halide Perovskites as Possible Origins of the Superior Solar Cell Performance. *Advanced Materials* **2014**, 26 (27), 4653-4658.

79. Yoshikawa, K.; Kawasaki, H.; Yoshida, W.; Irie, T.; Konishi, K.; Nakano, K.; Uto, T.; Adachi, D.; Kanematsu, M.; Uzu, H.; Yamamoto, K., Silicon Heterojunction Solar Cell with Interdigitated Back Contacts for a Photoconversion Efficiency over 26%. *Nature Energy* **2017**, 2, 17032.

80. Boix, P. P.; Raga, S. R.; Mathews, N., Working Principles of Perovskite Solar Cells. *Halide Perovskites: Photovoltaics, Light Emitting Devices, and Beyond* **2018**, 81-99.

81. De Wolf, S.; Holovsky, J.; Moon, S.-J.; Löper, P.; Niesen, B.; Ledinsky, M.; Haug, F.-J.; Yum, J.-H.; Ballif, C., Organometallic Halide Perovskites: Sharp Optical Absorption Edge and Its Relation to Photovoltaic Performance. *The Journal of Physical Chemistry Letters* **2014**, 5 (6), 1035-1039.

82. Shao, Y.; Yuan, Y.; Huang, J., Correlation of Energy Disorder and Open-Circuit Voltage in Hybrid Perovskite Solar Cells. *Nature Energy* **2016**, 1, 15001.

83. Eperon, G. E.; Stranks, S. D.; Menelaou, C.; Johnston, M. B.; Herz, L. M.; Snaith, H. J., Formamidinium Lead Trihalide: A Broadly Tunable Perovskite for Efficient Planar Heterojunction Solar Cells. *Energy & Environmental Science* **2014**, 7 (3), 982-988.

84. Sutton, R. J.; Eperon, G. E.; Miranda, L.; Parrott, E. S.; Kamino, B. A.; Patel, J. B.;

- Hörlantner, M. T.; Johnston, M. B.; Haghighirad, A. A.; Moore, D. T.; Snaith, H. J., Bandgap-Tunable Cesium Lead Halide Perovskites with High Thermal Stability for Efficient Solar Cells. *Advanced Energy Materials* **2016**, 6 (8), 1502458.
85. Wang, L.; Yuan, G. D.; Duan, R. F.; Huang, F.; Wei, T. B.; Liu, Z. Q.; Wang, J. X.; Li, J. M., Tunable Bandgap in Hybrid Perovskite $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_{3-y}\text{X}_y)$ Single Crystals and Photodetector Applications. *AIP Advances* **2016**, 6 (4), 045115.
86. Ju, D.; Dang, Y.; Zhu, Z.; Liu, H.; Chueh, C.-C.; Li, X.; Wang, L.; Hu, X.; Jen, A. K. Y.; Tao, X., Tunable Band Gap and Long Carrier Recombination Lifetime of Stable Mixed $\text{CH}_3\text{NH}_3\text{Pb}_x\text{Sn}_{1-x}\text{Br}_3$ Single Crystals. *Chemistry of Materials* **2018**, 30 (5), 1556-1565.
87. Kulkarni, S. A.; Baikie, T.; Boix, P. P.; Yantara, N.; Mathews, N.; Mhaisalkar, S., Band-Gap Tuning of Lead Halide Perovskites Using a Sequential Deposition Process. *Journal of Materials Chemistry A* **2014**, 2 (24), 9221-9225.
88. Yang, T. C.-J.; Fiala, P.; Jeangros, Q.; Ballif, C., High-Bandgap Perovskite Materials for Multijunction Solar Cells. *Joule* **2018**, 2 (8), 1421-1436.
89. Song, Z.; Chen, C.; Li, C.; Awni, R. A.; Zhao, D.; Yan, Y., Wide-Bandgap, Low-Bandgap, and Tandem Perovskite Solar Cells. *Semiconductor Science and Technology* **2019**, 34 (9), 093001.
90. Xing, G.; Mathews, N.; Sun, S.; Lim, S. S.; Lam, Y. M.; Grätzel, M.; Mhaisalkar, S.; Sum, T. C., Long-Range Balanced Electron- and Hole-Transport Lengths in Organic-Inorganic $\text{CH}_3\text{NH}_3\text{PbI}_3$. *Science* **2013**, 342 (6156), 344-347.
91. Stranks, S. D.; Eperon, G. E.; Grancini, G.; Menelaou, C.; Alcocer, M. J. P.; Leijtens, T.; Herz, L. M.; Petrozza, A.; Snaith, H. J., Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in an Organometal Trihalide Perovskite Absorber. *Science* **2013**, 342 (6156), 341-344.
92. Chen, Y.; Yi, H. T.; Wu, X.; Haroldson, R.; Gartstein, Y. N.; Rodionov, Y. I.; Tikhonov, K. S.; Zakhidov, A.; Zhu, X. Y.; Podzorov, V., Extended Carrier Lifetimes and Diffusion in Hybrid Perovskites Revealed by Hall Effect and Photoconductivity Measurements. *Nature Communications* **2016**, 7, 12253.
93. de Quilletes, D. W.; Vorpahl, S. M.; Stranks, S. D.; Nagaoka, H.; Eperon, G. E.; Ziffer, M. E.; Snaith, H. J.; Ginger, D. S., Impact of Microstructure on Local Carrier

Lifetime in Perovskite Solar Cells. *Science* **2015**, 348 (6235), 683-686.

94. Jung, H. S.; Park, N.-G., Perovskite Solar Cells: From Materials to Devices. *Small* **2015**, 11 (1), 10-25.
95. Ponseca, C. S., Jr.; Savenije, T. J.; Abdellah, M.; Zheng, K.; Yartsev, A.; Pascher, T.; Harlang, T.; Chabera, P.; Pullerits, T.; Stepanov, A.; Wolf, J.-P.; Sundström, V., Organometal Halide Perovskite Solar Cell Materials Rationalized: Ultrafast Charge Generation, High and Microsecond-Long Balanced Mobilities, and Slow Recombination. *Journal of the American Chemical Society* **2014**, 136 (14), 5189-5192.
96. Wehrenfennig, C.; Eperon, G. E.; Johnston, M. B.; Snaith, H. J.; Herz, L. M., High Charge Carrier Mobilities and Lifetimes in Organolead Trihalide Perovskites. *Advanced Materials* **2014**, 26 (10), 1584-1589.
97. D’Innocenzo, V.; Grancini, G.; Alcocer, M. J. P.; Kandada, A. R. S.; Stranks, S. D.; Lee, M. M.; Lanzani, G.; Snaith, H. J.; Petrozza, A., Excitons Versus Free Charges in Organo-Lead Tri-Halide Perovskites. *Nature Communications* **2014**, 5, 3586.
98. Ball, J. M.; Petrozza, A., Defects in Perovskite-Halides and Their Effects in Solar Cells. *Nature Energy* **2016**, 1, 16149.
99. Manser, J. S.; Christians, J. A.; Kamat, P. V., Intriguing Optoelectronic Properties of Metal Halide Perovskites. *Chemical Reviews* **2016**, 116 (21), 12956-13008.
100. Huang, J.; Yuan, Y.; Shao, Y.; Yan, Y., Understanding the Physical Properties of Hybrid Perovskites for Photovoltaic Applications. *Nature Reviews Materials* **2017**, 2, 17042.
101. Grätzel, M., The Light and Shade of Perovskite Solar Cells. *Nature Materials* **2014**, 13 (9), 838-842.
102. Kumar, M. H.; Dharani, S.; Leong, W. L.; Boix, P. P.; Prabhakar, R. R.; Baikie, T.; Shi, C.; Ding, H.; Ramesh, R.; Asta, M.; Graetzel, M.; Mhaisalkar, S. G.; Mathews, N., Lead-Free Halide Perovskite Solar Cells with High Photocurrents Realized through Vacancy Modulation. *Advanced Materials* **2014**, 26 (41), 7122-7127.
103. Kang, J.; Wang, L.-W., High Defect Tolerance in Lead Halide Perovskite CsPbBr₃. *The Journal of Physical Chemistry Letters* **2017**, 8 (2), 489-493.
104. Wang, F.; Bai, S.; Tress, W.; Hagfeldt, A.; Gao, F., Defects Engineering for High-Performance Perovskite Solar Cells. *npj Flexible Electronics* **2018**, 2 (1), 22.

105. Kim, J.; Chung, C.-H.; Hong, K.-H., Understanding of the Formation of Shallow Level Defects from the Intrinsic Defects of Lead Tri-Halide Perovskites. *Physical Chemistry Chemical Physics* **2016**, *18* (39), 27143-27147.
106. Yin, W.-J.; Yang, J.-H.; Kang, J.; Yan, Y.; Wei, S.-H., Halide Perovskite Materials for Solar Cells: A Theoretical Review. *Journal of Materials Chemistry A* **2015**, *3* (17), 8926-8942.
107. Chen, Q.; De Marco, N.; Yang, Y.; Song, T.-B.; Chen, C.-C.; Zhao, H.; Hong, Z.; Zhou, H.; Yang, Y., Under the Spotlight: The Organic–Inorganic Hybrid Halide Perovskite for Optoelectronic Applications. *Nano Today* **2015**, *10* (3), 355-396.
108. Sha, W. E.; Ren, X.; Chen, L.; Choy, W. C., The Efficiency Limit of $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Solar Cells. *Applied Physics Letters* **2015**, *106* (22), 221104.
109. Veldhuis, S. A.; Boix, P. P.; Yantara, N.; Li, M.; Sum, T. C.; Mathews, N.; Mhaisalkar, S. G., Perovskite Materials for Light-Emitting Diodes and Lasers. *Advanced Materials* **2016**, *28* (32), 6804-6834.
110. Zou, Y.; Yuan, Z.; Bai, S.; Gao, F.; Sun, B., Recent Progress toward Perovskite Light-Emitting Diodes with Enhanced Spectral and Operational Stability. *Materials Today Nano* **2019**, *5*, 100028.
111. Wei, Z.; Xing, J., The Rise of Perovskite Light-Emitting Diodes. *The Journal of Physical Chemistry Letters* **2019**, *10* (11), 3035-3042.
112. Kim, Y.-H.; Cho, H.; Lee, T.-W., Metal Halide Perovskite Light Emitters. *Proceedings of the National Academy of Sciences* **2016**, *113* (42), 11694-11702.
113. Xing, G.; Mathews, N.; Lim, S. S.; Yantara, N.; Liu, X.; Sabba, D.; Grätzel, M.; Mhaisalkar, S.; Sum, T. C., Low-Temperature Solution-Processed Wavelength-Tunable Perovskites for Lasing. *Nature Materials* **2014**, *13* (5), 476-480.
114. Tan, Z.-K.; Moghaddam, R. S.; Lai, M. L.; Docampo, P.; Higler, R.; Deschler, F.; Price, M.; Sadhanala, A.; Pazos, L. M.; Credgington, D.; Hanusch, F.; Bein, T.; Snaith, H. J.; Friend, R. H., Bright Light-Emitting Diodes Based on Organometal Halide Perovskite. *Nature Nanotechnology* **2014**, *9* (9), 687-692.
115. Chin, X. Y.; Cortecchia, D.; Yin, J.; Bruno, A.; Soci, C., Lead Iodide Perovskite Light-Emitting Field-Effect Transistor. *Nature communications* **2015**, *6*, 7383.
116. Light-Emitting Diodes. In *Kirk - Othmer Encyclopedia of Chemical Technology*, pp

1-20.

117. Wang, J.; Wang, N.; Jin, Y.; Si, J.; Tan, Z.-K.; Du, H.; Cheng, L.; Dai, X.; Bai, S.; He, H.; Ye, Z.; Lai, M. L.; Friend, R. H.; Huang, W., Interfacial Control toward Efficient and Low-Voltage Perovskite Light-Emitting Diodes. *Advanced Materials* **2015**, *27* (14), 2311-2316.
118. Bade, S. G. R.; Li, J.; Shan, X.; Ling, Y.; Tian, Y.; Dilbeck, T.; Besara, T.; Geske, T.; Gao, H.; Ma, B.; Hanson, K.; Siegrist, T.; Xu, C.; Yu, Z., Fully Printed Halide Perovskite Light-Emitting Diodes with Silver Nanowire Electrodes. *ACS Nano* **2016**, *10* (2), 1795-1801.
119. Li, G.; Tan, Z.-K.; Di, D.; Lai, M. L.; Jiang, L.; Lim, J. H.-W.; Friend, R. H.; Greenham, N. C., Efficient Light-Emitting Diodes Based on Nanocrystalline Perovskite in a Dielectric Polymer Matrix. *Nano Letters* **2015**, *15* (4), 2640-2644.
120. Cho, H.; Jeong, S.-H.; Park, M.-H.; Kim, Y.-H.; Wolf, C.; Lee, C.-L.; Heo, J. H.; Sadhanala, A.; Myoung, N.; Yoo, S.; Im, S. H.; Friend, R. H.; Lee, T.-W., Overcoming the Electroluminescence Efficiency Limitations of Perovskite Light-Emitting Diodes. *Science* **2015**, *350* (6265), 1222-1225.
121. Meredith, P.; Armin, A., LED Technology Breaks Performance Barrier. Nature Publishing Group: 2018.
122. Fan, R.; Huang, Y.; Wang, L.; Li, L.; Zheng, G.; Zhou, H., The Progress of Interface Design in Perovskite-Based Solar Cells. *Advanced Energy Materials* **2016**, *6* (17), 1600460.
123. Zhou, H.; Chen, Q.; Li, G.; Luo, S.; Song, T.-b.; Duan, H.-S.; Hong, Z.; You, J.; Liu, Y.; Yang, Y., Interface Engineering of Highly Efficient Perovskite Solar Cells. *Science* **2014**, *345* (6196), 542-546.
124. Jiang, Y.; Cho, S.-Y.; Shim, M., Light-Emitting Diodes of Colloidal Quantum Dots and Nanorod Heterostructures for Future Emissive Displays. *Journal of Materials Chemistry C* **2018**, *6* (11), 2618-2634.
125. Olthof, S., Research Update: The Electronic Structure of Hybrid Perovskite Layers and Their Energetic Alignment in Devices. *APL Materials* **2016**, *4* (9), 091502.
126. Mahmood, K.; Sarwar, S.; Mehran, M. T., Current Status of Electron Transport Layers in Perovskite Solar Cells: Materials and Properties. *RSC Advances* **2017**, *7* (28), 17044-17062.

127. Mohammadian-Sarcheshmeh, H.; Mazloum-Ardakani, M., Recent Advancements in Compact Layer Development for Perovskite Solar Cells. *Heliyon* **2018**, *4* (11), e00912.
128. Luceño-Sánchez, J. A.; Díez-Pascual, A. M.; Peña Capilla, R., Materials for Photovoltaics: State of Art and Recent Developments. *International Journal of Molecular Sciences* **2019**, *20* (4), 976.
129. Kumawat, N. K.; Gupta, D.; Kabra, D., Recent Advances in Metal Halide-Based Perovskite Light-Emitting Diodes. *Energy Technology* **2017**, *5* (10), 1734-1749.
130. Wang, Z.; Li, Z.; Zhou, D.; Yu, J., Low Turn-on Voltage Perovskite Light-Emitting Diodes with Methanol Treated PEDOT:PSS as Hole Transport Layer. *Applied Physics Letters* **2017**, *111* (23), 233304.
131. Yu, J. C.; Hong, J. A.; Jung, E. D.; Kim, D. B.; Baek, S.-M.; Lee, S.; Cho, S.; Park, S. S.; Choi, K. J.; Song, M. H., Highly Efficient and Stable Inverted Perovskite Solar Cell Employing PEDOT:GO Composite Layer as a Hole Transport Layer. *Scientific Reports* **2018**, *8* (1), 1070.
132. Wu, M.; Zhao, D.; Wang, Z.; Yu, J., High-Luminance Perovskite Light-Emitting Diodes with High-Polarity Alcohol Solvent Treating PEDOT:PSS as Hole Transport Layer. *Nanoscale Research Letters* **2018**, *13* (1), 128.
133. Li, Z.; Chen, Z.; Yang, Y.; Xue, Q.; Yip, H.-L.; Cao, Y., Modulation of Recombination Zone Position for Quasi-Two-Dimensional Blue Perovskite Light-Emitting Diodes with Efficiency Exceeding 5%. *Nature Communications* **2019**, *10* (1), 1027.
134. Berhe, T. A.; Su, W.-N.; Chen, C.-H.; Pan, C.-J.; Cheng, J.-H.; Chen, H.-M.; Tsai, M.-C.; Chen, L.-Y.; Dubale, A. A.; Hwang, B.-J., Organometal Halide Perovskite Solar Cells: Degradation and Stability. *Energy & Environmental Science* **2016**, *9* (2), 323-356.
135. Yantara, N.; Bhaumik, S.; Yan, F.; Sabba, D.; Dewi, H. A.; Mathews, N.; Boix, P. P.; Demir, H. V.; Mhaisalkar, S., Inorganic Halide Perovskites for Efficient Light-Emitting Diodes. *The Journal of Physical Chemistry Letters* **2015**, *6* (21), 4360-4364.
136. Kulbak, M.; Gupta, S.; Kedem, N.; Levine, I.; Bendikov, T.; Hodes, G.; Cahen, D., Cesium Enhances Long-Term Stability of Lead Bromide Perovskite-Based Solar Cells. *The Journal of Physical Chemistry Letters* **2016**, *7* (1), 167-172.
137. Sutton, R. J.; Eperon, G. E.; Miranda, L.; Parrott, E. S.; Kamino, B. A.; Patel, J. B.; Hörantner, M. T.; Johnston, M. B.; Haghighirad, A. A.; Moore, D. T.; Snaith, H. J.,

Bandgap-Tunable Cesium Lead Halide Perovskites with High Thermal Stability for Efficient Solar Cells. *Advanced Energy Materials* **2016**, 6 (8), 1502458.

138. Kulbak, M.; Cahen, D.; Hodes, G., How Important Is the Organic Part of Lead Halide Perovskite Photovoltaic Cells? Efficient CsPbBr₃ Cells. *The Journal of Physical Chemistry Letters* **2015**, 6 (13), 2452-2456.

139. Zhang, X.; Lin, H.; Huang, H.; Reckmeier, C.; Zhang, Y.; Choy, W. C. H.; Rogach, A. L., Enhancing the Brightness of Cesium Lead Halide Perovskite Nanocrystal Based Green Light-Emitting Devices through the Interface Engineering with Perfluorinated Ionomer. *Nano Letters* **2016**, 16 (2), 1415-1420.

140. Ling, Y.; Tian, Y.; Wang, X.; Wang, J. C.; Knox, J. M.; Perez-Orive, F.; Du, Y.; Tan, L.; Hanson, K.; Ma, B.; Gao, H., Enhanced Optical and Electrical Properties of Polymer-Assisted All-Inorganic Perovskites for Light-Emitting Diodes. *Advanced Materials* **2016**, 28, 8983-8989.

141. Zhou, Y.; Game, O. S.; Pang, S.; Padture, N. P., Microstructures of Organometal Trihalide Perovskites for Solar Cells: Their Evolution from Solutions and Characterization. *The Journal of Physical Chemistry Letters* **2015**, 6 (23), 4827-4839.

142. Wang, Q.; Shao, Y.; Dong, Q.; Xiao, Z.; Yuan, Y.; Huang, J., Large Fill-Factor Bilayer Iodine Perovskite Solar Cells Fabricated by a Low-Temperature Solution-Process. *Energy & Environmental Science* **2014**, 7 (7), 2359-2365.

143. Shi, D.; Adinolfi, V.; Comin, R.; Yuan, M.; Alarousu, E.; Buin, A.; Chen, Y.; Hoogland, S.; Rothenberger, A.; Katsiev, K.; Losovyj, Y.; Zhang, X.; Dowben, P. A.; Mohammed, O. F.; Sargent, E. H.; Bakr, O. M., Low Trap-State Density and Long Carrier Diffusion in Organolead Trihalide Perovskite Single Crystals. *Science* **2015**, 347 (6221), 519-522.

144. Zheng, X.; Chen, B.; Wu, C.; Priya, S., Room Temperature Fabrication of CH₃NH₃PbBr₃ by Anti-Solvent Assisted Crystallization Approach for Perovskite Solar Cells with Fast Response and Small J–V Hysteresis. *Nano Energy* **2015**, 17, 269-278.

145. Xia, B.; Wu, Z.; Dong, H.; Xi, J.; Wu, W.; Lei, T.; Xi, K.; Yuan, F.; Jiao, B.; Xiao, L.; Gong, Q.; Hou, X., Formation of Ultrasoft Perovskite Films toward Highly Efficient Inverted Planar Heterojunction Solar Cells by Micro-Flowing Anti-Solvent Deposition in Air. *Journal of Materials Chemistry A* **2016**, 4 (17), 6295-6303.

146. Zhou, Y.; Yang, M.; Wu, W.; Vasiliev, A. L.; Zhu, K.; Padture, N. P., Room-Temperature Crystallization of Hybrid-Perovskite Thin Films via Solvent-Solvent Extraction for High-Performance Solar Cells. *Journal of Materials Chemistry A* **2015**, *3* (15), 8178-8184.
147. Chen, W.; Wu, Y.; Yue, Y.; Liu, J.; Zhang, W.; Yang, X.; Chen, H.; Bi, E.; Ashraful, I.; Grätzel, M.; Han, L., Efficient and Stable Large-Area Perovskite Solar Cells with Inorganic Charge Extraction Layers. *Science* **2015**, *350* (6263), 944-948.
148. Lee, J.-W.; Choi, Y. J.; Yang, J.-M.; Ham, S.; Jeon, S. K.; Lee, J. Y.; Song, Y.-H.; Ji, E. K.; Yoon, D.-H.; Seo, S.; Shin, H.; Han, G. S.; Jung, H. S.; Kim, D.; Park, N.-G., In-Situ Formed Type I Nanocrystalline Perovskite Film for Highly Efficient Light-Emitting Diode. *ACS Nano* **2017**, *11* (3), 3311-3319.
149. Ling, Y.; Tian, Y.; Wang, X.; Wang, J. C.; Knox, J. M.; Perez-Orive, F.; Du, Y.; Tan, L.; Hanson, K.; Ma, B.; Gao, H., Enhanced Optical and Electrical Properties of Polymer-Assisted All-Inorganic Perovskites for Light-Emitting Diodes. *Advanced Materials* **2016**, *28* (40), 8983-8989.
150. Zhang, L.; Yang, X.; Jiang, Q.; Wang, P.; Yin, Z.; Zhang, X.; Tan, H.; Yang, Y.; Wei, M.; Sutherland, B. R.; Sargent, E. H.; You, J., Ultra-Bright and Highly Efficient Inorganic Based Perovskite Light-Emitting Diodes. *Nature Communications* **2017**, *8*, 15640.
151. Tang, L.; Qiu, J.; Wei, Q.; Gu, H.; Du, B.; Du, H.; Hui, W.; Xia, Y.; Chen, Y.; Huang, W., Enhanced Performance of Perovskite Light-Emitting Diodes via Diamine Interface Modification. *ACS Applied Materials & Interfaces* **2019**, *11* (32), 29132-29138.
152. Song, L.; Guo, X.; Hu, Y.; Lv, Y.; Lin, J.; Fan, Y.; Zhang, N.; Liu, X., Improved Performance of CsPbBr₃ Perovskite Light-Emitting Devices by Both Boundary and Interface Defects Passivation. *Nanoscale* **2018**, *10* (38), 18315-18322.
153. Zhang, Q.; Tavakoli, M. M.; Gu, L.; Zhang, D.; Tang, L.; Gao, Y.; Guo, J.; Lin, Y.; Leung, S.-F.; Poddar, S.; Fu, Y.; Fan, Z., Efficient Metal Halide Perovskite Light-Emitting Diodes with Significantly Improved Light Extraction on Nanophotonic Substrates. *Nature Communications* **2019**, *10* (1), 727.
154. Shen, Y.; Cheng, L.-P.; Li, Y.-Q.; Li, W.; Chen, J.-D.; Lee, S.-T.; Tang, J.-X., High-Efficiency Perovskite Light-Emitting Diodes with Synergetic Outcoupling Enhancement. *Advanced Materials* **2019**, *31* (24), 1901517.

155. Lin, K.; Xing, J.; Quan, L. N.; de Arquer, F. P. G.; Gong, X.; Lu, J.; Xie, L.; Zhao, W.; Zhang, D.; Yan, C.; Li, W.; Liu, X.; Lu, Y.; Kirman, J.; Sargent, E. H.; Xiong, Q.; Wei, Z., Perovskite Light-Emitting Diodes with External Quantum Efficiency Exceeding 20 Per Cent. *Nature* **2018**, *562* (7726), 245-248.
156. Cao, Y.; Wang, N.; Tian, H.; Guo, J.; Wei, Y.; Chen, H.; Miao, Y.; Zou, W.; Pan, K.; He, Y.; Cao, H.; Ke, Y.; Xu, M.; Wang, Y.; Yang, M.; Du, K.; Fu, Z.; Kong, D.; Dai, D.; Jin, Y.; Li, G.; Li, H.; Peng, Q.; Wang, J.; Huang, W., Perovskite Light-Emitting Diodes Based on Spontaneously Formed Submicrometre-Scale Structures. *Nature* **2018**, *562* (7726), 249-253.
157. Xu, W.; Hu, Q.; Bai, S.; Bao, C.; Miao, Y.; Yuan, Z.; Borzda, T.; Barker, A. J.; Tyukalova, E.; Hu, Z.; Kawecki, M.; Wang, H.; Yan, Z.; Liu, X.; Shi, X.; Uvdal, K.; Fahlman, M.; Zhang, W.; Duchamp, M.; Liu, J.-M.; Petrozza, A.; Wang, J.; Liu, L.-M.; Huang, W.; Gao, F., Rational Molecular Passivation for High-Performance Perovskite Light-Emitting Diodes. *Nature Photonics* **2019**, *13* (6), 418-424.
158. Zhao, B.; Bai, S.; Kim, V.; Lamboll, R.; Shivanna, R.; Auras, F.; Richter, J. M.; Yang, L.; Dai, L.; Alsari, M.; She, X.-J.; Liang, L.; Zhang, J.; Lilliu, S.; Gao, P.; Snaith, H. J.; Wang, J.; Greenham, N. C.; Friend, R. H.; Di, D., High-Efficiency Perovskite-Polymer Bulk Heterostructure Light-Emitting Diodes. *Nature Photonics* **2018**, *12* (12), 783-789.
159. Yu, J. C.; Park, J. H.; Lee, S. Y.; Song, M. H., Effect of Perovskite Film Morphology on Device Performance of Perovskite Light-Emitting Diodes. *Nanoscale* **2019**, *11* (4), 1505-1514.
160. Zhang, B.; Wang, H.; Xie, Z., Chapter 10 - Nanomaterials for Polymer and Perovskite Light-Emitting Diodes. In *Advanced Nanomaterials for Solar Cells and Light Emitting Diodes*, Gao, F., Ed. Elsevier: 2019; pp 371-421.
161. Fakharuddin, A.; Qiu, W.; Croes, G.; Devižis, A.; Gegevičius, R.; Vakhnin, A.; Rolin, C.; Genoe, J.; Gehlhaar, R.; Kadashchuk, A., Reduced Efficiency Roll - Off and Improved Stability of Mixed 2D/3D Perovskite Light Emitting Diodes by Balancing Charge Injection. *Advanced Functional Materials* **2019**, 1904101.
162. Quan, L. N.; Zhao, Y.; García de Arquer, F. P.; Sabatini, R.; Walters, G.; Voznyy, O.; Comin, R.; Li, Y.; Fan, J. Z.; Tan, H.; Pan, J.; Yuan, M.; Bakr, O. M.; Lu, Z.; Kim, D. H.; Sargent, E. H., Tailoring the Energy Landscape in Quasi-2D Halide Perovskites Enables

Efficient Green-Light Emission. *Nano Letters* **2017**, *17* (6), 3701-3709.

163. Yuan, M.; Quan, L. N.; Comin, R.; Walters, G.; Sabatini, R.; Voznyy, O.; Hoogland, S.; Zhao, Y.; Beauregard, E. M.; Kanjanaboos, P.; Lu, Z.; Kim, D. H.; Sargent, E. H., Perovskite Energy Funnels for Efficient Light-Emitting Diodes. *Nature Nanotechnology* **2016**, *11* (10), 872-877.

164. Byun, J.; Cho, H.; Wolf, C.; Jang, M.; Sadhanala, A.; Friend, R. H.; Yang, H.; Lee, T.-W., Efficient Visible Quasi-2D Perovskite Light-Emitting Diodes. *Advanced Materials* **2016**, *28* (34), 7515-7520.

165. Yantara, N.; Bruno, A.; Iqbal, A.; Jamaludin, N. F.; Soci, C.; Mhaisalkar, S.; Mathews, N., Designing Efficient Energy Funneling Kinetics in Ruddlesden–Popper Perovskites for High-Performance Light-Emitting Diodes. *Advanced Materials* **2018**, *30* (33), 1800818.

166. Yang, X.; Zhang, X.; Deng, J.; Chu, Z.; Jiang, Q.; Meng, J.; Wang, P.; Zhang, L.; Yin, Z.; You, J., Efficient Green Light-Emitting Diodes Based on Quasi-Two-Dimensional Composition and Phase Engineered Perovskite with Surface Passivation. *Nature Communications* **2018**, *9* (1), 570.

167. Yue, H.; Song, D.; Zhao, S.; Xu, Z.; Qiao, B.; Wu, S.; Meng, J., Highly Bright Perovskite Light-Emitting Diodes Based on Quasi-2D Perovskite Film through Synergetic Solvent Engineering. *RSC Advances* **2019**, *9* (15), 8373-8378.

168. Ruddlesden, S. N.; Popper, P., New Compounds of the K_2NiF_4 Type. *Acta Crystallographica* **1957**, *10* (8), 538-539.

169. Ruddlesden, S. N.; Popper, P., The Compound $Sr_3Ti_2O_7$ and Its Structure. *Acta Crystallographica* **1958**, *11* (1), 54-55.

170. Saparov, B.; Mitzi, D. B., Organic–Inorganic Perovskites: Structural Versatility for Functional Materials Design. *Chemical Reviews* **2016**, *116* (7), 4558-4596.

171. Liu, Y.; Xiao, H.; Goddard, W. A., Two-Dimensional Halide Perovskites: Tuning Electronic Activities of Defects. *Nano Letters* **2016**, *16* (5), 3335-3340.

172. Zhang, L.; Liu, Y.; Yang, Z.; Liu, S., Two Dimensional Metal Halide Perovskites: Promising Candidates for Light-Emitting Diodes. *Journal of Energy Chemistry* **2019**, *37*, 97-110.

173. Xiao, Z.; Kerner, R. A.; Zhao, L.; Tran, N. L.; Lee, K. M.; Koh, T.-W.; Scholes, G.

D.; Rand, B. P., Efficient Perovskite Light-Emitting Diodes Featuring Nanometre-Sized Crystallites. *Nature Photonics* **2017**, *11* (2), 108-115.

174. Miyata, A.; Mitiglu, A.; Plochocka, P.; Portugall, O.; Wang, J. T.-W.; Stranks, S. D.; Snaith, H. J.; Nicholas, R. J., Direct Measurement of the Exciton Binding Energy and Effective Masses for Charge Carriers in Organic–Inorganic Tri-Halide Perovskites. *Nature Physics* **2015**, *11*, 582.

175. Wu, X.; Trinh, M. T.; Niesner, D.; Zhu, H.; Norman, Z.; Owen, J. S.; Yaffe, O.; Kudisch, B. J.; Zhu, X. Y., Trap States in Lead Iodide Perovskites. *Journal of the American Chemical Society* **2015**, *137* (5), 2089-2096.

176. Yu, J. C.; Kim, D. B.; Jung, E. D.; Lee, B. R.; Song, M. H., High-Performance Perovskite Light-Emitting Diodes via Morphological Control of Perovskite Films. *Nanoscale* **2016**, *8* (13), 7036-7042.

177. Park, M.-H.; Jeong, S.-H.; Seo, H.-K.; Wolf, C.; Kim, Y.-H.; Kim, H.; Byun, J.; Kim, J. S.; Cho, H.; Lee, T.-W., Unravelling Additive-Based Nanocrystal Pinning for High Efficiency Organic-Inorganic Halide Perovskite Light-Emitting Diodes. *Nano Energy* **2017**, *42*, 157-165.

178. Li, F.; Yang, L.; Cai, Z.; Wei, K.; Lin, F.; You, J.; Jiang, T.; Wang, Y.; Chen, X., Enhancing Exciton Binding Energy and Photoluminescence of Formamidinium Lead Bromide by Reducing Its Dimensions to 2D Nanoplates for Producing Efficient Light Emitting Diodes. *Nanoscale* **2018**, *10* (44), 20611-20617.

179. Mauck, C. M.; Tisdale, W. A., Excitons in 2D Organic–Inorganic Halide Perovskites. *Trends in Chemistry* **2019**, *1* (4), 380-393.

180. Blancon, J. C.; Stier, A. V.; Tsai, H.; Nie, W.; Stoumpos, C. C.; Traoré, B.; Pedesseau, L.; Kepenekian, M.; Katsutani, F.; Noe, G. T.; Kono, J.; Tretiak, S.; Crooker, S. A.; Katan, C.; Kanatzidis, M. G.; Crochet, J. J.; Even, J.; Mohite, A. D., Scaling Law for Excitons in 2D Perovskite Quantum Wells. *Nature Communications* **2018**, *9* (1), 2254.

181. Huang, X.; Cui, Q.; Bi, W.; Li, L.; Jia, P.; Hou, Y.; Hu, Y.; Lou, Z.; Teng, F., Two-Dimensional Additive Diethylammonium Iodide Promoting Crystal Growth for Efficient and Stable Perovskite Solar Cells. *RSC Advances* **2019**, *9* (14), 7984-7991.

182. Wu, G.; Zhou, J.; Zhang, J.; Meng, R.; Wang, B.; Xue, B.; Leng, X.; Zhang, D.; Zhang, X.; Bi, S.; Zhou, Q.; Wei, Z.; Zhou, H.; Zhang, Y., Management of the

Crystallization in Two-Dimensional Perovskite Solar Cells with Enhanced Efficiency within a Wide Temperature Range and High Stability. *Nano Energy* **2019**, *58*, 706-714.

183. Zhang, F.; Kim, D. H.; Zhu, K., 3D/2D Multidimensional Perovskites: Balance of High Performance and Stability for Perovskite Solar Cells. *Current Opinion in Electrochemistry* **2018**, *11*, 105-113.

184. Meng, L.; Zhang, F.; Ma, W.; Zhao, Y.; Zhao, P.; Fu, H.; Wang, W.; Meng, S.; Guo, X., Improving Photovoltaic Stability and Performance of Perovskite Solar Cells by Molecular Interface Engineering. *The Journal of Physical Chemistry C* **2019**, *123* (2), 1219-1225.

185. Yuan, J.; Jiang, Y.; He, T.; Shi, G.; Fan, Z.; Yuan, M., Two-Dimensional Perovskite Capping Layer for Stable and Efficient Tin-Lead Perovskite Solar Cells. *SCIENCE CHINA Chemistry* **2019**, *62* (1674-7291), 629.

186. Xiao, Z.; Meng, W.; Wang, J.; Mitzi, D. B.; Yan, Y., Searching for Promising New Perovskite-Based Photovoltaic Absorbers: The Importance of Electronic Dimensionality. *Materials Horizons* **2017**, *4* (2), 206-216.

187. Stoumpos, C. C.; Cao, D. H.; Clark, D. J.; Young, J.; Rondinelli, J. M.; Jang, J. I.; Hupp, J. T.; Kanatzidis, M. G., Ruddlesden–Popper Hybrid Lead Iodide Perovskite 2D Homologous Semiconductors. *Chemistry of Materials* **2016**, *28* (8), 2852-2867.

188. Zheng, H.; Liu, G.; Chen, X.; Zhang, B.; Alsaedi, A.; Hayat, T.; Pan, X.; Dai, S., High-Performance Mixed-Dimensional Perovskite Solar Cells with Enhanced Stability against Humidity, Heat and UV Light. *Journal of Materials Chemistry A* **2018**, *6* (41), 20233-20241.

189. Cortecchia, D.; Neutzner, S.; Srimath Kandada, A. R.; Mosconi, E.; Meggiolaro, D.; De Angelis, F.; Soci, C.; Petrozza, A., Broadband Emission in Two-Dimensional Hybrid Perovskites: The Role of Structural Deformation. *Journal of the American Chemical Society* **2017**, *139* (1), 39-42.

190. Du, K.-z.; Tu, Q.; Zhang, X.; Han, Q.; Liu, J.; Zauscher, S.; Mitzi, D. B., Two-Dimensional Lead(II) Halide-Based Hybrid Perovskites Templated by Acene Alkylamines: Crystal Structures, Optical Properties, and Piezoelectricity. *Inorganic Chemistry* **2017**, *56* (15), 9291-9302.

191. Robinson, K.; Gibbs, G. V.; Ribbe, P. H., Quadratic Elongation: A Quantitative

Measure of Distortion in Coordination Polyhedra. *Science* **1971**, 172 (3983), 567-570.

192. Momma, K.; Izumi, F., Vesta 3 for Three-Dimensional Visualization of Crystal, Volumetric and Morphology Data. *Journal of Applied Crystallography* **2011**, 44 (6), 1272-1276.

193. Thomas, N., Crystal Structure-Physical Property Relationships in Perovskites. *Acta Crystallographica Section B* **1989**, 45 (4), 337-344.

194. Knutson, J. L.; Martin, J. D.; Mitzi, D. B., Tuning the Band Gap in Hybrid Tin Iodide Perovskite Semiconductors Using Structural Templating. *Inorganic Chemistry* **2005**, 44 (13), 4699-4705.

195. Zhang, F.; Kim, D. H.; Lu, H.; Park, J.-S.; Larson, B. W.; Hu, J.; Gao, L.; Xiao, C.; Reid, O. G.; Chen, X.; Zhao, Q.; Ndione, P. F.; Berry, J. J.; You, W.; Walsh, A.; Beard, M. C.; Zhu, K., Enhanced Charge Transport in 2D Perovskites via Fluorination of Organic Cation. *Journal of the American Chemical Society* **2019**, 141 (14), 5972-5979.

196. Gao, L.; Zhang, F.; Xiao, C.; Chen, X.; Larson, B. W.; Berry, J. J.; Zhu, K., Improving Charge Transport via Intermediate - Controlled Crystal Growth in 2D Perovskite Solar Cells. *Advanced Functional Materials* **2019**, 29 (47), 1901652.

197. Misra, R. K.; Cohen, B.-E.; Iagher, L.; Etgar, L., Low-Dimensional Organic-Inorganic Halide Perovskite: Structure, Properties, and Applications. *ChemSusChem* **2017**, 10 (19), 3712-3721.

198. Chen, C.-H.; Li, Z.; Xue, Q.; Su, Y.-A.; Lee, C.-C.; Yip, H.-L.; Chen, W.-C.; Chueh, C.-C., Engineering of Perovskite Light-Emitting Diodes Based on Quasi-2D Perovskites Formed by Diamine Cations. *Organic Electronics* **2019**, 75, 105400.

199. Koh, T. M.; Shanmugam, V.; Schlipf, J.; Oesinghaus, L.; Müller-Buschbaum, P.; Ramakrishnan, N.; Swamy, V.; Mathews, N.; Boix, P. P.; Mhaisalkar, S. G., Nanostructuring Mixed-Dimensional Perovskites: A Route toward Tunable, Efficient Photovoltaics. *Advanced Materials* **2016**, 28 (19), 3653-3661.

200. Vashishtha, P.; Ng, M.; Shivarudraiah, S. B.; Halpert, J. E., High Efficiency Blue and Green Light-Emitting Diodes Using Ruddlesden-Popper Inorganic Mixed Halide Perovskites with Butylammonium Interlayers. *Chemistry of Materials* **2019**, 31 (1), 83-89.

201. Han, Y.; Park, S.; Kim, C.; Lee, M.; Hwang, I., Phase Control of Quasi-2D Perovskites and Improved Light-Emitting Performance by Excess Organic Cations and

Nanoparticle Intercalation. *Nanoscale* **2019**, *11* (8), 3546-3556.

202. Si, J.; Liu, Y.; He, Z.; Du, H.; Du, K.; Chen, D.; Li, J.; Xu, M.; Tian, H.; He, H.; Di, D.; Lin, C.; Cheng, Y.; Wang, J.; Jin, Y., Efficient and High-Color-Purity Light-Emitting Diodes Based on in Situ Grown Films of CsPbX₃ (X = Br, I) Nanoplates with Controlled Thicknesses. *ACS Nano* **2017**, *11* (11), 11100-11107.

203. Conings, B.; Drijkoningen, J.; Gauquelin, N.; Babayigit, A.; D'Haen, J.; D'Olieslaeger, L.; Ethirajan, A.; Verbeeck, J.; Manca, J.; Mosconi, E.; Angelis, F. D.; Boyen, H.-G., Intrinsic Thermal Instability of Methylammonium Lead Trihalide Perovskite. *Advanced Energy Materials* **2015**, *5* (15), 1500477.

204. Quan, L. N.; Quintero-Bermudez, R.; Voznyy, O.; Walters, G.; Jain, A.; Fan, J. Z.; Zheng, X.; Yang, Z.; Sargent, E. H., Highly Emissive Green Perovskite Nanocrystals in a Solid State Crystalline Matrix. *Advanced Materials* **2017**, *29* (21), 1605945.

205. Li, C.; Zang, Z.; Han, C.; Hu, Z.; Tang, X.; Du, J.; Leng, Y.; Sun, K., Highly Compact CsPbBr₃ Perovskite Thin Films Decorated by ZnO Nanoparticles for Enhanced Random Lasing. *Nano Energy* **2017**, *40*, 195-202.

206. Shi, Y.; Wu, W.; Dong, H.; Li, G.; Xi, K.; Divitini, G.; Ran, C.; Yuan, F.; Zhang, M.; Jiao, B.; Hou, X.; Wu, Z., A Strategy for Architecture Design of Crystalline Perovskite Light-Emitting Diodes with High Performance. *Advanced Materials* **2018**, *30* (25), 1800251.

207. Cohen, B.-E.; Wierzbowska, M.; Etgar, L., High Efficiency Quasi 2D Lead Bromide Perovskite Solar Cells Using Various Barrier Molecules. *Sustainable Energy & Fuels* **2017**, *1* (9), 1935-1943.

208. Grancini, G.; Nazeeruddin, M. K., Dimensional Tailoring of Hybrid Perovskites for Photovoltaics. *Nature Reviews Materials* **2019**, *4* (1), 4-22.

209. Gao, P.; Bin Mohd Yusoff, A. R.; Nazeeruddin, M. K., Dimensionality Engineering of Hybrid Halide Perovskite Light Absorbers. *Nature Communications* **2018**, *9* (1), 5028.

210. Hu, J.; Oswald, I. W. H.; Stuard, S. J.; Nahid, M. M.; Zhou, N.; Williams, O. F.; Guo, Z.; Yan, L.; Hu, H.; Chen, Z.; Xiao, X.; Lin, Y.; Yang, Z.; Huang, J.; Moran, A. M.; Ade, H.; Neilson, J. R.; You, W., Synthetic Control over Orientational Degeneracy of Spacer Cations Enhances Solar Cell Efficiency in Two-Dimensional Perovskites. *Nature Communications* **2019**, *10* (1), 1276.

Chapter 3

Experimental Methodology

Chapter 3 introduces and rationalizes the principles behind the experimental methods and characterization techniques used in this thesis. The synthesis procedure of the various chemicals used is first presented, followed by the general method of thin film deposition by solution processes. Thereafter, the device fabrication procedure for PeLEDs is elaborated, showing how the various transport layers and electrodes are deposited, along with the rationale of choosing specific materials for these layers. The last part of this chapter will touch on the characterization tools employed, including structural, morphological, optical and electrical aspects. Detailed descriptions of each tool adopted for each analysis are presented, along with justification for their employment so as to understand how the characterization studies come together to achieve the objectives of this thesis.

3.1 Material Synthesis

3.1.1 Chemicals

Perovskite precursors: CsBr (99.9%), PbBr₂ (99.999%), all phenyl alkyl ammonium bromides and all naphthyl-based precursors (synthesis of ammonium salts are elaborated in the next section 3.1.2) were purchased from Sigma Aldrich.

Transport materials: Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate or PEDOT:PSS (AI 4083) was purchased from Heraeus Clevios™. Bathophenanthroline or Bphen (97%) was purchased from Sigma Aldrich, while 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) or TPBi (sublimed > 99.5%) was purchased from LumTec. The chemical structures of the organic compounds used as charge transport layers are shown in Figure 3.1.

Figure 3.1 Molecular structure of various transport materials used: (left) PEDOT:PSS, (middle) Bphen, and (right) TPBi.

All chemicals were used as received, except the naphthyl-based ligand molecules, which required additional synthesis steps from the purchased precursors. The detailed synthesis procedures will be described in the next section.

3.1.2 Synthesis of Naphthyl-based Ligand Molecules*

The synthesis routes of the naphthalene alkyl amine ligand molecules (for Chapter 7) are illustrated in Figure 3.2 and the steps are elaborated further below.

Figure 3.2 Synthesis route of various naphthyl alkyl amine ligand molecules used in this work.

2-Azidonaphthalene (2): To a DMSO solution of (1) (1.0 eq), excess NaN_3 (1.2 eq) was added. The mixture obtained was stirred for at least 4 h at room temperature (RT). Subsequently, deionized H_2O was added and upon cooling to RT, the aqueous solution was extracted 3 times with ethyl acetate. The organic phases were merged, and washed with H_2O (twice) and brine (once). After drying over MgSO_4 , all residual solvent was removed in vacuo to give (2) as a white powder (2.11 g; 91%).

2-Aminonaphthalene (3): To the solid (2) (1.0 eq), PPh_3 (1.5 eq) was added with a THF-

*Syntheses of all ligand molecules were performed by Benny Febriansyah.

H₂O solvent mixture (10:1). For each gram of compound (2), 22 mL of solvent was used. Upon completion of reaction, the THF was removed under reduced pressure. The resulting residue was dissolved in CH₂Cl₂, and washed twice with 1 M aqueous HCl. The combined acidic aqueous layers were washed with ethyl acetate (four times) and carefully basified (pH ~ 10) by the addition of 3 M aqueous NaOH. The resulting mixture was extracted with CH₂Cl₂ (3 times), and the combined organic portions were dried (MgSO₄) and all volatiles removed under vacuum to give the product (3) as a light yellow solid (0.77 g; 73%).

2-Cyanonaphthalene (4): Under a flow of N₂ gas, (1) (1 eq) was added in small portions to a two-necked round-bottomed flask containing a stirring suspension of KCN (1.2 eq) in DMSO. After being stirred at 60 °C for 16 h, plus overnight at RT, the reaction mixture was poured into cold H₂O. The beige solid obtained was filtered off, washed with cold H₂O and dried under reduced pressure to afford the desired product (4) (1.52 g; 72%).

2-Aminoethylnaphthalene (5): Under an argon gas atmosphere, a solution of AlCl₃ (3.0 eq) in dry THF was added dropwise to a suspension of LiAlH₄ (3.0 eq), also in dry THF. The resulting mixture was stirred for ~ 10 mins at RT. Subsequently, a solution of (4) (1.0 eq) dissolved in dry THF was added dropwise to it, and the mixture was heated under reflux for at least 12 h. After cooling to RT, H₂O was added dropwise with ice bath cooling, followed by 10% aqueous HCl. The resulting mixture was washed with ethyl acetate and the aqueous layer made alkaline using 2 M aqueous NaOH. CHCl₃ was then added and the resultant mixture was shaken vigorously. The emulsion obtained was passed through a pad of Celite, after which the organic phase was separated, washed with brine, dried over MgSO₄, filtered, and concentrated to afford (5) as a beige powder (0.63 g; 79%).

1-Cyanonaphthalene (7): Under a flow of N₂ gas, (6) (1 eq) was added in small portions to a two-necked round-bottomed flask containing a stirring suspension of KCN (1.2 eq) in DMSO. After being stirred at 60 °C for 16 h, plus overnight at RT, the reaction mixture was poured into cold H₂O. The beige solid obtained was filtered off, washed with cold H₂O and dried under reduced pressure to afford the desired product (7) (1.21 g; 69%).

1-Aminoethylnaphthalene (8): Under an argon gas atmosphere, a solution of AlCl_3 (3.0 eq) in dry THF was added dropwise to a suspension of LiAlH_4 (3.0 eq), also in dry THF. The resulting mixture was stirred for ~ 10 mins at RT. Subsequently, a solution of (4) (1.0 eq) dissolved in dry THF was added dropwise to it, and the mixture was heated under reflux for at least 12 h. After cooling to RT, H_2O was added dropwise with ice bath cooling, followed by 10% aqueous HCl. The resulting mixture was washed with ethyl acetate and the aqueous layer made alkaline using 2 M aqueous NaOH. CHCl_3 was then added and the resultant mixture shaken vigorously. The emulsion obtained was passed through a pad of Celite, after which the organic phase was separated, washed with brine, dried over MgSO_4 , filtered, and concentrated to afford (5) as a beige powder (0.82 g; 72%).

Procedures for protonating the amines 1-NMA, compounds (3), (5), and (8) are described as such: General procedure for preparation of the ammonium bromide salts. To a round bottom flask containing ethanol and the requisite amine cooled to $0\text{ }^\circ\text{C}$, a stoichiometric amount of concentrated hydrobromic acid was added. After stirring the solution for 1 hour, all volatiles were removed using a rotary evaporator. The solids, thereby, obtained were washed with copious amounts of diethyl ether and dried under vacuum at $50\text{ }^\circ\text{C}$ overnight.

3.1.3 Characterization of Synthesized Products

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ nuclear magnetic resonance (NMR) spectra of the final organic compounds were generally recorded in DMSO-d_6 solution using a Bruker Avance 400 spectrometer and shown in Appendix. Chemical shift values (δ in ppm) were referenced against residual protic solvent peaks.

1-Naphthylmethylammonium bromide (1-NMABr). ^1H NMR (DMSO-d_6 , 400 MHz): δ = 8.40 (s, 3H), 8.17-7.98 (m, 3H), 7.67-7.55 (m, 4H), 4.55 (s, 2H). ^{13}C NMR (DMSO-d_6 , 100 MHz): δ = 133.70, 131.13, 130.28, 129.61, 129.14, 127.86, 127.24, 126.74, 125.84, 123.96, 39.75. Spectral data (Appendix Figure A.1) correspond closely to published data.¹⁻

2-Naphthylmethyllammonium bromide (2-NMABr). ^1H NMR (DMSO- d_6 , 400 MHz): δ = 8.38 (s, 3H), 7.99-7.90 (m, 4H), 7.64-7.55 (m, 3H), 4.22 (s, 2H). ^{13}C NMR (DMSO- d_6 , 100 MHz): δ = 132.62, 132.57, 131.48, 128.24, 127.97, 127.73, 127.67, 126.64, 126.58, 126.50, 42.38. Spectral data (Appendix Figure A.2) correspond closely to published data.³

1-Naphthylethylammonium bromide (1-NEABr). ^1H NMR (DMSO- d_6 , 400 MHz): δ = 8.16 (d, 1H), 7.94 (s, 3H), 7.85 (d, 1H), 7.62-7.42 (m, 4H), 3.41-3.37 (m, 2H), 3.14-3.09 (m, 2H). ^{13}C NMR (DMSO- d_6 , 100 MHz): δ = 133.50, 133.36, 131.27, 128.75, 127.47, 126.97, 126.40, 125.86, 125.69, 123.45, 39.56, 30.15. Spectral data (Appendix Figure A.3) correspond closely to published data.³⁻⁵

2-Naphthylethylammonium bromide (2-NEABr). ^1H NMR (DMSO- d_6 , 400 MHz): δ = 6.90 (s, 3H), 6.85-6.79 (m, 3H), 6.72 (s, 1H), 6.51-6.44 (m, 3H), 3.05-3.01 (m, 2H), 2.98-2.96 (m, 2H). ^{13}C NMR (DMSO- d_6 , 100 MHz): δ = 134.88, 133.08, 131.96, 128.14, 127.51, 127.42, 127.14, 126.96, 126.18, 125.67, 39.80, 33.00. NMR spectra are shown in Appendix Figure A.4.

3.1.4 Perovskite Solution Preparation

All chemical precursors were transferred into an argon-filled glove box before weighing. For Chapters 4 – 6, the standard CsPbBr_3 solution was prepared as previously reported, with a 2:1 molar ratio of CsBr to PbBr_2 .⁶ The chemical precursors were mixed and dissolved in DMSO solvent at a concentration of 0.5 M and stirred (without heating) overnight. The solution was then filtered through a 0.25 μm pore size polyvinylidene fluoride (PVDF) filter and the clear supernatant was used for subsequent spin-coating steps. For Chapter 7, the molar ratio of CsBr to PbBr_2 was re-optimized to 1.2:1 at a concentration of 0.3 M with respect to Pb.

For the mixed-dimensional perovskites in Chapter 6 and 7, the different ligand molecules

were separately weighed and mixed in a stock solution of CsPbBr₃ at different excess concentration. The excess addition of PEABr is illustrated in Figure 3.3 for example. The composition can be represented either by a ratio or mol% excess. For instance, the ligand molecule to CsPbBr₃ molar ratio of 1:1 is equivalent to 100 mol% excess ligand molecule.

Figure 3.3 Schematic illustration of the preparation of mixed-dimensional CsPbBr₃ perovskite solution.

The mixtures were mixed thoroughly using a vortex mixer before film deposition.

3.2 Perovskite Thin Film Deposition

The standard solution-processed thin film deposition of the perovskite material is through a widely-used one-step spin-coating process as shown earlier in Figure 1.1b.⁷⁻¹⁴ The precursor solution was first dropped on the substrate to fully cover the active area before spinning at a speed of 4000 rpm for 30s. This method is employed for the control sample in Chapter 4, while in Chapters 6 and 7 the spin speed has been optimized to 5000 rpm for all perovskite thin film deposition. Two other modified deposition procedures used in

Chapters 4 and 5 are described in details in the following sub-sections.

3.2.1 N₂-Facilitated Spin-Coating

For Chapter 4, the grain size was modulated using a modified gas-assisted spin-coating process previously demonstrated in PSCs.¹⁵⁻²¹ The N₂-facilitated sample was spin-coated at 5000 rpm for 12 s with N₂ gas introduced at a pressure of 1-bar (14.5 psi) from an approximate distance of 2 cm above the spinning substrate. The gas flow was initiated 3 s from the start of the spin-coating process and allowed to continue right to the end. A schematic illustrating the N₂-facilitated spin-coating process is shown in Figure 3.4. For convenience, the terms “conventional” and “N₂-facilitated” are used to refer to the standard and N₂ gas-facilitated processes in that order. Thereafter, the films were left to dry for 30 min at ambient temperature before annealing at 70 °C for 5 min.

Figure 3.4 Schematic illustration of the N₂-facilitated film formation during the spin-coating process.

3.2.2 Sequential Deposition

For Chapter 5, a sequential deposition route was employed for the deposition of CsPbBr₃ thin film. This two-step method is similar to those used in earlier works to deposit MAPbI₃.²²⁻²⁸

Figure 3.5 Schematic illustration of the sequential deposition process for CsPbBr₃.

A simplified illustration of the sequential deposition process is shown in Figure 3.5. A layer of PbBr₂ is first deposited from solutions of varying concentrations (0.2, 0.5 and 1.0 M) and annealed to dry. The films were subsequently exposed to a 10 mg mL⁻¹ solution of CsBr (dissolved in methanol) for various durations (5, 10 and 20 min) to facilitate the phase conversion, before rinsing with anhydrous isopropanol (IPA) and spin-dried. The resultant films were lastly annealed at 70 °C for 30 min.

3.3 PeLED Device Fabrication

PeLED devices were made on indium-doped tin oxide (ITO, 7 Ω cm⁻²) coated glass substrates. Firstly, the substrates were cleaned sequentially using decon soap, deionised water, acetone, IPA and ethanol. This was then followed by drying and plasma treatment for 30 mins. PEDOT:PSS was spin-coated at 4000 rpm for 60 s and annealed for 15 mins at 130 °C. The steps thus far were done in ambient conditions. Subsequent steps were conducted in an Ar-filled glove box. The perovskite films were deposited as per discussed

in the previous section (Chapter 3.2). The ETL (Bphen in Chapter 4 and TPBi in Chapter 5 – 7) and cathode (aluminium) were then thermally evaporated under high vacuum ($< 1 \times 10^{-6}$ Torr) and thereafter encapsulated using a UV-curable epoxy prior to testing. The final cell size was around 8 mm^2 . A layout of the device architecture using Bphen is schematically illustrated in Figure 3.6a, along with the energy band levels of each layer in Figure 3.6b.

Figure 3.6 Schematic illustration of (a) CsPbBr₃ device architecture and (b) energy band level diagram for each layer.

The direction of current flow through the PeLED is indicated in Figure 3.6a, showing electron injection through the aluminium cathode and hole injection through the ITO anode. The energy band levels in Figure 3.6b also manifest efficient blocking ability of the charge transport layers against opposite charge carriers, thereby confining the injected carriers within the active perovskite EML.

3.4 Characterization

Various characterization techniques are employed for each project chapters, including phase, morphological, optical and electrical as described in details below.

3.4.1 Crystal Structure and Phase Identification

X-ray diffraction (XRD) is one of the most commonly used technique to characterize and analyse the crystal structure and phase of a crystalline material. Since crystals are made up of periodic arrangement of atoms on the lattice sites, when an X-ray beam is irradiated on the sample, interaction with the crystalline structure causes elastic scattering and diffraction of the beam. The diffraction along different planes can produce either constructive or destructive interference, and constructive interference occurs when Bragg's Law is satisfied:²⁹

$$2d \sin \vartheta = n\lambda$$

where d is the spacing between lattice planes, θ is the incidence angle of the X-ray beam on the sample surface, λ is the wavelength of the X-ray source, and n is a positive integral number. When scanned across a range of θ values, a characteristic diffraction pattern is obtained with a set of d-spacings unique to a particular material, much like a fingerprint, which then allows identification of the material, phase, crystal structure along with other information such as lattice constants and crystallite size (using Scherrer equation).

In this work, XRD was used to characterize the phase and crystal structure of the deposited perovskite films and determine the purity and crystallinity of the material. The diffraction patterns were obtained using a Bruker D8 Advance X-ray diffractometer with Ni-filtered Cu K α radiation (wavelength, $\lambda = 1.54 \text{ \AA}$). The samples were scanned from θ values ranging from 10 to 60° under room temperature and pressure.

3.4.2 Morphological

In traditional optical microscopes, visible light is used to irradiate a sample and the transmitted or reflected light is collected by optical lens to form a magnified image. The spatial resolution is dependent on the wavelength of the light and thus is limited to μm range. In scanning electron microscopes (SEM) however, the spatial resolution is dependent on the spot size of the electron beam, which is controlled by the wavelength of the electrons and the electromagnetic lens that focus the beam, and thus the spatial resolution can be as low as a few nm. The most common type of SEM is based on secondary electron imaging. The electron beam is first generated from a source, accelerated and focused on the sample surface. The beam is then scanned across the sample in a raster pattern, where the interaction between the beam and the atoms produces secondary electrons which are collected and used to generate a topographic image of the sample surface with high spatial resolution. SEM can be used to characterize the surface morphology of a solid sample, for example surface topography, film coverage, grain sizes and shapes. Cross-sectional SEM can also be used to observe smoothness of the film surface as well as thickness. Additional modes like backscattered electron imaging and energy-dispersive X-ray spectroscopy can be used to reveal further information such as phase and composition of the sample.

In this work, field emission scanning electron microscopy (FESEM) imaging of perovskite films was used to examine the topology and microstructures of the perovskite films including top and cross-sectional views. The electron beam is generated by a field emission gun where electrons emit from the tip of a metal conductor under a very strong electric field. The imaging of thin film samples was conducted on ITO/PEDOT:PSS substrates using a JEOL JSM-7600F scanning electron microscope at 5-10 kV with a working distance of ~ 8 mm.

3.4.3 Optical

The optical properties are characterized using several spectroscopic tools.

The absorbance of a sample is measured using ultraviolet-visible (UV-vis) spectroscopy. When light passes through a sample, the absorbance of the material is related to the attenuation of the light according to Beer–Lambert’s Law:

$$A = \log_{10} \frac{I_0}{I}$$

where A is the absorbance of the sample and I_0 and I are the intensities of the incident and transmitted light respectively. The light intensity is usually measured using a spectrometer and the light source comes from a lamp along with a rotating grating and slits that allows measurement of the absorbance across a wide range of wavelengths. UV-vis spectroscopy is particularly useful in perovskite optoelectronics in determining the absorption coefficient as well as band gap of the material. In this work, the absorbance spectra of perovskite thin films are recorded using a UV-vis-NIR spectrophotometer (UV-3600, Shimadzu) equipped with an integrating sphere. The absorbance at different wavelengths gives information about presence of different phases, especially for the mixed-dimensional perovskite systems.

The photoluminescence (PL) spectroscopy is used to characterize the emission properties of a sample. The sample is first irradiated with a ray of photons, which is absorbed by the sample. This excites electrons from the ground state to the higher energy electronic states, which upon relaxation back to the ground state, emits a photon with a wavelength closely related to the band gap of the material through the following equation:

$$E = \frac{hc}{\lambda}$$

where E is the photon energy or band gap, h and c are constants representing Planck constant and the speed of light in vacuum respectively, and λ is the wavelength of the emitted photon. In this study, the steady-state PL spectra were recorded and measured using Fluoromax-4 (Horiba Jobin Yvon) spectrofluorometer. The excitation is kept at a wavelength of 350 nm and the PL intensities collected were corrected against the number of absorbed photons at the same excitation wavelength. This allows relative comparison of the emission intensities across different samples. In addition, PL excitation spectroscopy

was also performed with the detector fixed at the strongest PL peak position (3D emission) while the samples were photo-excited across a range of wavelengths. This was used to characterize mixed-dimensional perovskites where the different PL intensities at different excitation wavelengths give information about the presence of different energy domains and demonstrate the energy funnelling phenomenon.

In addition, time-resolved PL (TRPL) was employed to study the photophysical properties and charge dynamics of the perovskite samples. This technique differs from the steady-state PL such that the measurement is done on the transient PL signals (in the ps – ns range), which gives information about the kinetics and lifetime decay of photoexcited charge carriers. In this work, the TRPL measurement is conducted using two different techniques. The first technique uses a streak camera system (Optronis OptoscopeTM) to resolve the transient signals. The 400 nm pump pulse was generated by frequency doubling the 800 nm pulse from the regenerative amplifier (Coherent LibraTM, pulse width 50 fs, repetition rate 1 KHz) using a BBO crystal. The second technique involves a Picoquant PicoHarp 300 time-correlated single photon counting (TCSPC) system in a micro-PL setup with Nikon microscope objective (20x magnification, NA = 0.3). A ps-pulsed laser diode emitting at 405 nm with 40 MHz repetition rate (Picoquant P-C-405B) was used to excite the sample. The output signal is then fiber-coupled to Acton SP-2300i monochromator (300 mm focal length) for spectral selection of the emission light. Another optical fiber connected to the output of the monochromator is used to couple spectral separated output light to an avalanche diode that is synchronized with the excitation laser via the TCSPC electronic. Overall, the FWHM of the system instrument respond function is expected to be at 50 ps. The first method was used in Chapter 4 to measure the average PL lifetime whereas the second method was used in Chapter 6 to measure the PL lifetime at specific emission wavelengths.

The PL quantum yield (PLQY) is a quantitative characterization of the PL of a sample, defined as the number of photons emitted divided by the number of photons absorbed. This absolute quantity can be used to compare the efficiencies of PL emission across different samples where the higher the PLQY, the more emissive is the material. This technique is

usually used for screening of materials to identify promising emitters for LEDs. The external quantum yield of LEDs is also limited by the maximum PLQY of the material. In this work, the absolute PLQY was measured using an OceanOptics USB4000 spectrometer connected to an integrating sphere and the sample is excited using a laser at a wavelength of 405 nm. The signals are collected and the PLQY is automatically calculated using a LabView program by integrating the emission spectrum and dividing it by the absorption of the sample.

3.4.4 Electrical

The fabricated LED devices are characterized through current injection using an applied voltage and measurement of the electroluminescence (EL). This is performed using an in-house built, integrated setup as shown in Figure 3.7.

Figure 3.7 Experimental setup for EL characterization of PeLED devices.³⁰ Reprinted with permission from Chin, X. Y.; Perumal, A.; Bruno, A.; Yantara, N.; Veldhuis, S. A.; Martínez-Sarti,

L.; Chandran, B.; Chirvony, V.; Lo, A. S.-Z.; So, J.; Soci, C.; Grätzel, M.; Bolink, H. J.; Mathews, N.; Mhaisalkar, S. G., Self-assembled hierarchical nanostructured perovskites enable highly efficient LEDs via an energy cascade. *Energy & Environmental Science* **2018**, *11* (7), 1770-1778. Copyright © 2019 Royal Society of Chemistry.

PeLED devices were tested at ambient conditions in a fully dark environment to eliminate contribution from stray light. The current density and voltage (J-V) characteristics were recorded using a Keithley 2612B source meter while the luminance (L) was collected in an integrating sphere (OceanOptics FOIS-1) coupled to an OceanOptics QE Pro spectrometer. The measurements were operated using Ciemo LabVIEW software from a computer. An OceanOptics HL-3 Plus vis-NIR LED, calibrated via the ISO 17025, IEC Guide 115 and JCGM100:2008 (GUM) protocols was employed to calibrate the spectrometer's quantification of absolute irradiance. Since the LED devices were set on the exterior of the integrating sphere with the active area placed at the centre of the sphere aperture, only the front emission is collected whereas the edge emission due to total internal reflection of the glass substrate is not captured.

From this characterization, information relating to the device performance and characteristics can be obtained and used to compare against other device systems. Various information include the luminance output of the device (brightness), current density with respect to voltage (J-V), current and luminance turn-on voltages, current efficiencies and EL spectra. The device emission can be assumed to have a lambertian emission pattern due to the configuration of the light output (in this case, bottom emission through the surface of a planar glass substrate), thus the power efficiency can also be calculated as follows:

$$\text{Power efficiency} = \frac{L \times \pi}{J \times V} = \frac{\text{Current efficiency} \times \pi}{V}$$

Based on the electrical and EL data, the number of electrons and photons can be computed and the external quantum efficiency (EQE) can be calculated as follows:

$$EQE = \frac{\# \text{ of photons}}{\# \text{ of electrons}}$$

The figure of merits are used to compare and evaluate the performance of each perovskite material system in LEDs, with the efficiency values being the most important parameters.

References

1. Chen, F.; Topf, C.; Radnik, J.; Kreyenschulte, C.; Lund, H.; Schneider, M.; Surkus, A.-E.; He, L.; Junge, K.; Beller, M., Stable and Inert Cobalt Catalysts for Highly Selective and Practical Hydrogenation of C≡N and C=O Bonds. *Journal of the American Chemical Society* **2016**, *138* (28), 8781-8788.
2. Yao, W.; Fang, H.; He, Q.; Peng, D.; Liu, G.; Huang, Z., A BEt₃-Base Catalyst for Amide Reduction with Silane. *The Journal of Organic Chemistry* **2019**, *84* (10), 6084-6093.
3. Gandhamsetty, N.; Jeong, J.; Park, J.; Park, S.; Chang, S., Boron-Catalyzed Silylative Reduction of Nitriles in Accessing Primary Amines and Imines. *The Journal of Organic Chemistry* **2015**, *80* (14), 7281-7287.
4. Kayser, K. J.; Glenn, M. P.; Sebt, S. M.; Cheng, J. Q.; Hamilton, A. D., Modifications of the GSK3β Substrate Sequence to Produce Substrate-Mimetic Inhibitors of Akt as Potential Anti-Cancer Therapeutics. *Bioorganic & Medicinal Chemistry Letters* **2007**, *17* (7), 2068-2073.
5. Reeves, J. T.; Tan, Z.; Marsini, M. A.; Han, Z. S.; Xu, Y.; Reeves, D. C.; Lee, H.; Lu, B. Z.; Senanayake, C. H., A Practical Procedure for Reduction of Primary, Secondary and Tertiary Amides to Amines. *Advanced Synthesis & Catalysis* **2013**, *355* (1), 47-52.
6. Yantara, N.; Bhaumik, S.; Yan, F.; Sabba, D.; Dewi, H. A.; Mathews, N.; Boix, P. P.; Demir, H. V.; Mhaisalkar, S., Inorganic Halide Perovskites for Efficient Light-Emitting Diodes. *The Journal of Physical Chemistry Letters* **2015**, *6* (21), 4360-4364.
7. Boix, P. P.; Nonomura, K.; Mathews, N.; Mhaisalkar, S. G., Current Progress and Future Perspectives for Organic/Inorganic Perovskite Solar Cells. *Materials Today* **2014**,

17 (1), 16-23.

8. Veldhuis, S. A.; Boix, P. P.; Yantara, N.; Li, M.; Sum, T. C.; Mathews, N.; Mhaisalkar, S. G., Perovskite Materials for Light-Emitting Diodes and Lasers. *Advanced Materials* **2016**, 28 (32), 6804-6834.
9. Antonietta Loi, M.; Hummelen, J. C., Perovskites under the Sun. *Nature Materials* **2013**, 12, 1087.
10. Colella, S.; Mazzeo, M.; Rizzo, A.; Gigli, G.; Listorti, A., The Bright Side of Perovskites. *The Journal of Physical Chemistry Letters* **2016**, 4322-4334.
11. Grätzel, M., The Light and Shade of Perovskite Solar Cells. *Nature Materials* **2014**, 13, 838.
12. Jung, H. S.; Park, N. G., Perovskite Solar Cells: From Materials to Devices. *Small* **2015**, 11 (1), 10-25.
13. Kim, Y.-H.; Cho, H.; Lee, T.-W., Metal Halide Perovskite Light Emitters. *Proceedings of the National Academy of Sciences* **2016**, 113 (42), 11694-11702.
14. You, J.; Hong, Z.; Yang, Y.; Chen, Q.; Cai, M.; Song, T.-B.; Chen, C.-C.; Lu, S.; Liu, Y.; Zhou, H.; Yang, Y., Low-Temperature Solution-Processed Perovskite Solar Cells with High Efficiency and Flexibility. *ACS Nano* **2014**, 8 (2), 1674-1680.
15. Huang, F.; Dkhissi, Y.; Huang, W.; Xiao, M.; Benesperi, I.; Rubanov, S.; Zhu, Y.; Lin, X.; Jiang, L.; Zhou, Y.; Gray-Weale, A.; Etheridge, J.; McNeill, C. R.; Caruso, R. A.; Bach, U.; Spiccia, L.; Cheng, Y.-B., Gas-Assisted Preparation of Lead Iodide Perovskite Films Consisting of a Monolayer of Single Crystalline Grains for High Efficiency Planar Solar Cells. *Nano Energy* **2014**, 10, 10-18.
16. Yun, J. S.; Ho-Baillie, A.; Huang, S.; Woo, S. H.; Heo, Y.; Seidel, J.; Huang, F.; Cheng, Y.-B.; Green, M. A., Benefit of Grain Boundaries in Organic-Inorganic Halide Planar Perovskite Solar Cells. *The Journal of Physical Chemistry Letters* **2015**, 6 (5), 875-880.
17. Dkhissi, Y.; Huang, F.; Rubanov, S.; Xiao, M.; Bach, U.; Spiccia, L.; Caruso, R. A.; Cheng, Y.-B., Low Temperature Processing of Flexible Planar Perovskite Solar Cells with Efficiency over 10%. *Journal of Power Sources* **2015**, 278, 325-331.
18. Della Gaspera, E.; Peng, Y.; Hou, Q.; Spiccia, L.; Bach, U.; Jasieniak, J. J.; Cheng, Y.-B., Ultra-Thin High Efficiency Semitransparent Perovskite Solar Cells. *Nano Energy*

2015, *13*, 249-257.

19. Luo, P.; Zhou, S.; Zhou, Y.; Xia, W.; Sun, L.; Cheng, J.; Xu, C.; Lu, Y., Fabrication of $\text{Cs}_x\text{FA}_{1-x}\text{PbI}_3$ Mixed-Cation Perovskites via Gas-Phase-Assisted Compositional Modulation for Efficient and Stable Photovoltaic Devices. *ACS Applied Materials & Interfaces* **2017**, *9* (49), 42708-42716.
20. Vidyasagar, C. C.; Muñoz Flores, B. M.; Jiménez Pérez, V. M., Recent Advances in Synthesis and Properties of Hybrid Halide Perovskites for Photovoltaics. *Nano-Micro Letters* **2018**, *10* (4), 68.
21. Prakasam, V.; Tordera, D.; Di Giacomo, F.; Abbel, R.; Langen, A.; Gelinck, G.; Bolink, H. J., Large Area Perovskite Light-Emitting Diodes by Gas-Assisted Crystallization. *Journal of Materials Chemistry C* **2019**, *7* (13), 3795-3801.
22. Burschka, J.; Pellet, N.; Moon, S.-J.; Humphry-Baker, R.; Gao, P.; Nazeeruddin, M. K.; Grätzel, M., Sequential Deposition as a Route to High-Performance Perovskite-Sensitized Solar Cells. *Nature* **2013**, *499* (7458), 316-319.
23. Luo, Y.; Meng, F.; Zhao, E.; Zheng, Y.-Z.; Zhou, Y.; Tao, X., Fine Control of Perovskite-Layered Morphology and Composition via Sequential Deposition Crystallization Process Towards Improved Perovskite Solar Cells. *Journal of Power Sources* **2016**, *311*, 130-136.
24. Wu, Y.; Islam, A.; Yang, X.; Qin, C.; Liu, J.; Zhang, K.; Peng, W.; Han, L., Retarding the Crystallization of PbI_2 for Highly Reproducible Planar-Structured Perovskite Solar Cells via Sequential Deposition. *Energy & Environmental Science* **2014**, *7* (9), 2934-2938.
25. Zhang, T.; Yang, M.; Zhao, Y.; Zhu, K., Controllable Sequential Deposition of Planar $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Films via Adjustable Volume Expansion. *Nano Letters* **2015**, *15* (6), 3959-3963.
26. Xu, G.; Xue, R.; Chen, W.; Zhang, J.; Zhang, M.; Chen, H.; Cui, C.; Li, H.; Li, Y.; Li, Y., New Strategy for Two-Step Sequential Deposition: Incorporation of Hydrophilic Fullerene in Second Precursor for High-Performance p-i-n Planar Perovskite Solar Cells. *Advanced Energy Materials* **2018**, *8* (12), 1703054.
27. Ummadisingu, A.; Grätzel, M., Revealing the Detailed Path of Sequential Deposition for Metal Halide Perovskite Formation. *Science Advances* **2018**, *4* (2), e1701402.

28. Guo, F.; He, W.; Qiu, S.; Wang, C.; Liu, X.; Forberich, K.; Brabec, C. J.; Mai, Y., Sequential Deposition of High-Quality Photovoltaic Perovskite Layers via Scalable Printing Methods. *Advanced Functional Materials* **2019**, 29 (24), 1900964.
29. Meyers, H.; Myers, H., *Introductory Solid State Physics*. CRC press: 1997.
30. Chin, X. Y.; Perumal, A.; Bruno, A.; Yantara, N.; Veldhuis, S. A.; Martínez-Sarti, L.; Chandran, B.; Chirvony, V.; Lo, A. S.-Z.; So, J.; Soci, C.; Grätzel, M.; Bolink, H. J.; Mathews, N.; Mhaisalkar, S. G., Self-Assembled Hierarchical Nanostructured Perovskites Enable Highly Efficient LEDs via an Energy Cascade. *Energy & Environmental Science* **2018**, 11 (7), 1770-1778.

Chapter 4

Charge Carrier Confinement through Grain Size Modulation*

The geometrical confinement is predominantly associated with the morphological structures of the deposited film, which is highly dependent on the film deposition and crystallization processes. In this chapter, geometrical confinement is achieved by tuning of the perovskite grain size. The film crystallization is enhanced by accelerating the supersaturation rate of the precursor solution through a simple gas-facilitated solution processing technique. The introduction of a nitrogen (N_2) gas flow during the spin-coating process induces rapid nucleation and crystallization along with suppressed grain growth to achieve smaller and less percolated $CsPbBr_3$ grains. Through this approach, stronger spatial charge confinement is realized through the geometric constraints, shown by enhanced radiative recombination. By optimizing the pressure and timing of the gas flow, highly luminescent green-emitting PeLEDs based on $CsPbBr_3$ were fabricated with device performance results several times better than the pristine $CsPbBr_3$ alone, emphasizing the importance of geometrical confinement through grain size tuning on the photo- and electroluminescence properties of the $CsPbBr_3$ perovskite emitter.

*This section is published substantially as Ng, Y. F.; Jamaludin, N. F.; Yantara, N.; Li, M.; Irukuvarjula, V. K. R.; Demir, H. V.; Sum, T. C.; Mhaisalkar, S.; Mathews, N., Rapid Crystallization of All-Inorganic $CsPbBr_3$ Perovskite for High-Brightness Light-Emitting Diodes. *ACS Omega* **2017**, 2 (6), 2757-2764.

4.1 Introduction

Film formation plays a pivotal role in determining the morphology, which in turn is responsible for the resultant properties of the perovskite film, especially charge carrier dynamics.¹ A major factor influencing it is the crystallization rate. Padture *et al.* have reported a comprehensive study to understand solution-processed perovskite film formation, with particular emphasis on the nucleation, growth, coarsening and evolution aspects.² The slow evaporation of commonly used solvents (*e.g.* DMF and DMSO) due to their high boiling points has somewhat hindered the perovskite crystallization during the spin-coating process. As a result, low nuclei density has led to acicular structures and incomplete coverage from conventional spin-coating process. A commonly used method to circumvent this problem and achieve highly efficient perovskite solar cells and PeLEDs is by using a solvent engineering method, whereby an antisolvent such as toluene or chloroform is introduced to supersaturate the perovskite precursor solution and induce precipitation.³⁻⁶ Using this method, the nucleation rate is greatly enhanced while the growth rate is suppressed simultaneously,⁷ resulting in a smooth and fine-grained film with good coverage. However, scale-up production of such devices remains hampered by low reproducibility arising from propensity for radial and inhomogeneous growth gradient as well as the toxic nature of commonly used antisolvents.⁸⁻⁹

In this chapter, the anti-solvent is replaced by simply using a N₂ gas flow directed at the center of the spinning film with an optimized pressure and time to facilitate the perovskite crystallization (illustration shown in Chapter 3.2.1). The substrate with the precursor solution dropped at the center is first spun at the same rate as the reference (conventional) sample (4000 rpm). The first 3 seconds allow the precursor solution to fully spread across the substrate and some of the solvent to evaporate so that the wet film reaches closer to supersaturation. At the end of the 3rd second, a flow of N₂ gas is discharged towards the center of the spinning film with a gas pressure of 1-bar. This is done by using a N₂ spray gun with its nozzle held approximately 2 cm above the spinning substrate, as illustrated in Figure 3.4. The aim of using this process is to enhance the crystallization rate of the perovskite and suppress crystal growth so as to achieve grains of smaller sizes in order to

elucidate the effect of grain size on the confinement of charge carriers. Since this technique does not involve any additives, the effect can be directly observed without contribution from any other factors.

4.2 Results and Discussions

4.2.1 Morphological Control with Gas-Facilitated Process

The effect of the gas-facilitated rapid crystallization process on the morphology of the perovskite film is visibly observed using surface topology and cross-section FESEM imaging of the deposited films (Figure 4.1), which shows the feasibility of this simple technique in controlling the morphological structures of the spin-coated film.

Figure 4.1 Surface (top row) and cross-sectional (bottom row) FESEM images of CsPbBr₃ films deposited on ITO/PEDOT:PSS substrates using (a,c) conventional and (b,d) N₂-facilitated process.

Here, stark dissimilarities in the film morphology are observed for the two films, where noticeably smaller and less percolated grains are present in the N₂-facilitated film. This is attributed to the rapid nucleation as a result of the sudden N₂ flow leading to the generation of a high nuclei density while suppressing grain growth. However, this also leads to a slightly reduced film coverage (Figure 4.1b). This was further verified using the ImageJ software, whereby the film prepared via the conventional process shows approximately 80% surface coverage whereas the N₂-facilitated film shows 65-70% surface coverage. Cross-section imaging indicates a thinner film (85 ± 10 nm) for the N₂-facilitated method (Figure 4.1d) compared to a (130 ± 10) nm thick film via the conventional process (Figure 4.1c). The thinner and smaller grains are postulated to more easily confine charges within the geometrical constraints, bringing about a higher probability of radiative recombination, which will be investigated in subsequent sections.

4.2.2 Crystal Structure and Phase Analysis

To confirm the phase purity and examine any changes in crystal structure, XRD was performed and the diffraction patterns of the films fabricated using the two methods are shown in Figure 4.2.

Figure 4.2 XRD spectra of conventional (black) and N_2 -facilitated (red) $CsPbBr_3$ films (* corresponds to ITO peaks).

From the XRD patterns in Figure 4.2, both samples reveal similar reflections at 2θ values of 15.15° , 21.55° , 30.35° and 34.50° , corresponding to the orthorhombic ($Pnma$) crystal structure of $CsPbBr_3$. Both films were preferentially oriented in the (202) direction with lattice parameters of $a = 8.22(6) \text{ \AA}$, $b = 11.80(3) \text{ \AA}$, and $c = 8.30(5) \text{ \AA}$ and $a = 8.22(9) \text{ \AA}$, $b = 11.79(9) \text{ \AA}$, and $c = 8.31(7) \text{ \AA}$ for the conventional and N_2 -facilitated films respectively, which are in good agreement with previous reports.¹⁰⁻¹¹ Negligible variance in lattice parameters indicates similar stress and strain levels in both films.¹² The absence of characteristic CsBr peaks in both patterns confirms the absence of crystalline CsBr in the samples despite the addition of excess precursor material, as is previously reported.¹⁰ By taking into consideration the full width at half maximum (FWHM) and the integral breadth of all peaks, the crystallite sizes were calculated to be *ca.* 20 nm for both deposition routes.

4.2.3 Optical Properties

The optical properties of the films fabricated using the two techniques are probed using steady-state PL and UV-vis spectroscopy. Figure 4.3 shows the normalized PL and absorbance spectra of both films.

Figure 4.3 Absorption and PL spectra of the conventional (black) and N₂-facilitated (red) CsPbBr₃ films.

Although both PL spectra exhibit narrow green emission with a FWHM of 17 nm, a slight blueshift (*ca.* 2 nm) was observed from 526 nm for the conventional to 524 nm for the N₂-facilitated film (Table 4.1). The blueshift in the steady state PL is attributed to the inner filter effect due to change in the optical density (OD) of the film. This is supported by the lower absorbance recorded across the scanned wavelengths for the N₂-facilitated sample. From the correlation between PL and absorption, it can be readily deduced that the PL emission exhibits band to band characteristics. It also needs to be noted that the presence

of excitonic peaks, detected in the absorption spectra of both films, contribute towards the enhancement of absorption near the band gap. The effective optical band gap of the films would thus deviate from the electronic band gap of 2.3 eV due to the need for exciton binding energy considerations in the calculation as previously reported by Kumawat et al.¹³

Table 4.1 Optical and photophysical properties of conventional and N₂-facilitated CsPbBr₃ films.

Sample	$\lambda_{\max}$ (nm)	FWHM (nm)	PLQY (%)	τ_{PL} (ns)	τ_{rad} (ns)	$\tau_{non-rad}$ (ns)
Conventional	526	17	10.9 ± 0.2	4.9	44.5	5.5
N ₂ -facilitated	524	17	13.0 ± 0.1	3.7	28.5	4.3

4.2.4 Verifying Absence of Cs₄PbBr₆ Impure Phase in Deposited CsPbBr₃ Films

Recent literature has reported the coexistence of both three-dimensional CsPbBr₃ and zero-dimensional Cs₄PbBr₆ (Bergerhoff–Schmitz–Dumont-type crystal structure)¹⁴ crystals in products obtained from solution growth.^{15–16} The large difference in solubility between CsBr and PbBr₂ in DMSO can result in different reactivity of both dissolved species, leading to CsBr-rich Cs₄PbBr₆ precipitating alongside CsPbBr₃. However, the absence of any characteristic XRD peaks in the films verifies that Cs₄PbBr₆ is not present. The single PL peak for both samples (at 524 and 526 nm) also confirms the absence of Cs₄PbBr₆, which emits at 520 nm. Since Cs₄PbBr₆ has a stronger emission at excitation wavelengths of $\lambda > 340$ nm,¹⁶ in order to substantiate our claim, additional PL measurements were taken at various excitation wavelengths ranging from 300 to 470 nm (Figure 4.4). Again, no additional PL peak was observed. Since Cs₄PbBr₆ is insoluble in DMSO, it was most likely precipitated in the precursor solution. XRD patterns shown in a previous report have confirmed the presence of Cs₄PbBr₆ in the precipitates.¹⁰ The resultant clear supernatant, which was used for subsequent spin-coating, is thus free of this impurity compound.

Figure 4.4 PL spectra as a function of excitation wavelengths for (a) conventional and (b) N₂-facilitated CsPbBr₃ films.

4.2.5 Charge Dynamics Comparison

To investigate the charge dynamics, PL quantum yield (PLQY) and time-resolved PL (TRPL) measurements were carried out and summarized in Table 4.1. The N₂-facilitated film shows a slightly higher PLQY of 13% as compared to 11% for the standard film. The TRPL decay spectra (following excitation at 400 nm) for both films are shown in Figure 4.5. The PL decay lifetimes were determined by fitting with a single exponential decay function (solid line). The characteristic PL lifetime (τ_{PL}) extracted is 4.9 ± 0.1 ns for the standard film and 3.7 ± 0.1 ns for the N₂-facilitated film. From here, the radiative (τ_{rad}) and non-radiative ($\tau_{non-rad}$) recombination lifetimes can be calculated using the following formulae:

$$\tau_{rad} = \tau_{PL} / \phi$$

$$\tau_{non-rad} = \tau_{PL} / (1 - \phi)$$

where ϕ represents PLQY.¹⁷ The much shorter radiative lifetime of 28.5 ns for the N₂-facilitated film is ascribed to the smaller and more isolated grains seen from the surface imaging of the film (Chapter 4.2.1), consequently restricting charge movement and triggering faster recombination. The non-radiative lifetime, however, was slightly shorter

for the N₂-facilitated film (4.3 ns), owing to the increased surface area of the isolated grains resulting in additional non-radiative recombination channels.¹⁸⁻¹⁹ Hence, the higher PLQY for the film with smaller grain size is a result of the enhanced radiative recombination rate inside the grains which overwhelms the enhanced non-radiative recombination rate at grain boundaries.

Figure 4.5 Time-resolved photoluminescence (TRPL) decay curves (solid lines are fitted curves) of conventional (black) and N₂-facilitated (red) CsPbBr₃ films.

4.2.6 PeLED Device Performance

To investigate the effect of the film morphology on the operation of the CsPbBr₃ emitters, complete PeLED devices were fabricated with CsPbBr₃ sandwiched between a HTL (PEDOT:PSS) and an ETL (Bathophenanthroline or Bphen), which is a phenanthroline organic molecule commonly used as an electron transporter. Figure 4.6 shows the device architecture along with the corresponding energy levels of each layer and the working

mechanism of the PeLED to give electroluminescence (EL). The electrons (represented by black spheres) are injected from the aluminium cathode to the LUMO of Bphen, before being transported and transferred to the conduction band of CsPbBr₃. Likewise, the holes (opposite of electrons), are injected from the ITO anode to the work function of PEDOT:PSS and then to the valence band of CsPbBr₃. Within the CsPbBr₃ EML, electrons and holes recombine to give radiative emission with each photon generated carrying an energy equivalent to the band gap of the emitter material.

Figure 4.6 3D schematic illustration of the device architecture, carrier movement and corresponding energy levels of various layers in the CsPbBr₃ PeLEDs used in this work.

The current density and luminance versus driving voltage (J - V - L data) is shown in Figure 4.7. From the J - V curves (logarithmic plot in Figure 4.7b), the conventional and N₂-facilitated devices exhibit ohmic conduction ($m=1$) up to 1.0 V and 1.6 V respectively. Higher current in the ohmic conduction region was observed for the N₂-facilitated devices,

which could be attributed to the lower surface coverage of the perovskite film. Trap limited conduction region ($m > 2$) was observed up to 5.0 V and 3.2 V for the conventional and N_2 -facilitated devices respectively, followed by pseudo space charge limited region ($m = 2$) at higher voltage where carrier recombination is limited by transport of charges from either the ETL or HTL or both.²⁰ Sharp current turn-on from the N_2 -facilitated device indicates that charge injection into the $CsPbBr_3$ layer upon overcoming the energy barrier is far more superior, owing to the undulating morphology of the perovskite lending it higher interfacial area for contact with the electron transporting material, thereby explaining the higher charge injection. On the other hand, the premature current turn-on voltage as well as the gentle slope at trap limited conduction region of the conventional device indicate higher defects in the film and lower conductivity of the material as compared to the N_2 -facilitated device.

Figure 4.7 (a) Current density (J) and luminance (L) versus driving voltage (V), and (b) Log J vs log V plot of conventional (black) and N_2 -facilitated (red) PeLEDs showing various regions of conduction regimes.

As compared to the conventional method, devices made with the N_2 -facilitated film show substantial improvement in luminance turn-on voltage (V_{th}), L_{max} , and current efficiency (Table 4.2). The remarkable V_{th} as low as 2.4 V, which is almost comparable to the electronic band gap of the active material (~ 2.3 eV), means that charge carrier transport and injection into the perovskite emitter are extremely efficient. Despite possessing higher current turn-on voltage, which signifies higher carrier injection barrier, the light turn-on

voltage for the N₂-facilitated devices is lower. This means that once the carriers are injected, they are recombining more effectively, which is explained by the enhanced spatial confinement effect imparted by the smaller grain volumes.²¹ The current efficiency (Figure 4.8a) enhances with increasing current density and the highest current efficiency was achieved at high current density ($\sim 1,000 \text{ mA cm}^{-2}$), indicating that the efficiency is limited by traps or defects within the device. The champion cell emanated an L_{max} of $8,218 \text{ cd m}^{-2}$ at an astonishingly low voltage of 5.0 V. In contrast, the reference device emitted a much weaker L_{max} of $2,964 \text{ cd m}^{-2}$. Interestingly, the luminance tripled (based on average L_{max}) even though the coverage is slightly reduced (Figure 4.1b). This improvement is again ascribed to the enhanced radiative recombination bestowed by the spatial constraints that more effectively trap injected charge carriers within the smaller and more isolated grains.²¹⁻
²² The high brightness at exceptionally low voltages ($\sim 5 \text{ V}$) also indicates superb carrier confinement within the perovskite emitter layer.²³ At higher voltages, a cross-over between the current curves was observed (Figure 4.7a), which means that a much higher luminance was achieved at a lower current density for the N₂-facilitated device. This is again due to the ease of charge recombination within the smaller domain of each grain, which leads to a huge enhancement in the current efficiency of the N₂-facilitated device at a much lower current density (Figure 4.8a), giving a maximum of 0.718 cd A^{-1} , more than 6 times that of the reference device. Comparison between the EQE (Fig 4.8b) shows a similar enhancement from 0.020% for the conventional to 0.088% for the N₂-facilitated device, indicating lower energy loss and reiterating the importance of the charge confinement effect.

Figure 4.8 (a) Current efficiency versus current density, and (b) EQE versus luminance curves of both devices.

Table 4.2 Comparison of device performance of conventional and N₂-facilitated CsPbBr₃ PeLEDs.

Sample	L _{max} (cd m ⁻²)		V _{th} (V)		Current Efficiency (cd A ⁻¹)	
	Best	Average	Best	Average	Best	Average
Conventional	2964	2300 ± 900	2.6	3.2 ± 0.5	0.118	0.08 ± 0.03
N ₂ -facilitated	8218	7000 ± 1000	2.4	2.7 ± 0.3	0.718	0.3 ± 0.2

4.2.7 Electroluminescence Spectra Comparison

The EL spectra of both devices measured from 5 to 6 V are plotted in Figure 4.9. Likewise, the N₂-facilitated device shows several-fold enhancement in the number of counts collected, corresponding to the higher luminance. At a low voltage (5 V or less), the EL spectra for the standard and N₂-facilitated device centralize at 526 and 524 nm respectively, which are in good agreement with the PL spectra of the respective films (Table 4.1). At higher voltages, a blueshift of 2-3 nm was observed for both EL spectra, resulting in final peaks at 523 and 522 nm. This phenomenon was also previously observed in organometal halide PeLEDs²⁴ and is likely due to Joule heating during device operation. More in-depth studies

on the thermochromic effects in perovskite films have been conducted by Wu *et al.*, relating the phenomenon to electron-phonon renormalization.²⁵

Figure 4.9 EL spectra of both devices at different driving voltages. Pictures in inset show the respective devices under applied bias.

4.2.8 Eliminating Thickness Effect

To prove that the enhanced device performance is more significantly due to spatial charge confinement within the smaller perovskite grains rather than the thickness difference, additional conventional devices were fabricated by increasing the spin-coating speed to 5000 rpm to achieve an average thickness of 82 nm, which is on par with that of the N₂-facilitated film. Cross-sectional FESEM as well as a summary of the device performance are shown in Figure 4.10 and Table 4.3 respectively. Here, it is shown that although both films have the same thickness, the N₂-facilitated device still outperforms the conventional one due to the formation of smaller grain structures, which reinforces the claim that the

grain size is the dominating factor in achieving stronger spatial confinement of charge carriers.

Figure 4.10 (a) Surface and (b) cross-sectional FESEM of conventionally spin-coated CsPbBr₃ films with increased spin speed at 5000 rpm.

Table 4.3 Comparison of device performance of CsPbBr₃ PeLEDs spin-coated using conventional and N₂-facilitated method with N₂ flow introduced at various timings and pressures.

Sample	Luminance (cd m ⁻²)		V _{th} (V)		Current Efficiency (cd A ⁻¹)	
	Best	Average	Best	Average	Best	Average
Conventional (4000 rpm)	2964	2274	2.6	3.2	0.118	0.084
Conventional (5000 rpm)	3615	3184	3.1	3.3	0.120	0.118
N ₂ -facilitated (1-bar) at 1s	6810	6231	2.5	2.7	0.240	0.205
N₂-facilitated (1-bar) at 3s	8218	6863	2.4	2.7	0.718	0.339
N ₂ -facilitated (1-bar) at 5s	8156	6509	2.4	2.6	0.246	0.220
N ₂ -facilitated (2-bar)	2617	1601	3.1	3.4	0.135	0.133

4.2.9 Effect of N₂ Gas Pressure and Introduction Time

Further studies were conducted to investigate the effect of the pressure of the N₂ gas flow and the timing at which it is introduced. It is found that by further increasing the pressure of the N₂ flow to 2-bar, no improvement in device performance was noted but rather, the luminance and current efficiency were somewhat diminished (Table 4.3). Although the grain size was reduced with higher N₂ pressure (Figure 4.11), the poorer device performance is likely ascribed to the additional non-radiative recombination channels as a result of the increased surface area of the more isolated grains.

Figure 4.11 Surface (top row) and cross sectional (bottom row) FESEM images of N_2 -facilitated CsPbBr_3 films deposited on ITO/PEDOT:PSS substrates using (a,c) 1-bar and (b,d) 2-bar pressure.

The N_2 pressure was then maintained at 1-bar and the timing of the N_2 gas introduction was varied at 1, 3 and 5 s from the start of the spin-coating process. The surface topography (Figure 4.12) show negligible difference while all 3 devices give comparable figures of merit (Table 4.3) with average L_{max} , V_{th} and current efficiency within $6,000\text{--}7,000 \text{ cd m}^{-2}$, 2.6-2.7 V, and $0.2\text{--}0.3 \text{ cd A}^{-1}$ respectively. It is henceforth concluded that the timing of N_2 introduction is not a critical factor in determining the performance of the N_2 -facilitated PeLEDs.

Figure 4.12 Surface FESEM images of CsPbBr₃ films deposited on ITO/PEDOT:PSS substrates with N₂ flow introduced at (a) 1 s, (b) 3 s, and (c) 5 s from initiation of spin coating.

4.3 Conclusion

In this work, the importance of charge confinement in PeLEDs is demonstrated through a solution-processed, N₂-facilitated film formation of CsPbBr₃, yielding enhanced EL and efficiency in LED operation. This modus operandi combines the action of rapid supersaturation and pinning of the nucleated crystals to achieve smaller grain sizes and less percolated microstructures. As a result, this led to better spatial confinement of charge carriers and thus improves the radiative recombination and light emission. By optimizing the pressure and timing of the N₂ gas flow, highly bright PeLEDs ($L_{\max} = 8,218 \text{ cd m}^{-2}$) along with improved efficiencies (current efficiency = 0.718 cd A^{-1} and EQE = 0.088%) and extremely low turn-on voltage ($V_{\text{th}} = 2.4 \text{ V}$) are achieved. The type of gas flow is not limited to N₂, but any inert dry gas should accomplish the task. Since no additional additives are present, this study directly confirms that smaller grains are desired for enhanced light emission.

While this work has shown how tuning of the grain size can improve carrier confinement geometrically, the poor morphological coverage is still glaringly evident. The smaller grain structures may have helped to confine injected charge carriers, but the vast uncovered area remains unconfined. Exposed areas allow for direct contact between the ETL and HTL, which will lead to undesired leakage current. This leakage carriers will result in non-radiative recombination losses, which could otherwise enhance the film emission have they

been effectively confined. The next chapter will endeavour to use alternative deposition techniques to improve the coverage and compactness of the film morphology, thereby improving the confinement of carriers within the perovskite film and maximising the surface area of light emission.

References

1. de Quilettes, D. W.; Vorpahl, S. M.; Stranks, S. D.; Nagaoka, H.; Eperon, G. E.; Ziffer, M. E.; Snaith, H. J.; Ginger, D. S., Impact of Microstructure on Local Carrier Lifetime in Perovskite Solar Cells. *Science* **2015**, *348* (6235), 683-686.
2. Zhou, Y.; Game, O. S.; Pang, S.; Padture, N. P., Microstructures of Organometal Trihalide Perovskites for Solar Cells: Their Evolution from Solutions and Characterization. *The Journal of Physical Chemistry Letters* **2015**, *6* (23), 4827-4839.
3. Jeon, N. J.; Noh, J. H.; Kim, Y. C.; Yang, W. S.; Ryu, S.; Seok, S. I., Solvent Engineering for High-Performance Inorganic–Organic Hybrid Perovskite Solar Cells. *Nature Materials* **2014**, *13* (9), 897-903.
4. Shi, D.; Adinolfi, V.; Comin, R.; Yuan, M.; Alarousu, E.; Buin, A.; Chen, Y.; Hoogland, S.; Rothenberger, A.; Katsiev, K.; Losovyj, Y.; Zhang, X.; Dowben, P. A.; Mohammed, O. F.; Sargent, E. H.; Bakr, O. M., Low Trap-State Density and Long Carrier Diffusion in Organolead Trihalide Perovskite Single Crystals. *Science* **2015**, *347* (6221), 519-522.
5. Zheng, X.; Chen, B.; Wu, C.; Priya, S., Room Temperature Fabrication of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ by Anti-Solvent Assisted Crystallization Approach for Perovskite Solar Cells with Fast Response and Small J–V Hysteresis. *Nano Energy* **2015**, *17*, 269-278.
6. Xia, B.; Wu, Z.; Dong, H.; Xi, J.; Wu, W.; Lei, T.; Xi, K.; Yuan, F.; Jiao, B.; Xiao, L.; Gong, Q.; Hou, X., Formation of Ultrasooth Perovskite Films toward Highly Efficient Inverted Planar Heterojunction Solar Cells by Micro-Flowing Anti-Solvent Deposition in Air. *Journal of Materials Chemistry A* **2016**, *4* (17), 6295-6303.
7. Zhou, Y.; Yang, M.; Wu, W.; Vasiliev, A. L.; Zhu, K.; Padture, N. P., Room-Temperature Crystallization of Hybrid-Perovskite Thin Films via Solvent-Solvent

Extraction for High-Performance Solar Cells. *Journal of Materials Chemistry A* **2015**, *3* (15), 8178-8184.

8. Li, X.; Bi, D.; Yi, C.; Décoppet, J.-D.; Luo, J.; Zakeeruddin, S. M.; Hagfeldt, A.; Grätzel, M., A Vacuum Flash-Assisted Solution Process for High-Efficiency Large-Area Perovskite Solar Cells. *Science* **2016**, *353* (6294), 58-62.

9. Chen, W.; Wu, Y.; Yue, Y.; Liu, J.; Zhang, W.; Yang, X.; Chen, H.; Bi, E.; Ashraful, I.; Grätzel, M.; Han, L., Efficient and Stable Large-Area Perovskite Solar Cells with Inorganic Charge Extraction Layers. *Science* **2015**, *350* (6263), 944-948.

10. Yantara, N.; Bhaumik, S.; Yan, F.; Sabba, D.; Dewi, H. A.; Mathews, N.; Boix, P. P.; Demir, H. V.; Mhaisalkar, S., Inorganic Halide Perovskites for Efficient Light-Emitting Diodes. *The Journal of Physical Chemistry Letters* **2015**, *6* (21), 4360-4364.

11. Stoumpos, C. C.; Malliakas, C. D.; Peters, J. A.; Liu, Z.; Sebastian, M.; Im, J.; Chasapis, T. C.; Wibowo, A. C.; Chung, D. Y.; Freeman, A. J.; Wessels, B. W.; Kanatzidis, M. G., Crystal Growth of the Perovskite Semiconductor CsPbBr₃: A New Material for High-Energy Radiation Detection. *Crystal Growth & Design* **2013**, *13* (7), 2722-2727.

12. Eperon, G. E.; Beck, C. E.; Snaith, H. J., Cation Exchange for Thin Film Lead Iodide Perovskite Interconversion. *Materials Horizons* **2016**, *3* (1), 63-71.

13. Kumawat, N. K.; Dey, A.; Kumar, A.; Gopinathan, S. P.; Narasimhan, K. L.; Kabra, D., Band Gap Tuning of CH₃NH₃Pb(Br_{1-x}Cl_x)₃ Hybrid Perovskite for Blue Electroluminescence. *ACS Applied Materials & Interfaces* **2015**, *7* (24), 13119-13124.

14. Bergerhoff, G.; Schmitz-Dumont, O., Die Kristallstruktur Des Kaliumhexachlorocadmats(II). *Zeitschrift für anorganische und allgemeine Chemie* **1956**, *284* (1-3), 10-19.

15. Rakita, Y.; Kedem, N.; Gupta, S.; Sadhanala, A.; Kalchenko, V.; Böhm, M. L.; Kulbak, M.; Friend, R. H.; Cahen, D.; Hodes, G., Low-Temperature Solution-Grown CsPbBr₃ Single Crystals and Their Characterization. *Crystal Growth & Design* **2016**, *16* (10), 5717-5725.

16. Saidaminov, M. I.; Almutlaq, J.; Sarmah, S.; Dursun, I.; Zhumekenov, A. A.; Begum, R.; Pan, J.; Cho, N.; Mohammed, O. F.; Bakr, O. M., Pure Cs₄PbBr₆: Highly Luminescent Zero-Dimensional Perovskite Solids. *ACS Energy Letters* **2016**, *1* (4), 840-845.

17. Bhaumik, S.; Veldhuis, S. A.; Ng, Y. F.; Li, M.; Muduli, S. K.; Sum, T. C.;

Damodaran, B.; Mhaisalkar, S.; Mathews, N., Highly Stable, Luminescent Core-Shell Type Methylammonium-Octylammonium Lead Bromide Layered Perovskite Nanoparticles. *Chemical Communications* **2016**, 52 (44), 7118-7121.

18. Bi, D.; Yi, C.; Luo, J.; Décoppet, J.-D.; Zhang, F.; Zakeeruddin, Shaik M.; Li, X.; Hagfeldt, A.; Grätzel, M., Polymer-Templated Nucleation and Crystal Growth of Perovskite Films for Solar Cells with Efficiency Greater Than 21%. *Nature Energy* **2016**, 1, 16142.

19. Yang, B.; Dyck, O.; Poplawsky, J.; Keum, J.; Paretzky, A.; Das, S.; Ivanov, I.; Rouleau, C.; Duscher, G.; Geohegan, D.; Xiao, K., Perovskite Solar Cells with near 100% Internal Quantum Efficiency Based on Large Single Crystalline Grains and Vertical Bulk Heterojunctions. *Journal of the American Chemical Society* **2015**, 137 (29), 9210-9213.

20. Agarwal, S.; Seetharaman, M.; Kumawat, N. K.; Subbiah, A. S.; Sarkar, S. K.; Kabra, D.; Namboothiry, M. A. G.; Nair, P. R., On the Uniqueness of Ideality Factor and Voltage Exponent of Perovskite-Based Solar Cells. *The Journal of Physical Chemistry Letters* **2014**, 5 (23), 4115-4121.

21. Cho, H.; Jeong, S.-H.; Park, M.-H.; Kim, Y.-H.; Wolf, C.; Lee, C.-L.; Heo, J. H.; Sadhanala, A.; Myoung, N.; Yoo, S.; Im, S. H.; Friend, R. H.; Lee, T.-W., Overcoming the Electroluminescence Efficiency Limitations of Perovskite Light-Emitting Diodes. *Science* **2015**, 350 (6265), 1222-1225.

22. Kim, Y.-H.; Cho, H.; Lee, T.-W., Metal Halide Perovskite Light Emitters. *Proceedings of the National Academy of Sciences* **2016**, 113 (42), 11694-11702.

23. Veldhuis, S. A.; Boix, P. P.; Yantara, N.; Li, M.; Sum, T. C.; Mathews, N.; Mhaisalkar, S. G., Perovskite Materials for Light-Emitting Diodes and Lasers. *Advanced Materials* **2016**, 28 (32), 6804-6834.

24. Tan, Z.-K.; Moghaddam, R. S.; Lai, M. L.; Docampo, P.; Higler, R.; Deschler, F.; Price, M.; Sadhanala, A.; Pazos, L. M.; Credgington, D.; Hanusch, F.; Bein, T.; Snaith, H. J.; Friend, R. H., Bright Light-Emitting Diodes Based on Organometal Halide Perovskite. *Nature Nanotechnology* **2014**, 9 (9), 687-692.

25. Wu, K.; Bera, A.; Ma, C.; Du, Y.; Yang, Y.; Li, L.; Wu, T., Temperature-Dependent Excitonic Photoluminescence of Hybrid Organometal Halide Perovskite Films. *Physical Chemistry Chemical Physics* **2014**, 16 (41), 22476-22481.

Chapter 5

Controlling Film Morphology through Sequential Deposition*

Film morphology has a major influence on the performance of halide perovskite semiconductors, as demonstrated in the previous chapter. While grain size plays an important role in spatial confinement of charge carriers, film coverage remains an issue which needs to be overcome. Poor coverage and pinholes are generally detrimental as these uncovered areas are unwanted pathways for charge carriers to travel. This results in the charge carriers not being able to be effectively confined within the perovskite emitter material, leading to undesirable current leakage. To tackle this, a sequential deposition technique is proposed whereby the deposition of the precursor solution is decoupled. This approach essentially nullifies the solubility problem of CsBr and the final perovskite film coverage now chiefly depends on the initial PbBr₂ concentration and the duration of exposure to the CsBr solution. With this alternative deposition route, over 90% film coverage can be achieved without the need for additives, along with working proof-of-concept devices, demonstrating the feasibility of this methodology for future device fabrication.

*This section is published substantially as Ng, Y. F.; Neo, W. J.; Jamaludin, N. F.; Yantara, N.; Mhaisalkar, S.; Mathews, N., Enhanced Coverage of All-Inorganic Perovskite CsPbBr₃ through Sequential Deposition for Green Light-Emitting Diodes. *Energy Technology* **2017**, 5 (10), 1859-1865.

5.1 Introduction

The limited solubility of Cs-based precursor (CsBr) in common aprotic solvents (DMF or DMSO) has restricted the efficacy of the solution-processed deposition. One-step spin-coated films usually results in poor surface coverage (Chapter 4.2.1), translating to high leakage currents and low efficiencies in devices.¹⁻² On the other hand, a more sophisticated two-step sequential deposition method permits a much better control over the deposition and growth of individual precursor compounds and thus the final film morphology can be easily modulated.³⁻⁶ In addition, due to the decoupling of the deposition procedure, the reaction principle, conversion kinetics, crystallization and growth behaviors can all be studied thoroughly,⁷ allowing morphological engineering according to the desired final film structure.

The 2 key parameters varied in this work are (a) PbBr_2 concentration and (b) duration of exposure to CsBr solution. While the former is crucial for templating growth of the final film, the latter on the other hand, determines the degree of conversion and phase transformation occurring in the resulting film. The sequential process is described in further details in Chapter 3.2.2, where a schematic illustration is depicted in Figure 3.5. The resultant films with the different deposition conditions are shown in Figure 5.1.

Figure 5.1 Photograph of sequentially-deposited CsPbBr₃ films with different PbBr₂ concentration and exposure time in a 10 mg ml⁻¹ CsBr solution.

5.2 Results and Discussions

5.2.1 Crystal Structure and Phase Analysis

In order to verify the conversion of PbBr₂ to the desired CsPbBr₃ phase, XRD was used and the diffraction patterns are presented in Figure 5.2.

Figure 5.2 XRD patterns of all CsPbBr₃ samples made via the sequential deposition technique with different initial PbBr₂ concentration and dipping duration in the CsBr solution. The bottom diffractogram corresponds to the Pnma orthorhombic structure of pristine CsPbBr₃ thin film.

The broad amorphous hump observed for the 0.2 M PbBr₂ samples is ascribed to incomplete coverage of the substrate as verified by the FESEM images *vide infra*. The low

characteristic peak intensities along with the amorphous signature fail to give a clear indication of a pure CsPbBr_3 phase. Meanwhile, samples formed using 0.5 M PbBr_2 base layer show excellent conversion for the various exposure times, with all characteristic peaks perfectly matching those of the reference Pnma CsPbBr_3 ,⁸ indicative of a more complete transformation. On the other hand, although all the 1.0 M PbBr_2 samples show distinctive CsPbBr_3 peaks, additional reflections corresponding to PbBr_2 and other lead-rich intermediates such as CsPb_2Br_5 were observed at 5 and 10 min CsBr exposure times. This is due to the insufficient time allowed for the penetration of CsBr precursor into the thick PbBr_2 base layer, thus resulting in incomplete conversion. Additional phase analysis using Match! can be seen in Figure 5.3, showing presence of impurities such as CsPb_2Br_5 and PbBr_2 . The longer exposure time needed for complete conversion of the 1.0 M PbBr_2 sample provides strong evidence of the crucial role concentration and time play in determining the resulting film's phase purity.

Figure 5.3 Match! analysis of CsPbBr₃ sample with 1.0 M initial PbBr₂ dipped 5 min in CsBr, showing presence of CsPbBr₃ (PDF#18-0364, green lines), CsPb₂Br₅ (PDF#25-0211, olive lines) and PbBr₂ (PDF#01-0623, brown lines).

5.2.2 Morphological Tuning via Deposition Conditions

Top-view FESEM images (Figure 5.4) were taken to examine the morphological evolution from the initial PbBr₂ (top row) to the converted CsPbBr₃ films upon dipping at various time intervals (subsequent rows). Estimation of the surface coverage is done using the ImageJ software and displayed at the bottom left hand corner of each figure.

Figure 5.4 Surface FESEM images of initial PbBr_2 films (top row), followed by converted CsPbBr_3 films upon dipping in CsBr solution for 5, 10 and 20 min (2nd, 3rd and 4th row respectively). The 3 columns represent the different starting PbBr_2 concentration increasing from 0.2, 0.5, to 1.0 M from left to right. Brackets in the bottom left corner of each image specifies the coverage of each converted perovskite film. All samples were deposited on ITO/PEDOT:PSS substrates. Scale bar represents 1 μm .

As shown in Figure 5.4, the initial PbBr_2 concentration is critical in influencing the morphology of the converted CsPbBr_3 film since the PbBr_2 crystals subsequently become active sites for chemical reaction with the incoming CsBr . A low PbBr_2 concentration of

0.2 M resulted in distinct streaks of sparse PbBr_2 crystals being scattered across the substrate surface, limiting the final film coverage to a meagre 51.8% on exposure to CsBr for 5 min (Figure 5.4a–b). Prolonged exposure time, however, reduced the surface coverage further to below 50% (Figure 5.4c–d) possibly due to Ostwald ripening-driven coalescence. The accompanying increase in thickness of nuclei with decrease in surface area coverage is due to the preferred vertical growth of the grains and volume conservation, forming more island-like structures as observed in the cross-sectional FESEM images (Figure 5.5). The thickness of each converted film is indicated at the bottom left hand corner of each figure, where an upward trend is noted with prolonged CsBr exposure time. Increasing the PbBr_2 precursor concentration to 0.5 M forms a fully covered and compact base layer which is necessary to achieve a coverage exceeding 90% on exposure to CsBr solution (Figure 5.4e–f). This is in sharp contrast to previously published reports of single-step deposition of pristine CsPbBr_3 showing surface coverage of less than 80%.^{1, 9} Longer exposure times likewise resulted in a reduction in coverage and increase in thickness (Figure 5.4g–h, 5.5e–f). In the case of the 1.0 M PbBr_2 sample, although a fully compact film was obtained, noticeable grain boundaries were observed likely due to stresses present and stacking of excess material. Consequently, the converted perovskite shows stacking of grains albeit having almost full coverage (Figures 5.4j–l, 5.5g–i). This is undesirable as charge transport across the perovskite layer can be hindered. The thicker films (252 – 369 nm) also give rise to higher resistivity and facilitate non-radiative recombination processes arising from bulk defects. This implies a possible trade-off between thickness and surface coverage offered by the various processing conditions, which can be statistically analyzed in the correlation plot as shown in Figure 5.6. Based on this, the best balance between thickness and coverage is achieved with 0.5 M concentration of PbBr_2 and 5 min of CsBr exposure time.

Figure 5.5 Cross-sectional FESEM images of converted CsPbBr₃ films. Columns from left to right show increasing initial PbBr₂ concentration (0.2 to 0.5 to 1.0 M) while rows from top to bottom show increasing dipping duration in CsBr solution (5 to 10 to 20 mins). Brackets in the bottom left corner of each image specifies the average thickness of each film. Scale bar represents 100 nm.

Figure 5.6 Plot of thickness against coverage based on FESEM results for all sequentially-deposited CsPbBr₃ films.

5.2.3 Optical Properties and Band Gap Determination

The effect of the film processing on optical properties was subsequently probed, with the optical absorption shown in Figure 5.7a. Regardless of the PbBr₂ concentration and CsBr exposure time, all samples show similar absorption onset at 525 nm. Based on the work by Kumar et al. and Elliot's theory of Wannier exciton,¹⁰⁻¹¹ the excitonic absorption peak was fitted against a model with the excitonic and band-to-band contributions deconvoluted (Figure 5.7b–d). The band gaps of all samples are calculated to be ~ 2.46 eV. However, presence of an additional peak at 312 nm, assigned to PbBr₂ band gap,¹² was observed for several samples. The presence of trace PbBr₂ is due to the insufficient time for diffusion and reaction of the CsBr species, thus leaving unreacted material at the base layer, although this was undetected from the XRD analysis. This additional peak decreases with longer CsBr exposure time, indicating increasing degree of conversion.

Figure 5.7 (a) UV-vis absorption for all sequentially-deposited CsPbBr_3 samples. The absorption spectra of 0.5 M PbBr_2 samples with different CsBr exposure time of (b) 5 min, (c) 10 min, and (d) 20 min are refitted using Elliot's theory for deconvolution of Wannier exciton (red dashed lines) and band-to-band (blue dashed lines) contributions. The electronic band gap is finally determined in each graph.

The normalized PL spectra are plotted in Figure 5.8a, showing green emission for all samples around 530 nm along with small shifts attributed to thickness-assisted self-absorption (Figure 5.9). By plotting the PL peak wavelength against the film thickness (Figure 5.8b), a clear trend of increasing peak wavelength with thickness is revealed, which is consistent with literature.¹³ This deviation in PL peak position is possibly due to scattering of rougher films. The energy shift with respect to the optical density (OD) of each sample is shown in Figure 5.10, showing a linear trend except at lower OD region, where more scattering is expected due to lower coverage and rougher surface of the films.

Figure 5.8 (a) PL spectra and (b) PL peak wavelength versus thickness trend for all sequentially-deposited CsPbBr₃ samples.

Figure 5.9 PL redshift with (a) increasing initial PbBr_2 concentration from 0.2 M (black), 0.5 M (red) to 1.0 M (blue) and (b-d) increasing dipping duration in CsBr solution.

Figure 5.10 Plot of energy shift (from calculated band gap energy of 2.46 eV) of PL peak with respect to optical density (obtained from absorbance data).

5.2.4 Device Performance with respect to Dipping Time

As proof of concept, PeLED devices were fabricated using samples with 0.5 M PbBr_2 concentration based on the optimal coverage and degree of conversion. The device architecture adopted is shown in Figure 5.11, where the electron transporting material is changed from Bphen (from the previous chapter) to TPBi due to its higher electron mobility. The current density and luminance versus driving voltage (J - V - L) curves of all three devices are plotted in Figure 5.12a, with the current efficiency reflected in Figure 5.12b. The EL spectra shown in Figure 5.13 confirm that the emission at 527 nm is similar for all devices, although the slight blueshift from its PL can be explained by thermochromic effects.¹⁴ A summary of all characteristic device parameters is tabulated in Table 5.1. The best device is achieved with 5 min CsBr exposure time, reaching an L_{max} of 167 cd m^{-2} and current efficiency of $7.6 \times 10^{-2} \text{ cd A}^{-1}$. On the other hand, increasing the exposure time

leads to higher current density associated with higher leakage channels. This is ascribed to the combined effect of increasing thickness and reduced surface coverage, which gives rise to more non-radiative recombination pathways and finally resulted in a drop in both $L_{\max}$ and efficiency, thus emphasizing the importance of film morphology and coverage on the geometrical confinement effect.¹⁵

Figure 5.11 Energy band levels of PeLED device architecture used in this work.

Figure 5.12 (a) Current density and luminance against voltage (J - V - L) and (b) current efficiency against luminance curves of sequential CsPbBr₃ PeLEDs fabricated using 0.5 M initial PbBr₂ concentration with different dipping durations.

Table 5.1 Comparison of device performance for sequentially-deposited CsPbBr₃ PeLEDs with different dipping durations.

0.5 M PbBr ₂	$L_{\max}$ (cd m ⁻²)	$CE_{\max}$ (cd A ⁻¹)	V_{th} (V)
Dip 5 min	166.5	7.6×10^{-2}	5.3
Dip 10 min	48.0	1.9×10^{-2}	5.2
Dip 20 min	22.7	1.3×10^{-2}	4.9

Figure 5.13 EL spectra of all devices at maximum luminance. Inset is a photograph of a 12 mm² device showing homogeneous green light emission.

5.3 Conclusion

In conclusion, this work has demonstrated the use of a sequential deposition process to yield CsPbBr₃ film with more than 90% coverage, a feat unachievable with single-step spin-coating method due to the low solubility of the CsBr precursor. The degree of phase transformation is governed by the initial PbBr₂ precursor concentration and the exposure

time in CsBr solution. It is found that a mono PbBr₂ base layer with sufficient coverage is required for optimal chemical reaction and conversion to CsPbBr₃ with the desired final morphology. The exposure time is also critical in ensuring sufficient time for diffusion and reaction to occur, but concomitantly, not excessively to cause significant grain growth. A proof of concept PeLED emitted green luminance of more than 100 cd m⁻² at a wavelength of 527 nm, almost equivalent to its PL peak position, showing the feasibility of this approach in future inorganic PeLED fabrication.

This work shows huge coverage improvement using the sequential deposition method, which implies lesser leakage pathways and non-radiative recombination, leading to better confinement of charge carriers within the perovskite layer. While this method allows control of coverage and compactness, the lack of control over grain size means that the spatial confinement within the perovskite grains is still weak. The preferred vertical growth of the CsPbBr₃ crystals upon conversion from PbBr₂ also means that it is difficult to reduce the thickness of the film without compromising on the degree of conversion. The rougher film morphology also means a thicker electron transporting layer is required, which will unfavourably increase the transport resistance. These drawbacks eventually lead to poorer devices as compared to the one-step method in Chapter 4, albeit the improvement in coverage from <80% to >90%. These limiting factors will need to be overcome to achieve PeLEDs with higher efficiencies. The next Chapter will see a different approach that aims to achieve an amalgamation of all the desired features seen in Chapters 4 and 5, i.e. reduced grain size and improved film coverage with minimum thickness and roughness.

References

1. Yantara, N.; Bhaumik, S.; Yan, F.; Sabba, D.; Dewi, H. A.; Mathews, N.; Boix, P. P.; Demir, H. V.; Mhaisalkar, S., Inorganic Halide Perovskites for Efficient Light-Emitting Diodes. *The Journal of Physical Chemistry Letters* **2015**, 6 (21), 4360-4364.
2. Wei, Z.; Perumal, A.; Su, R.; Sushant, S.; Xing, J.; Zhang, Q.; Tan, S. T.; Demir, H. V.; Xiong, Q., Solution-Processed Highly Bright and Durable Cesium Lead Halide

Perovskite Light-Emitting Diodes. *Nanoscale* **2016**, 8 (42), 18021-18026.

3. Burschka, J.; Pellet, N.; Moon, S.-J.; Humphry-Baker, R.; Gao, P.; Nazeeruddin, M. K.; Gratzel, M., Sequential Deposition as a Route to High-Performance Perovskite-Sensitized Solar Cells. *Nature* **2013**, 499 (7458), 316-319.
4. Hu, L.; Peng, J.; Wang, W.; Xia, Z.; Yuan, J.; Lu, J.; Huang, X.; Ma, W.; Song, H.; Chen, W.; Cheng, Y.-B.; Tang, J., Sequential Deposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ on Planar NiO Film for Efficient Planar Perovskite Solar Cells. *ACS Photonics* **2014**, 1 (7), 547-553.
5. Zhang, T.; Yang, M.; Zhao, Y.; Zhu, K., Controllable Sequential Deposition of Planar $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Films via Adjustable Volume Expansion. *Nano Letters* **2015**, 15 (6), 3959-3963.
6. Li, H.; Li, S.; Wang, Y.; Sarvari, H.; Zhang, P.; Wang, M.; Chen, Z., A Modified Sequential Deposition Method for Fabrication of Perovskite Solar Cells. *Solar Energy* **2016**, 126, 243-251.
7. Chen, H., Two-Step Sequential Deposition of Organometal Halide Perovskite for Photovoltaic Application. *Advanced Functional Materials* **2017**, 27 (8), 1605654.
8. Stoumpos, C. C.; Malliakas, C. D.; Peters, J. A.; Liu, Z.; Sebastian, M.; Im, J.; Chasapis, T. C.; Wibowo, A. C.; Chung, D. Y.; Freeman, A. J.; Wessels, B. W.; Kanatzidis, M. G., Crystal Growth of the Perovskite Semiconductor CsPbBr_3 : A New Material for High-Energy Radiation Detection. *Crystal Growth & Design* **2013**, 13 (7), 2722-2727.
9. Wu, C.; Zou, Y.; Wu, T.; Ban, M.; Pecunia, V.; Han, Y.; Liu, Q.; Song, T.; Duhm, S.; Sun, B., Improved Performance and Stability of All-Inorganic Perovskite Light-Emitting Diodes by Antisolvent Vapor Treatment. *Advanced Functional Materials* **2017**, 1700338.
10. Kumar, A.; Kumawat, N. K.; Maheshwari, P.; Kabra, D. In *Role of Halide Anion on Exciton Binding Energy and Disorder in Hybrid Perovskite Semiconductors*, 2015 IEEE 42nd Photovoltaic Specialist Conference (PVSC), 14-19 June 2015; 2015; pp 1-4.
11. Elliott, R. J., Intensity of Optical Absorption by Excitons. *Physical Review* **1957**, 108 (6), 1384-1389.
12. Kramarenko, N. K.; Miloslavskii, V. K., Thickness Effect on the Exciton Spectrum of Thin PbBr_2 Films. *physica status solidi (b)* **1971**, 48 (2), K177-K180.
13. D'Innocenzo, V.; Srimath Kandada, A. R.; De Bastiani, M.; Gandini, M.; Petrozza, A., Tuning the Light Emission Properties by Band Gap Engineering in Hybrid Lead Halide

Perovskite. *Journal of the American Chemical Society* **2014**, *136* (51), 17730-17733.

14. Wu, K.; Bera, A.; Ma, C.; Du, Y.; Yang, Y.; Li, L.; Wu, T., Temperature-Dependent Excitonic Photoluminescence of Hybrid Organometal Halide Perovskite Films. *Physical Chemistry Chemical Physics* **2014**, *16* (41), 22476-22481.

15. Kumawat, N. K.; Jain, N.; Dey, A.; Narasimhan, K. L.; Kabra, D., Quantitative Correlation of Perovskite Film Morphology to Light Emitting Diodes Efficiency Parameters. *Advanced Functional Materials* **2017**, *27* (3), 1603219.

Chapter 6

Elucidating the Energy Cascade Phenomena in CsPbBr₃ Mixed-Dimensional Perovskites*

Chapters 4 and 5 saw the impact of geometrical confinement on the optical and EL properties of CsPbBr₃. In this chapter, a dimensional tuning method was employed, showing that carrier confinement can be achieved through an electronic approach, introducing the concept of energy funnelling from a multidimensional structured perovskite. This is done by incorporating a large ligand molecule into the 3D framework of CsPbBr₃. By carefully tuning the molar ratio, highly uniform, smooth and nano-sized grains were achieved with efficient energy channelling through an energy cascade as proven by various spectroscopic analyses. The significance of this energy landscape is demonstrated, highlighting its importance in confining carriers electronically. The benefits are nicely reflected in PeLEDs made from this quasi-2D mix, giving more than fifty-fold increment in device luminance and efficiency. This chapter shows that the electronic confinement through dimensional engineering outperforms the geometrical approach shown in the previous two chapters, and suggests that this multidimensional perovskite has a bright future in achieving better performing PeLEDs.

*This section is published substantially as Ng, Y. F.; Kulkarni, S. A.; Parida, S.; Jamaludin, N. F.; Yantara, N.; Bruno, A.; Soci, C.; Mhaisalkar, S.; Mathews, N., Highly Efficient Cs-based Perovskite Light-Emitting Diodes Enabled by Energy Funnelling. *Chemical Communications* **2017**, 53 (88), 12004-12007.

6.1 Introduction

Multi, or mixed-dimensional perovskites (the terms are synonymous), have been shown to yield interesting properties that the 3D perovskites lack (further elaboration can be found in Chapter 2.4.4), in particular a modulated energy landscape that enables energy or carrier funnelling. These properties are especially important for LEDs where carrier confinement is key in defining the radiative recombination and light generation of the device. While several mixed-dimensional systems have been synthesized for the organic-inorganic hybrid perovskites, this study demonstrates for the first time a quasi-2D perovskite based on the fully inorganic Cs-based perovskite for light emission. In addition, the funnelling mechanism is explored deeper in this chapter through excitation and time-resolved spectroscopies by closely observing the emission properties of the various phases present using different excitation energies. The electronic confinement imparted by the energy cascade is nicely reflected in PeLEDs showing significant improvement in both luminance and efficiency.

The CsPbBr₃ precursor was prepared using an excess of CsBr as previously reported (also described in Chapter 2.1.3).¹ The perovskite solutions with excess of PEABr addition were prepared in different molar ratios, i.e. PEABr:CsPbBr₃ = 0:1, 0.05:1, 0.1:1, 0.2:1, 0.3:1, 0.5:1, 0.8:1 and 1:1 to study the effect of PEABr addition. The molecular structure and a simple schematic illustration of the solution preparation are depicted in Figure 3.3, with further elaboration in Chapter 3.1.4.

6.2 Results and Discussions

6.2.1 Optical Properties of Mixed-Dimensional PEABr–CsPbBr₃ Perovskite

The effect of PEABr on the optical properties of CsPbBr₃ is first probed using UV-vis and PL spectroscopies, with the absorption and emission spectra shown in Figure 6.1. The emission of the film under UV light is shown in Figure 6.2.

Figure 6.1 (a) UV-vis absorption (plotted with a constant offset, arrow indicates the absorption peak due to quasi-2D / 2D perovskite formation), (b) PL (absorbance-corrected), and (c) normalized PL spectra of CsPbBr₃ perovskite films prepared with different molar excess addition of PEABr.

Figure 6.2 Photographs of CsPbBr₃ perovskite films formed with different PEABr:CsPbBr₃ mole ratios under UV illumination.

The typical absorption (Figure 6.1a) peak onset at 525 nm (band gap = 2.34 eV)² for 3D CsPbBr₃ perovskite is noted for all films prepared with the different PEABr addition. Interestingly, films formed with PEABr:CsPbBr₃ ratios above 0.2:1 were found to exhibit secondary absorption peaks at lower wavelengths (< 500 nm), which are attributed to the quasi-2D excitonic absorption. With further addition of PEABr, the quasi-2D absorption becomes more dominant with the attenuation of the 3D peak, indicating a transition from 3D towards a more layered perovskite structure. The absorption peak at ~400 nm corresponds to the pure 2D (PEA)₂PbBr₄ phase ($n = 1$)³⁻⁴ whereas the other peaks (centred at ~430, 460 and 480 nm) are signatures of layered perovskites with $n = 2, 3, 4$ or higher order.⁵⁻⁶ At 1:1 ratio, the 3D absorption is almost diminished, implying that the film is mainly composed of quasi-2D phases. With increasing PEABr:CsPbBr₃ ratios up to 0.8:1, enhancement in absorbance-corrected PL intensity (Figure 6.1b) is observed. Most of the emission originates mainly from the 3D perovskite phase (511 – 522 nm), corresponding to the band gap of 2.34 eV, which is lower than that of the quasi-2D (~2.78 eV) and pure 2D (~3.06 eV) phase. The huge enhancement in PL intensity of the 0.8:1 quasi-2D perovskite is likely due to i) efficient funnelling of the photoexcitation energy and ii) spatial charge confinement due to morphological improvement, both of which will be verified subsequently. It is also possible that the larger PEA cations can passivate defects at lattice surfaces and grain boundaries as speculated by Jen and co-workers,⁷ thereby reducing shunt paths and non-radiative recombination losses. From the normalized PL spectra (Figure 6.1c), gradual blueshifts in PL peak position with increasing PEABr:CsPbBr₃ ratio was

observed from 522 nm (0:1) to 511 nm (0.8:1) due to the reduced domains of the perovskite structure. At ratios of 0.2:1 and above, additional PL emission with low but appreciable intensities are detected at wavelengths of 483 nm, 467 nm, 436 nm and 405 nm. These extra peaks are attributed to the reduced dimensionality of the perovskite⁸ and are closely in line with the quasi-2D absorption signatures. At a higher ratio of 1:1 however, emission from the 3D perovskite (~511 nm) becomes diminished while the quasi-2D emission dominates due to the formation of more layered perovskite phases. Following the PL spectra, all samples emit green light under UV excitation except the 1:1 sample which gives a bluish-green tinge (Figure 6.2).

6.2.2 Energy Funnelling Observed through PL Excitation Spectra and Transient Spectroscopy

While the additional quasi-2D emission peaks at lower wavelengths may affect the purity of the emitted light, they could be beneficial in fine-tuning the energy landscape and revamping the behaviour of charge carriers.⁹⁻¹⁰ In order to investigate this effect, the PL excitation spectra were measured and shown in Figure 6.3.

Figure 6.3 PL excitation spectra (plotted with a constant offset) of CsPbBr₃ perovskite films prepared with different molar excess addition of PEABr.

For the pure CsPbBr₃ film, there is no significant contribution to the emission below 500 nm. However, for the PEABr:CsPbBr₃ samples, the signature peaks of the quasi-2D structure can be observed in the excitation spectra starting from PEABr ratios as low as 0.3:1, with more obvious magnitudes at ratios of 0.5:1 and above. The presence of these peaks implies that the quasi-2D domains (larger band gap) significantly contribute to the emission of the 3D phase due to the efficient energy funnelling from the larger band gap to the lower band gap domains. The funnelling effect is further probed by a systematic wavelength-dependent study of TRPL decays as shown in Figure 6.4.

Figure 6.4 TRPL spectra for (a) pristine CsPbBr_3 , (b) $\text{PEABr}:\text{CsPbBr}_3 = 0.3:1$, and (c) $\text{PEABr}:\text{CsPbBr}_3 = 0.8:1$ perovskite films. The colour of the curves (a-c) corresponds to the specific wavelengths measured as shown in each graph.

Table 6.1 TRPL lifetimes and decay parameters of CsPbBr₃ perovskite films prepared with different mole ratio of PEABr:CsPbBr₃ (0:1, 0.3:1 and 0.8:1) at different wavelengths.

PEABr:CsPbBr ₃ ratio	Wavelength (nm)	A _f	τ _f (ns)	A _s	τ _s (ns)	τ _{ave} (ns)
0:1 (pristine CsPbBr ₃)	496	0.845	1.532	0.176	4.225	1.9962
	516	0.640	1.769	0.390	5.420	3.1514
	526	0.502	2.767	0.485	8.449	5.5591
0.3:1	436	0.632	0.493	0.102	1.561	0.6414
	466	0.865	0.659	0.142	2.843	0.967
	496	0.523	1.807	0.477	6.805	4.191
	516	0.467	2.100	0.515	11.298	6.9238
	526	0.465	2.117	0.516	9.812	6.1645
0.8:1	436	1.02	0.437	—	—	0.437
	466	0.729	0.711	0.258	4.144	1.6084
	496	0.503	2.481	0.504	7.947	5.2167
	516	0.369	2.099	0.632	8.761	6.3052
	526	0.272	3.142	0.680	14.714	11.408

The TRPL decays are well described by a bi-exponential decay function comprising of a fast component (either due to presence of defects or due to energy transfer processes), related to non-radiative processes, and a slow decay component related to the radiative recombination.^{3, 11} Both characteristic decay times and the calculated average lifetime values are tabulated in Table 6.1. The PL decay curves are fitted using the following bi-exponential decay function: $I(t) = A_f e^{-t/\tau_f} + A_s e^{-t/\tau_s}$, where A_f and A_s refer to the decay amplitudes (i.e., weighting factors) of the fit and τ_f and τ_s refer to the decay time constants of the fast and slow components respectively. The average lifetime τ_{avg} was calculated using the formula: $\tau_{avg} = \frac{A_f \tau_f + A_s \tau_s}{A_f + A_s}$.

The TRPL decays were measured for various emission wavelengths corresponding to the peaks observed in the steady-state PL emission (Figure 6.1b and c). The measured lifetimes strongly depend on the emission wavelength, consistent with the different nature of the 2D

and 3D domains present in the samples.⁹ Indeed, the lifetime increases by almost one order of magnitude from hundreds of ps to a few ns across the different emission wavelengths (in both samples with 0.3:1 and 0.8:1 ratio), consistently in line with the presence of different structures. Even more interestingly, by comparing the fluorescence lifetime at the same emission wavelength across the different samples, it is observed that with increasing PEABr content, the decay of the 2D phase (436 nm signal) becomes slightly faster while the 3D component (526 nm) becomes significantly longer (*e.g.* from 5.56 ns in CsPbBr₃ to 6.16 ns in 0.3:1 and 11.41 ns in 0.8:1 sample), suggesting that the energy transfer from the higher energy states to the 3D domains increases the carrier density in these domains, thereby overwhelming the charge carrier trap states. The lifetimes also confirm that the highest radiative recombination occurs with the addition of 80 mol% excess PEABr (ratio of 0.8:1), which is consistent with the highest PL intensity measured with this PEABr concentration (Figure 6.1b).

6.2.3 Morphological Enhancement with Mixed-Dimensional System

The morphological change with PEABr addition was observed with FESEM as shown in Figure 6.5 (top-view) and 6.6 (cross-section). The FESEM images of pure CsPbBr₃ film shows large and non-uniform grains with visible pinholes along with a rough top surface as seen from the cross-section image (Figure 6.5a and 6.6a). At a PEABr:CsPbBr₃ ratio of 0.3:1 however, the grain size is reduced and less pinholes were observed (Figure 6.5e and 6.6e). Beyond this ratio, the quasi-2D films become pinhole-free. With a ratio of 0.5:1, nano-sized grains, uniform, and flat top surface were achieved (Figure 6.5g and 6.6g). This morphological evolution can be explained by the fact that the bulky PEA chains could not fit inside the 3D lattice of CsPbBr₃,¹² thus they function as ligands that surround the 3D crystallites.⁸ As a result, the growth of 3D perovskite grains becomes inhibited while layered structures are preferentially formed, leading to smaller grains and smoother film. These morphological refinements are expected facilitate charge injection, confinement, and improve radiative recombination. From the cross-section imaging (Figure 6.6), all films show similar thicknesses of ~ 85 nm.

Figure 6.5 Field emission scanning electron microscopic (FESEM) top-view images of CsPbBr_3 perovskite films prepared using different mole ratio of $\text{PEABr}:\text{CsPbBr}_3$, showing reduction in grain size with increasing compactness and smoothness of the film with increasing PEABr content.

Figure 6.6 FESEM cross-section images of CsPbBr₃ perovskite films prepared using different mole ratio of PEABr:CsPbBr₃, showing smoother and flatter films with increasing PEABr content. Thicknesses of all films are closely similar (~ 85 nm).

6.2.4 Crystal Structure and Phase Analysis

The crystal structure and phase were checked with XRD. The diffraction patterns (Figure 6.7) show orthorhombic (Pnma) crystal structure of CsPbBr₃, in agreement with reported literature.¹³ While the XRD peak positions of CsPbBr₃ are invariant with PEABr addition in Figure 6.7a, the quasi-2D phase formation was confirmed in the XRD spectra of thicker films prepared via drop-casting (Figure 6.7b).

Figure 6.7 Superimposed XRD patterns of perovskite films prepared using different mole ratio of PEABr:CsPbBr₃: (a) As prepared films after vacuum drying and (b) thicker films prepared using drop-casting and subsequent annealing at 100 °C for 20 mins.

6.2.5 Device Comparison

PeLEDs (device architecture shown in Figure 6.8a) were then fabricated and tested, with the resultant current density–voltage–luminance (J - V - L) curves shown in Figure 6.8b. The efficiencies were extracted and plotted in Figure 6.9. The $L_{\max}$, V_{th} , current efficiency, and EQE of the best and average devices are tabulated in Table 6.2. The $L_{\max}$ of the pure CsPbBr₃ PeLED only obtained a maximum of 271 cd m⁻² while increasing the PEABr:CsPbBr₃ ratio to 0.2:1 and above achieved close to or greater than 10,000 cd m⁻². The V_{th} is reduced from 4 V to 3 V after PEABr addition, while the current efficiency escalated rapidly from 0.13 cd A⁻¹ to more than 1 cd A⁻¹. The best device was achieved at a PEABr:CsPbBr₃ ratio of 0.8:1, yielding a current efficiency of 6.16 cd A⁻¹ and EQE of 1.97%, which is ~50 times that of the pure CsPbBr₃. The substantial enhancement in device performance is attributable to the combinatorial effect of the charge dynamics and film morphology. The energy landscape created by the quasi-2D states (which is absent in the pure 3D perovskite) allows efficient energy transfer from the larger band gap to the smallest band gap region, thereby amplifying electron-hole capture and radiative recombination rates.⁹ Concomitantly, the formation of compact film with nano-sized grains is key to suppressing leakage currents and spatially confine injected charge carriers.¹⁴ These two effects contribute concurrently to achieve high luminance and better efficiency of the quasi-2D devices. Increasing uniformity and smoothness of the PEABr-CsPbBr₃ films also allows better interfacial contact with the electron transport layer, thereby reducing V_{th} . However, at higher PEABr:CsPbBr₃ ratio of 1:1, formation of 3D perovskite phase becomes impeded (Figure 6.1), which considerably hinders the charge transport and reduces the emissive area, thereby resulting in a drop in the device performance.

Figure 6.8 (a) Energy level alignment of the device architecture used in this work. (b) J-V-L of PeLEDs fabricated with CsPbBr₃ perovskites prepared using different PEABr:CsPbBr₃ molar ratios.

Figure 6.9 (a) Current efficiency, and (b) EQE curves of PeLEDs fabricated with CsPbBr₃ perovskites prepared using different PEABr:CsPbBr₃ molar ratios.

Table 6.2 Summary of device performance of CsPbBr₃ light-emitting diodes (PeLEDs) with different mole ratio of PEABr:CsPbBr₃.

PEABr: CsPbBr ₃ ratio	L _{max} (cd m ⁻²)		V _{th} (V)		Current Eff (cd A ⁻¹)		EQE (%)		λ _{emission peak} (nm)	
	Best	Average	Best	Average	Best	Average	Best	Average	PL	EL
0:1	271	147	4.0	4.3	0.13	0.06	0.035	0.016	522	523
0.1:1	8116	6364	3.0	3.2	1.91	1.38	0.553	0.430	516	518
0.2:1	10096	7778	3.3	3.4	3.05	2.49	0.985	0.761	516	518
0.3:1	10857	7847	3.2	3.6	3.37	2.91	1.136	0.956	515	517
0.5:1	11536	8405	3.0	3.6	5.12	4.41	1.717	1.246	515	514
0.8:1	9957	8984	3.0	3.1	6.16	5.07	1.973	1.603	511	514
1:1	1853	1342	3.2	3.2	3.91	2.46	1.369	0.862	466, 482, 509	512

6.2.6 Electroluminescence Shift and Analysis

The EL spectra are plotted in Figure 6.10. Interestingly, only single emission peaks for all devices, even at high biases (Figure 6.11) are shown for all samples. The peak positions closely match the lowest band gap PL wavelength of each film and no additional quasi-2D emission is observed, indicating the successful energy funnelling and carrier confinement in the lowest band gap phase. All devices show narrowband green emission (inset of Figure 6.11) with full width at half maximum (FWHM_{EL}) of 20-22 nm.

Figure 6.10 Normalized EL spectra of all devices (in (a) linear scale and (b) log scale) under an applied bias of 6 V, showing single emission for all PEABr:CsPbBr₃ compositions.

Figure 6.11 EL spectra of 0.8:1 PeLED device under different applied biases from 3 – 7 V, showing only a single emission peak even at high voltages. Inset shows an image of the device under an applied bias of 4 V.

6.3 Conclusion

This work presents the first study of quasi-2D CsPbBr₃ based perovskite framework for LEDs. The integration of PEABr and CsPbBr₃ in a mixed-dimensional configuration brings about a threefold benefit of i) smooth and pinhole-free film morphology, ii) nano-sized grains, and iii) constructive energy channelling towards the smallest band gap phase. The eventual outcome is the realization of highly luminous ($L_{\max} > 10,000 \text{ cd m}^{-2}$) and efficient PeLEDs (current efficiency $> 6 \text{ cd A}^{-1}$, EQE $\sim 2\%$) with pure green emission (FWHM_{EL} $\sim 20 \text{ nm}$). The device performance shows more than 50 times improvement as compared to the standard. The methodology involved in this work is simple, allowing ample opportunity for large scale production.

This chapter of results employs a mixed-dimensional perovskite to explore the effect of reduced dimensionality on the electronic confinement of charge carriers, with the energetics further investigated using excitation and time-resolved spectroscopy techniques. The tremendous improvement in both optical and electroluminescence properties as compared to the previous two chapters strongly suggest that future work should be focused in this direction. While PEABr is the ligand molecule studied in this work, the influence of the choice of such molecules should be further researched. It is likely that the molecular structure of this spacer molecule can change the properties of the mixed-dimensional perovskite, for instance, distortion and defects in the lattice, charge transport and electrical properties, and even effectiveness of energy funnelling. Comparison of various ligand molecules based on factors like size, conjugation, and position of functional groups will then give a clearer idea of how a good spacer cation should be designed.

References

1. Yantara, N.; Bhaumik, S.; Yan, F.; Sabha, D.; Dewi, H. A.; Mathews, N.; Boix, P. P.; Demir, H. V.; Mhaisalkar, S., Inorganic Halide Perovskites for Efficient Light-Emitting Diodes. *The Journal of Physical Chemistry Letters* **2015**, 6 (21), 4360-4364.
2. de Jong, E. M. L. D.; Yamashita, G.; Gomez, L.; Ashida, M.; Fujiwara, Y.;

Gregorkiewicz, T., Multiexciton Lifetime in All-Inorganic CsPbBr₃ Perovskite Nanocrystals. *The Journal of Physical Chemistry C* **2017**, *121* (3), 1941-1947.

3. Byun, J.; Cho, H.; Wolf, C.; Jang, M.; Sadhanala, A.; Friend, R. H.; Yang, H.; Lee, T.-W., Efficient Visible Quasi-2D Perovskite Light-Emitting Diodes. *Advanced Materials* **2016**, *28* (34), 7515-7520.

4. Liang, D.; Peng, Y.; Fu, Y.; Shearer, M. J.; Zhang, J.; Zhai, J.; Zhang, Y.; Hamers, R. J.; Andrew, T. L.; Jin, S., Color-Pure Violet-Light-Emitting Diodes Based on Layered Lead Halide Perovskite Nanoplates. *ACS Nano* **2016**, *10* (7), 6897-6904.

5. Quan, L. N.; Yuan, M.; Comin, R.; Voznyy, O.; Beauregard, E. M.; Hoogland, S.; Buin, A.; Kirmani, A. R.; Zhao, K.; Amassian, A.; Kim, D. H.; Sargent, E. H., Ligand-Stabilized Reduced-Dimensionality Perovskites. *Journal of the American Chemical Society* **2016**, *138* (8), 2649-2655.

6. Bhaumik, S.; Veldhuis, S. A.; Ng, Y. F.; Li, M.; Muduli, S. K.; Sum, T. C.; Damodaran, B.; Mhaisalkar, S.; Mathews, N., Highly Stable, Luminescent Core-Shell Type Methylammonium-Octylammonium Lead Bromide Layered Perovskite Nanoparticles. *Chemical Communications* **2016**, *52* (44), 7118-7121.

7. Li, N.; Zhu, Z.; Chueh, C.-C.; Liu, H.; Peng, B.; Petrone, A.; Li, X.; Wang, L.; Jen, A. K. Y., Mixed Cation FA_xPEA_{1-x}PbI₃ with Enhanced Phase and Ambient Stability toward High-Performance Perovskite Solar Cells. *Advanced Energy Materials* **2017**, *7* (1), 1601307.

8. Xiao, Z.; Kerner, R. A.; Zhao, L.; Tran, N. L.; Lee, K. M.; Koh, T.-W.; Scholes, G. D.; Rand, B. P., Efficient Perovskite Light-Emitting Diodes Featuring Nanometre-Sized Crystallites. *Nature Photonics* **2017**, *11* (2), 108-115.

9. Yuan, M.; Quan, L. N.; Comin, R.; Walters, G.; Sabatini, R.; Voznyy, O.; Hoogland, S.; Zhao, Y.; Beauregard, E. M.; Kanjanaboos, P.; Lu, Z.; Kim, D. H.; Sargent, E. H., Perovskite Energy Funnels for Efficient Light-Emitting Diodes. *Nature Nanotechnology* **2016**, *11* (10), 872-877.

10. Quan, L. N.; Zhao, Y.; García de Arquer, F. P.; Sabatini, R.; Walters, G.; Voznyy, O.; Comin, R.; Li, Y.; Fan, J. Z.; Tan, H.; Pan, J.; Yuan, M.; Bakr, O. M.; Lu, Z.; Kim, D. H.; Sargent, E. H., Tailoring the Energy Landscape in Quasi-2D Halide Perovskites Enables Efficient Green-Light Emission. *Nano Letters* **2017**, *17* (6), 3701-3709.

11. Liang, P.-W.; Liao, C.-Y.; Chueh, C.-C.; Zuo, F.; Williams, S. T.; Xin, X.-K.; Lin, J.; Jen, A. K. Y., Additive Enhanced Crystallization of Solution-Processed Perovskite for Highly Efficient Planar-Heterojunction Solar Cells. *Advanced Materials* **2014**, *26* (22), 3748-3754.
12. Mitzi, D. B.; Wang, S.; Feild, C. A.; Chess, C. A.; Guloy, A. M., Conducting Layered Organic-Inorganic Halides Containing <110>-Oriented Perovskite Sheets. *Science* **1995**, *267* (5203), 1473-1476.
13. Stoumpos, C. C.; Malliakas, C. D.; Peters, J. A.; Liu, Z.; Sebastian, M.; Im, J.; Chasapis, T. C.; Wibowo, A. C.; Chung, D. Y.; Freeman, A. J.; Wessels, B. W.; Kanatzidis, M. G., Crystal Growth of the Perovskite Semiconductor CsPbBr₃: A New Material for High-Energy Radiation Detection. *Crystal Growth & Design* **2013**, *13* (7), 2722-2727.
14. Cho, H.; Jeong, S.-H.; Park, M.-H.; Kim, Y.-H.; Wolf, C.; Lee, C.-L.; Heo, J. H.; Sadhanala, A.; Myoung, N.; Yoo, S.; Im, S. H.; Friend, R. H.; Lee, T.-W., Overcoming the Electroluminescence Efficiency Limitations of Perovskite Light-Emitting Diodes. *Science* **2015**, *350* (6265), 1222-1225.

Chapter 7

Ligand Design for Modulation of Mixed-Dimensional Perovskites for Enhanced LED Performance*

Chapter 6 has shown the use of one type of ligand molecule, PEABr, to obtain mixed-dimensional CsPbBr₃ perovskite, demonstrating the effect of reduced dimensionality on the electronic confinement of charge carriers. The exceptional enhancement to both the optical and electroluminescence properties as compared to the pure 3D CsPbBr₃ indicates this multidimensional system is more superior and deserves more attention. This chapter aims to build up on the previous one by exploring various ligand molecules for forming quasi-2D CsPbBr₃ perovskites. Although PEA has been commonly used for both LEDs and PSCs, not much has been known how the choice of ligand molecule affects the different phase formation. Through a systematic screening of different families of spacer structures, it is observed that increasing the size of the ligand molecule leads to suppression of the quasi-2D states. This chapter then moves on to focus on a particular acene family of spacer structure, the naphthyl group, along with its regioisomers, to access how this spacer structure affects the various phase formation and its electroluminescence properties. Finally, a list of criteria for screening effective ligand molecules is established, which will be beneficial for the future design of mixed-dimensional perovskites.

*This chapter is currently being prepared as a manuscript.

7.1 Introduction

In Chapter 6, it was concluded that the mixed-dimensional system is much superior to the pure 3D CsPbBr₃ system in terms of carrier confinement. The addition of an optimized ratio of the selected ligand molecule, PEABr, has shown remarkable improvement to the optical and electroluminescence properties of the mixed-dimensional CsPbBr₃ perovskite, a result of a combination of energy cascading and morphological improvement. Based on these findings, there is a strong motivation to explore this mixed-dimensional system further, in terms of the ligand molecule used and its effect on the formation of quasi-2D phases. While PEABr has been used in quite a number of literatures, other ligand molecules are seldom reported. On top of that, most literature reports the use of specific ligand molecules in various concentrations to form mixed-dimensional perovskites, similar to the work done in Chapter 6. The choice of ligand molecules and a comparison with other molecules are not usually discussed and therefore the question of how to judiciously choose or even design a ligand molecule for a mixed-dimensional perovskite system remains unanswered (Chapter 2.5). Nevertheless, researchers have speculated that a more bulky organic molecule may be a more stable spacer ligand due to its steric hindrance and stronger dispersion interactions.¹⁻² It has also been shown that 2D iodide-based perovskites exhibit enhanced internal quantum efficiencies (IQE) with longer alkyl spacer groups due to increased radiative recombination rates.³ With a better 2D system, it is more likely to obtain a more efficient funnelling process and enhanced radiative recombination in the 3D domains.

In this Chapter, it is hypothesized that a larger ligand molecule will be more difficult to incorporate in between the 3D perovskite framework. From this aspect, the formation of quasi-2D phases ($n = 2, 3, 4 \dots$), as observed from the absorption and PL data from Chapter 6, may be more finely controlled. The main intention of this is to not only achieve morphological improvement and energy cascade of the mixed-dimensional system, but also to minimize the formation of the lower dimensional phases ($n = 2, 3, 4 \dots$) such that the majority phase in the perovskite is still the 3D part. The reason is simply because the 3D phase is still the main contribution of light emission in both film and its corresponding

device configuration. While the ligand molecule is still required to optimize film morphology and attain energy funnelling, the 3D phase should still be maximized in the final film. From here, the choice of ligand molecules is identified as the most important factor in determining the formation of various phases in the mixed-dimensional perovskite film.

There are many ways to increase the size of a ligand molecule, the simplest of which is to have a longer alkyl chain length. To form a mixed-dimensional perovskite, an ammonium functional group is required to bind to the PbBr_6^{4-} octahedra. The ligand molecules are thus selected based on the spacer structure covalently bonded to the ammonium bromide functional group. They can be classified as alkyl, phenyl, and naphthyl molecules, families with increasing size and conjugation. Some of the ligand molecules including OABr, PhABr, PMABr and PEABr were purchased commercially, while the rest were synthesized according to the procedure shown in Chapter 3.1. The next few sections will show and discuss in details how different spacer structures of the ligand molecules affect the phase formation of the mixed-dimensional CsPbBr_3 and the corresponding effect on the film properties and device performances.

7.2 Results and Discussions

7.2.1 Preliminary Study with Octylammonium Spacer Groups

The first study of the effect of ligand molecules was performed using the n-alkyl group of spacer structures, more specifically octylammonium bromide (OABr) (Figure 7.1). This molecule has been widely used as a ligand in nanoparticle and quantum dot synthesis due to its long carbon chain (consisting of 8 carbons in the chain), which allows formation of stable nanoscale structures (nanoparticles, nanoplatelets, nanorods, nanocrystals etc.)⁴⁻¹¹ due to the alkyl capping layer that prevents particle agglomeration. Since its molecular structure is much longer than the PEABr molecule, it was used as a preliminary study to quickly test the hypothesis.

Figure 7.1 (Left) Molecular structure of octylammonium bromide (OABr). (Right) Photograph of a spin-coated mixed-dimensional CsPbBr_3 film with OABr as the spacer ligand.

The OABr is added at an excess concentration of 60, 80, and 100 mol% to a solution of CsPbBr_3 , which is around the best concentration used for PEABr in the previous chapter. The solution is mixed properly and used for spin-coating thereafter, in exactly the same procedure as used for the PEABr system. However, it was observed that after spin-coating, streaky patterns appear from the centre of the substrate in a radial direction (Figure 7.1) for any concentration of OABr used, which could likely be a result of the long oily chain of the octyl group that affected film formation. Nevertheless, these films were characterized to obtain some preliminary results to test the hypothesis. The UV-vis absorption and PL spectra of both PEABr and OABr mixed-dimensional perovskite films are shown in Figure 7.2.

Figure 7.2 Absorption and PL spectra of (a, b) PEABr-CsPbBr₃ and (c, d) OABr-CsPbBr₃ films with different excess concentration (mol%) of ligand additives.

By comparing the absorption spectra of both the PEA (Figure 7.2a) and OA (Figure 7.2c) mixed-dimensional perovskites, it can be evidently observed that with the same concentration of OABr, the excitonic absorption peaks from the lower dimensional phases (< 500 nm) become much more suppressed as compared to the PEABr samples. This means that by merely changing the ligand molecule, the quasi-2D phase formation can be controlled. This gives support to the hypothesis, although it is not entirely conclusive since only one ligand molecule was tested. Further comparison with different ligand molecules were necessary to confirm the hypothesis. Although the formation of lower dimensional phases is suppressed with OABr, a quick comparison of the PL spectra (Figure 7.2b and d) shows that the OA-CsPbBr₃ films can reach similar level of PL intensity as the PEA-

CsPbBr₃ films. This means that the carrier confinement within the OA-CsPbBr₃ system is still enhanced significantly. This improvement is assumed to be of a similar effect as the PEA-CsPbBr₃ system, where energy funnelling and morphological improvement leads to spatial and electronic confinement of charge carriers. Furthermore, this shows that a reduction in the quasi-2D phases does not necessarily lead to a reduction in the 3D emission. This means that if a particular ligand molecule is found to give minimal quasi-2D phases and maximal 3D phase while concomitantly sufficient ligand molecules are incorporated to achieve a compact and flat morphology, then this ligand molecule is conjectured to be the best candidate for mixed-dimensional perovskite light emitters.

7.2.2 Electroluminescence of Mixed-dimensional CsPbBr₃ with OABr Spacer Groups

On another note, the electrical properties of the ligand molecule should not be overlooked, especially considering the need for current injection in LED applications. For instance, a long OA ligand may hinder charge transport within the perovskite layer due to its long insulating carbon chain.¹²⁻¹⁶ A quick comparison of the performance of the electrically biased devices will be able to verify this. The J-V-L and current efficiency curves of the PEABr- and OABr-CsPbBr₃ PeLED devices are shown in Figure 7.3, along with the summary of the device characteristics tabulated in Table 7.1.

Figure 7.3 (a) J-V-L and (b) current efficiency curves of mixed-dimensional PeLEDs fabricated with 80% PEABr (black), 80% OABr (green), and 100% OABr (orange).

Table 7.1 Summary of device performance of mixed-dimensional CsPbBr₃-based PeLEDs comparing PEABr and OABr as ligand molecules.

Device	$L_{\max}$ (cd m ⁻²)	V_{th} (V)	Current Eff. (cd A ⁻¹)
80% PEABr	12.4k	2.8	5.41
80% OABr	2.1k	4.5	0.84
100% OABr	1.6k	4.4	0.85

From the J-V curves in Figure 7.3a, OABr devices show a much lower current density as compared to the PEABr devices due to the longer insulating octyl chain. The slope of the current injection onset appears to be gentler, as compared to the steep injection onset of the PEABr device, and along with the high V_{th} of the OABr devices (> 4 V), implies that the current injection is impeded and the charge carrier transport through the perovskite is retarded. As a result, the luminance and efficiency are much lower as compared to the PEABr devices (Table 7.1).

7.2.3 Mixed-dimensional CsPbBr₃ with Phenyl Alkyl Spacer Groups

While OABr shows a promising trend towards validating the hypothesis of this work, issues such as film non-uniformity and insulating spacer structure have led to poor current injection and device performance. To overcome that and to further verify the trend, four other ligand molecules that are more similar to PEABr were selected and systematically screened. The phenyl group was retained for its conjugated structure while the size of the ligand molecules was varied through the length of the alkyl chain linking the benzene ring to the ammonium functional group, which leads to the four different ligand molecules alongside PEABr as shown in Figure 7.4.

Figure 7.4 Molecular structure of (a) phenylammonium bromide (PhABr), (b) phenylmethyammonium bromide (PMABr), (c) phenylethylammonium bromide (PEABr), (d) phenylpropylammonium bromide (PPABr), and (e) phenylbutylammonium bromide (PBABr).

The ligand molecules used are listed in order of increasing alkyl chain length: phenylammonium bromide (PhABr), phenylmethylanmonium bromide (PMABr), phenylethylanmonium bromide (PEABr), phenylpropylanmonium bromide (PPABr), and phenylbutylanmonium bromide (PBABr). Due to the huge sample size, the concentration variation for each ligand molecule is kept to four: 25, 50, 75 and 100 mol% excess additive.

7.2.4 Optical Properties of Mixed-dimensional CsPbBr₃ with Phenyl Alkyl Spacer Groups

In order to confirm the trend observed from the OABr study, UV-vis and PL spectroscopy were first conducted. However, it is noticed that the PhABr sample does not form mixed-dimensional perovskite as observed from its absorption curve, where no excitonic absorption from the low dimensional phase is detected even at high concentration (100 mol%) of PhABr additive (Figure 7.5a). Similarly, no PL enhancement is observed (Figure 7.5b) due to the lack of energy funnelling. In literature, this PhA ligand has never been used to make 2D perovskites, which implies that a minimum alkyl chain is required for flexibility of the ammonium functional group, otherwise the ligand may become too rigid and may not bind properly in between the PbBr₆⁴⁻ octahedra.

Figure 7.5 (a) UV-vis absorption and (b) PL spectra of PhABr-CsPbBr₃ samples.

On the other hand, all four other ligand molecules (PMABr – PBABr) are able to form mixed-dimensional perovskites with CsPbBr₃, as seen from the low dimensional excitonic absorption in the absorption spectra (Figure 7.6).

Figure 7.6 UV-vis absorption spectra of (a) PMABr-CsPbBr₃, (b) PEABr-CsPbBr₃, (c) PPABr-CsPbBr₃, and (d) PBABr-CsPbBr₃ mixed-dimensional perovskite films.

The lower dimensional absorption peaks ($n = 1, 2$ or 3) become noticeable at 50% addition of ligand molecules for the PMABr and PEABr samples (Figure 7.6a and b), whereas for the longer ligand molecule (PPABr and PBABr) samples, they only become apparent at high concentrations of 100% (Figure 7.6c and d). By comparing the absorption curves of the four different mixed-dimensional perovskites, it can be distinctly observed that the quasi-2D absorption peaks are gradually reduced in intensity from the PMABr to PBABr samples. This trend becomes more obvious when the same mol% of each ligand molecule is plotted alongside one another as shown in Figure 7.7.

Figure 7.7 Absorbance spectra (plots stacked with a constant offset of 0.1) of (a) 75% and (b) 100% excess ligand additives showing a diminution of the quasi-2D phases with increasing length of the spacer molecule. (c) Overlapped absorbance spectra of the 75% excess ligand additives (zoomed in to the 3D CsPbBr_3 absorption region).

From Figure 7.7a, the suppression of the lower dimensional absorption peaks with increasing length of the ligand molecule indicates that the formation of these lower dimensional phases is somewhat diminished, in line with the trend observed for the OABr samples and further substantiating the hypothesis. The trend is even more distinct for the 100% excess ligand molecule samples in Figure 7.7b. However, it should also be noted that the 3D component is also affected as shown by the absorption region around 510 – 520 nm (Figure 7.7c). In this case, although PPABr and PBABr show strong diminution of the quasi-2D peaks, the 3D absorption is also slightly reduced, implying that there is also lesser

3D phase in these films. The PEABr sample retains the highest proportion of its 3D phase among the different samples.

The same trend for the suppression of quasi-2D phase is again noticed in the PL spectra in Figure 7.8 and 7.9, with the logarithmic plots shown on the right for a clearer perspective of the quasi-2D emission.

Figure 7.8 PL spectra of (a) PMABr-CsPbBr₃ and (c) PEABr-CsPbBr₃ mixed-dimensional perovskite films. (b) and (d) show the corresponding graphs plotted in logarithmic scale.

Figure 7.9 PL spectra of (a) PPABr-CsPbBr₃ and (c) PBABr-CsPbBr₃ mixed-dimensional perovskite films. (b) and (d) show the corresponding graphs plotted in logarithmic scale.

Figure 7.10 PL spectra of (a) 75% and (b) 100% excess ligand additives. Graphs on the right show the magnified logarithmic plot of the region of interest (boxed in green).

From Figure 7.8 and 7.9, it is similarly shown that the emission from the lower dimensional (high band gap) phases become suppressed with increasing length of the phenyl alkyl ligand molecule. Figure 7.10 gives a clearer magnified comparison of the same concentration of each molecule at the lower wavelength region, where the reduction of the quasi-2D emission becomes apparent. The suppression of the quasi-2D phases with increasing length of the ligand molecule is likely due to the increasing difficulty of incorporating these larger spacer structures in the perovskite framework. In addition, it is also observed that the PL intensity increases with longer alkyl chains (Figure 7.9a and c),

along with an increasing blueshift in the PL spectra (Figure 7.10). Both of these observations have previously been reported in literatures, where it is proposed that the longer organic ligand molecules have higher relative internal quantum yield, although this study was done on the 2D iodide perovskite systems.³

7.2.5 Device Electroluminescence of Mixed-dimensional CsPbBr₃ with Phenyl Alkyl Spacer Groups

The impact of the various phenyl alkyl ligand molecules on the corresponding PeLED performance is investigated in device EL measurement, with the J-V-L and efficiency graphs plotted in Figure 7.11 and 7.12 respectively. The characteristic device parameters are summarized in Table 7.2.

Figure 7.11 J-V-L graphs of (a) PhABr, (b) PMABr, (c) PEABr, (d) PPABr, and (e) PBABr mixed-dimensional CsPbBr₃ PeLEDs.

Figure 7.12 Current efficiency graphs of (a) PhABr, (b) PMABr, (c) PEABr, (d) PPABr, and (e) PBABr mixed-dimensional CsPbBr₃ PeLEDs.

Table 7.2 Summary of device performance of mixed-dimensional CsPbBr₃-based PeLEDs with PhABr, PMABr, PEABr, PPABr and PBABr as ligand molecules.

Excess ligand molecule (mol%)		$L_{\max}$ (cd m ⁻²)	V_{th} (V)	Current Eff. (cd A ⁻¹)
PhABr	25%	0.5k	3.9	0.18
	50%	1.1k	3.4	0.50
	75%	1.2k	3.5	0.70
	100%	0.7k	3.7	0.54
PMABr	25%	0.4k	4.4	0.14
	50%	3.3k	3.7	1.17
	75%	1.3k	3.3	1.95
	100%	0.3k	3.3	2.17
PEABr	25%	0.9k	3.7	0.13
	50%	11.5k	3.2	3.10
	75%	13.6k	3.0	9.07
	100%	7.1k	3.0	7.27
PPABr	25%	1.3k	3.7	0.23
	50%	4.4k	3.2	1.93
	75%	4.7k	2.9	6.21
	100%	1.8k	2.8	4.78
PBABr	25%	4.3k	3.4	0.80
	50%	5.3k	3.0	4.85
	75%	3.3k	2.8	4.87
	100%	1.9k	2.8	4.97

From Figure 7.11, the current density curves appear to drop slightly with increasing alkyl chain length of the phenyl alkyl spacer molecules from PhABr to PBABr, similar to the OABr devices although the drop is less, again ascribed to the reduction in electrical conductivity of the EML with increasing alkyl length of the spacer molecule.¹⁷ The devices with PhABr do not see any significant improvement due to the absence of energy funnelling as discussed previously. While longer alkyl lengths (PPABr and PBABr) have led to suppression of lower dimensional phases along with enhancement in 3D PL emission

intensity (Figure 7.8 – 7.10) as seen previously, the EL of devices with PPABr and PBABr saw a decline as compared to PEABr. This is likely due to a few reasons: 1) the absorption from Figure 7.7c saw a reduction in 3D phase for the PPABr and PBABr mixed-dimensional perovskite films, and 2) the slight increase in the insulating alkyl chain length affected the charge transport. From the summarized comparison of the device performance (Figure 7.13), PEABr still yields more superior PeLEDs, which means that while some extent of alkyl chain length is needed (PEABr > PMABr), too much of it may affect the charge transport and the 3D phase formation.

Figure 7.13 Comparison of (a) current efficiency and (b) luminance of mixed-dimensional CsPbBr₃ PeLEDs with the five different ligand molecules.

While this study, along with the preliminary work with OABr, has proven that the quasi-2D phase formation can be modulated with increasing alkyl length of the ligand molecule in alignment with the initial hypothesis, other factors come into play in determining the final performance of the electrically-driven PeLED devices, more importantly, the 3D phase component and the charge transport properties. In order to overcome these hurdles, a more careful and systematic study towards the design of future ligand molecules is needed. Progressing from here, there is motivation to shift towards larger ligand molecules which are concomitantly more conjugated so that the problem of charge transport can be eliminated.

7.2.6 Towards Naphthyl-based Systems

Based on the study conducted on the alkyl and phenyl systems, it can be briefly concluded that the PL properties of the mixed-dimensional CsPbBr₃ perovskite improve with longer or larger spacer cation, but the EL suffers due to the long insulating alkyl chains that hinder charge transport. The other element that is realized to have an important effect is the amount of 3D phase component. The 3D phase should be maximized along with minimization of the quasi-2D phases to obtain the highest proportion of emitter states while just having enough ligand molecules to achieve funnelling and improve morphology. To eliminate the charge transport limitation with alkyl ligands, ligand molecules that are large, yet having decent charge transport properties, are desired. The most obvious route is to find molecules that are more conjugated, which motivated the decision to explore molecules with polycyclic aromatic hydrocarbon groups. The acene family of molecules presents a series of linearly fused benzene rings that are fully conjugated, including naphthalene, anthracene, tetracene, pentacene and so on, with increasing number of linearly fused benzene rings for spacer size but also having good charge transport at the same time.

Two naphthyl-based ligand molecules are selected with at least a methyl or ethyl group (based on results from the previous sub-chapter) connecting the spacer structure to the ammonium bromide functional group. However, due to the slight asymmetry of the double benzene rings as compared to the fully symmetric phenyl structure, the position of the methyl or ethyl ammonium branch now matters (as opposed to the PEA system, where the position of the alkyl ammonium branch is inconsequential and always results in the same molecule). In this case, position isomerism, or regioisomerism, has to be taken into consideration, which leads to each naphthyl molecule having two regioisomers. Finally, the four selected ligand molecules for this study are listed as such: 1-naphthylmethyammonium bromide (1-NMA), 2-naphthylmethyammonium bromide (2-NMA), 1-naphthylethylammonium bromide (1-NEA), and 2-naphthylethylammonium bromide (2-NEA), with their molecular structures shown in Figure 7.14.

Figure 7.14 Molecular structures of the naphthyl-based 1-NMA, 2-NMA, 1-NEA and 2-NEA ligand molecules used for making mixed-dimensional CsPbBr_3 perovskites.

7.2.7 Characterization of 2D Naphthyl-based Lead Bromide Perovskites

While most of the alkyl and phenyl alkyl ligand molecules have been widely demonstrated to form 2D lead bromide perovskites, the naphthyl-based molecules have not been frequently used. As mentioned in Chapter 2.4.4, the successful synthesis and characterization of the 2D crystal structures for 2-NMA and 2-NEA lead bromide perovskites have been previously reported.¹⁸ While it is highly probable that the isomers will likewise form 2D perovskites due to their similar molecular structures, all four ligand molecules were nevertheless characterized to confirm the formation of 2D layered perovskite structures. The naphthyl ligand molecules were dissolved with PbBr_2 in the composition L_2PbBr_4 (more information regarding 2D perovskite composition can be found in Chapter 2.4.4), where $\text{L} = 1\text{-NMA}, 2\text{-NMA}, 1\text{-NEA}$ or 2-NEA . The solutions were then spin-coated and characterized with XRD, with their diffraction patterns shown in Figure 7.15.

Figure 7.15 XRD patterns of 2D naphthyl-based perovskites: $(1\text{-NMA})_2\text{PbBr}_4$ (black), $(2\text{-NMA})_2\text{PbBr}_4$ (red), $(1\text{-NEA})_2\text{PbBr}_4$ (blue), and $(2\text{-NEA})_2\text{PbBr}_4$ (magenta).

From Figure 7.15, the thin film XRD patterns show regular 2-theta spacings for all four naphthyl ligand molecules, which is characteristic of 2D perovskites. The diffraction peaks of 2-NMA and 2-NEA also match with those in literatures.¹⁸ By taking the 2-theta values of the diffraction peaks and using Bragg's Law, the d-spacing for the (001) plane of the 2D perovskites is calculated as follows: 1-NMA (2.07 nm), 2-NMA (1.88 nm), 1-NEA (2.05 nm), and 2-NEA (1.97 nm). It is noted that increasing the alkyl group from methyl to ethyl

does not significantly alter the d-spacing. By changing the position of the alkyl ammonium branch from position 1 to 2, the d-spacing seems to reduce slightly, although it is not significant either.

The optical properties of the pure 2D compounds are measured using UV-vis and PL spectroscopy as shown in Figure 7.16.

Figure 7.16 (a) UV-vis absorption and (b) PL spectra of 2D naphthyl-based perovskites.

From the absorption spectra in Figure 7.16a, all four 2D naphthyl perovskites show very strong excitonic absorption close to 400 nm, which is another feature of 2D perovskites due to the higher exciton binding energy. The absorption onset, however, is shifted slightly with different naphthyl molecules. The same shift is also observed in the PL spectra, where the emission peak positions are more redshifted for 2-NEA and blueshifted for 2-NMA. By comparing the relative absorption and PL intensities, it is observed that 1-NMA exhibits the strongest excitonic absorption and highest emission intensity (black curves). The same is not true for the other samples, where 2-NEA shows the lowest excitonic absorption but second highest PL intensity, and 2-NMA shows the second highest excitonic absorption but lowest PL intensity, which could be due to intrinsic factors such as small distortions in the crystal structure, although this was not pursued further. Nevertheless, this might have an effect on the mixed-dimensional system as the higher absorption and PL intensity of the 2D (1-NMA)₂PbBr₄ may mean more energy for funnelling. Figure 7.17 shows the combined absorption and PL spectra of each naphthyl ligand molecule. All four 2D

naphthyl perovskites show PL emission peaks close to the excitonic absorption, with small Stokes shift of ~ 6 to 9 nm.

Figure 7.17 UV-vis absorption and PL spectra of (a) $(1\text{-NMA})_2\text{PbBr}_4$, (b) $(2\text{-NMA})_2\text{PbBr}_4$, (c) $(1\text{-NEA})_2\text{PbBr}_4$, and (d) $(2\text{-NEA})_2\text{PbBr}_4$ 2D perovskites.

7.2.8 Morphological and Optical Characterization of Mixed-Dimensional CsPbBr_3 Perovskites using Naphthyl-based Ligand Molecules

The mixed-dimensional perovskites are synthesized in the same way as the previous studies, where different concentrations of each ligand molecule are added to a fixed volume of CsPbBr_3 solution. The solutions were blended and left overnight in the glovebox for complete mixing before they were used for spin-coating. The deposited films with different

concentrations of naphthyl ligand molecules are first checked under UV light as shown in Figure 7.18.

Figure 7.18 Comparison of photoemission under UV light between 3D CsPbBr_3 (left) and mixed-dimensional CsPbBr_3 perovskites using naphthyl-based ligand molecules.

The different shade of colour at the border of each sample is due to the epoxy used to encapsulate each sample to prevent any possible degradation from oxygen and moisture. The epoxy is deposited along the border of the sample and another piece of glass is placed on top such that the perovskite film is sandwiched between two pieces of glass. The epoxy is then UV-cured for 3 min to complete the encapsulation. From Figure 7.18, it is shown that the mixed-dimensional systems appear much brighter than the pure CsPbBr_3 alone, which was also seen previously for the PEA work (Chapter 6). The mixed-dimensional films remain green with 40 – 60 mol% excess naphthyl ligand additives, although the 2-NMA, 1-NEA and 2-NEA samples appear slightly bluish at 60 mol%. At 100 mol%, all except the 1-NMA sample become evidently blueshifted. The surface morphologies of the

mixed-dimensional CsPbBr_3 perovskite films can be observed in the FESEM images in Figure 7.19 and 7.20, with the pristine CsPbBr_3 shown in Figure 7.19e for comparison.

Figure 7.19 Top-view FESEM images of CsPbBr_3 perovskite films prepared using different concentration of NMA ligand molecules: (a) 40 mol% and (b) 60 mol% 1-NMA; (c) 40 mol% and (d) 60 mol% 2-NMA. The pristine CsPbBr_3 is shown in (e) for comparison. Scale bars (bottom right) represents 100 nm.

Figure 7.20 Top-view FESEM images of CsPbBr₃ perovskite films prepared using different concentration of NEA ligand molecules: (a) 40 mol% and (b) 60 mol% 1-NEA; (c) 40 mol% and (d) 60 mol% 2-NEA. Scale bars (bottom right) represents 100 nm.

As compared to the pristine CsPbBr₃ (Figure 7.19e), the mixed-dimensional films show better morphologies that are fully compact and covered. Similar to the PEA system in Chapter 6.2.3, a fully compact film morphology can be achieved with excess NMA and NEA ligand additives of ~ 40 to 60 mol%, along with reduction in grain size. At 60 mol% 1-NMA and 2-NMA, the grains can still be distinguished (Figure 7.19b and d), whereas for the 1-NEA and 2-NEA samples, the grains appear to be less distinct (Figure 7.20b and d). These compositions (at 40 and 60 mol%) seem to be sufficient enough to realize optimum film morphologies, and subsequent optical characterizations will be focused on these compositions.

The optical properties of the 40 and 60 mol% samples were further probed using UV-vis absorption spectroscopy. Due to the strong suppression of the quasi-2D excitonic

absorption signatures, the 100 mol% excess composition for each ligand molecule was also tested for comparison. The absorption spectra of the mixed-dimensional CsPbBr_3 perovskite film with each naphthyl ligand molecule are separately plotted in Figure 7.21.

Figure 7.21 UV-vis absorption spectra of mixed-dimensional CsPbBr_3 perovskite films with different mol% excess concentration of (a) 1-NMA, (b) 2-NMA, (c) 1-NEA, and (d) 2-NEA ligand molecules.

From Figure 7.21, it can be seen that the absorption spectra of the mixed-dimensional CsPbBr_3 perovskite with all four naphthyl ligand molecules show lesser quasi-2D excitonic signatures as compared to the PEA system (Figure 7.6b). Although the concentration used in both studies are different, it is apparent that the higher energy states start appearing at a concentration of 50 mol% for the PEA samples, while the higher energy states are still very much suppressed for the naphthyl samples even at 60 mol%. This again reinforces the

hypothesis that larger ligand molecules are harder to incorporate into the perovskite structure, and therefore form lesser quasi-2D states. By comparing the four different naphthyl mixed-dimensional systems, it is noticed that with increasing concentration of ligand molecules, the formation of quasi-2D phases seems to vary. While 1-NMA seems to show only one obvious excitonic peak at 392 nm, which corresponds to the absorption of the $n=1$ phase, the other three samples show multiple excitonic peaks corresponding to the $n=1$, 2, and 3 phases, although it has not been reported how this will affect the funnelling process. On a different note, it is also observed that the 3D absorption component for the 1-NMA samples is more retained with increasing 1-NMA concentration, where the slope at 525 nm remains sharp albeit a reduction in the intensity. All three other naphthyl samples, however, saw a huge diminution of the 3D absorption peak with increasing concentration of ligand molecule, along with formation of more quasi-2D phases. This could possibly explain the bluish-green tinge seen from the 100 mol% samples (2-NMA, 1-NEA, and 2-NEA) in Figure 7.18. This observation is more clearly distinguished by plotting the same concentration of different ligand molecules in the same graph as shown in Figure 7.22.

Figure 7.22 UV-vis absorption spectra of mixed-dimensional CsPbBr_3 perovskites with (a) 40 mol%, (b) 60 mol%, and (c) 100 mol% excess naphthyl ligand molecules.

From Figure 7.22, it is evidently seen that for all three concentrations, the 1-NMA samples always retain the most 3D component (black curves), implying that the dominant phase in the film is still 3D CsPbBr_3 . At a concentration of 40 mol% (Figure 7.22a), 2-NEA shows the second highest 3D component, while at 60 mol% (Figure 7.22b), it has dropped below 1-NEA. At 100 mol%, the 3D component for 2-NMA, 1-NEA and 2-NEA samples seem to have all but completely faded, whereas it is still enduring for the 1-NMA sample. It is speculated that the differences in the solubility of the ligand molecules may have affected the crystallization dynamics of the system. The presence of each phase can be more clearly identified in the transient absorption (TA) spectra for the 100 mol% samples in Figure 7.23.

Figure 7.23 Transient absorption (TA) spectra of mixed-dimensional CsPbBr₃ perovskite films with 100 mol% excess of (a) 1-NMA, (b) 2-NMA, (c) 1-NEA, and (d) 2-NEA at different delay times.

From the TA spectra at different delay times, it can be clearly seen that at a high concentration of 100 mol% ligand molecule, the 1-NMA sample (Figure 7.23a) still exhibits a strong 3D absorption component with a long absorption lifetime. However, all three other samples no longer show any signal at this wavelength (Figure 7.23b-d), and the majority of the absorption is contributed by the quasi-2D states corresponding to the excitonic peaks in Figure 7.21b-d. The 2-NMA sample in particular, only displays intense but short-lived absorption signals in the low *n* regions (~ 430 and 460 nm), indicating that majority of the film is constituted by lower dimensional phases (Figure 7.23b). Both NEA

samples show weak and short-lived low dimensional signals but a broader and long-lived absorption close to 500 nm was observed, indicating that the dominant phases here are a mix of higher n species, although the 3D phase is still absent. As discussed in the previous section when comparing the phenyl alkyl ligand molecules, the 3D absorption component may play an important role in device performance since this is the main light-emitting phase.

The PL spectra of each naphthyl-based mixed-dimensional CsPbBr_3 are plotted in Figure 7.24, while spectra for the same concentration of each sample are combined and replotted in Figure 7.25.

Figure 7.24 Normalized PL spectra of mixed-dimensional CsPbBr_3 perovskite films with different mol% excess concentration of (a) 1-NMA, (b) 2-NMA, (c) 1-NEA, and (d) 2-NEA ligand molecules.

Figure 7.25 Normalized PL spectra of mixed-dimensional CsPbBr₃ perovskites with (a) 40 mol%, (b) 60 mol%, and (c) 100 mol% excess naphthyl ligand molecules. Graph on the right of (c) shows the magnified logarithmic plot of the region of interest (boxed in green), showing absence of quasi-2D emission.

As compared to the PL spectra of the phenyl alkyl study (Figure 7.10), the PL spectra of the naphthyl-based samples here do not exhibit any quasi-2D emission, even if the lower wavelength region has been magnified for the 100 mol% excess ligand concentrations (Figure 7.25c). From the normalized curves in Figure 7.24, all samples show blueshift in the peak emission with increasing concentration of ligand molecules, which is in line with the previous studies with other ligand molecules, although the shift for the 1-NMA samples is more gradual as compared to the other three naphthyl molecules. This can be better observed from Figure 7.25a-c, where the black curves corresponding to the 1-NMA samples always lie closest to the 3D emission peak at 525 nm (orange curve), whereas the

other three samples have emission peaks moving further and further away. This is likely due to the increase in quasi-2D phases as seen in the absorption spectra, which once again explains the blueshift in the photograph images of 2-NMA, 1-NEA and 2-NEA samples with 100 mol% excess ligand additives in Figure 7.18.

Apart from the blueshift, the presence of the quasi-2D phases for 2-NMA, 1-NEA and 2-NEA may have affected the colour purity of the PL emission. The full width at half maximum (FWHM) of the PL spectrum of each sample is plotted against the concentration of excess ligand molecule as shown in Figure 7.26.

Figure 7.26 Full width at half maximum (FWHM) of the PL spectrum of each naphthyl-based mixed-dimensional CsPbBr_3 perovskite sample plotted against the concentration of ligand molecule (in excess mol%).

While the FWHM of the 1-NMA sample increases slightly with concentration, high colour purity is still retained ($\text{FWHM} \leq 20$ nm) even at a high concentration of 100 mol% excess ligand molecule. On the other hand, the 2-NMA, 1-NEA and 2-NEA samples show peak broadening to a larger extent as a result of the extra quasi-2D phases, which results in poorer colour purity of the emission.

7.2.9 Electroluminescence Characteristics of Naphthyl-based Mixed-Dimensional PeLEDs

PeLED devices of each naphthyl ligand molecule were fabricated with different excess concentrations from 20 to 100 mol%. The J-V-L characteristics are plotted in Figure 7.27, with the current efficiency and EQE graphs shown in Figure 7.28 and 7.29 respectively. A summary of the characteristic device parameters is tabulated in Table 7.3.

Figure 7.27 J-V-L graphs of mixed-dimensional CsPbBr₃ PeLEDs fabricated with different concentration of naphthyl ligand molecules: (a) 1-NMA, (b) 2-NMA, (c) 1-NEA, and (d) 2-NEA.

Figure 7.28 Current efficiency versus luminance graphs of mixed-dimensional CsPbBr₃ PeLEDs fabricated with different concentration of naphthyl ligand molecules: (a) 1-NMA, (b) 2-NMA, (c) 1-NEA, and (d) 2-NEA.

Figure 7.29 EQE versus current density graphs of mixed-dimensional CsPbBr_3 PeLEDs fabricated with different concentration of naphthyl ligand molecules: (a) 1-NMA, (b) 2-NMA, (c) 1-NEA, and (d) 2-NEA.

Table 7.3 Summary of device performance of mixed-dimensional CsPbBr₃-based PeLEDs with 1-NMA, 2-NMA, 1-NEA, and 2-NEA as ligand molecules.

Excess ligand (mol%)	L _{max} (cd m ⁻²)	V _{th} (V)	Curr. Eff. (cd A ⁻¹)	EQE (%)	Offset btw J _{th} and V _{th} (V)	λ _{EL} (nm)	FWHM _{EL} (nm)
3D CsPbBr₃	800	4	0.27	0.07	1.87	524	19
1-NMA	20%	5.2k	3	1.57	0.45	519	20
	40%	9.3k	2.7	15.42	4.46	518	20
	60%	13.2k	2.6	20.2	6.01	516	20
	80%	8.3k	2.6	14.28	4.34	515	21
	100%	2.2k	2.7	5.42	1.63	515	22
2-NMA	20%	10.1k	3.1	2.36	0.78	514	21
	40%	11.8k	3.1	3.91	1.22	514	22
	60%	1.0k	3.2	0.70	0.26	507	26
	80%	0.3k	3.2	0.78	0.38	499	28
	100%	0.04k	3.3	0.60	0.35	494	30
1-NEA	20%	9.5k	3.2	2.06	0.66	513	22
	40%	8.9k	3.2	3.59	1.14	513	23
	60%	5.2k	3.1	6.79	2.45	509	25
	80%	0.03k	3.8	0.12	0.06	497	28
	100%	0.008k	4.6	0.06	0.05	490	29
2-NEA	20%	18.9k	3.1	3.84	1.24	512	23
	40%	15.0k	3.2	5.86	1.98	511	24
	60%	2.5k	3.2	3.77	1.57	504	26
	80%	0.5k	3.3	0.99	0.51	498	27
	100%	0.02k	3.8	0.30	0.17	495	29

As compared to the 3D CsPbBr₃ device, all four naphthyl ligand molecules produce an improvement in device performance, with lower turn-on voltage, higher luminance and efficiencies, in line with the previous study with PEA. The best ligand concentration lies around 40 or 60 mol% for all multidimensional devices. Comparing the four different naphthyl devices, 1-NMA outperforms the other three molecules, with current efficiency

and EQE of 20.2 cd A^{-1} and 6.01% respectively, which is almost 2 orders of magnitude higher than the 3D CsPbBr₃. The best efficiencies for 2-NMA, 1-NEA and 2-NEA are 3.91 cd A^{-1} (1.22%), 6.79 cd A^{-1} (2.45%), and 5.86 cd A^{-1} (1.98%) respectively. The current efficiency (Figure 7.28) and EQE (Figure 7.29) curves look similar as the emission wavelengths are not too far apart (Table 7.3). The V_{th} for 1-NMA is lower at 2.6 V as compared to the other three naphthyl devices, which show turn-on voltage of more than 3 V. All four naphthyl PeLEDs show high luminance of close to or even higher than 10 k cd m^{-2} , as compared to the 3D CsPbBr₃ PeLED, which gave less than 1 k cd m^{-2} . The offset between current turn-on (J_{th}) and luminance turn-on (V_{th}) is calculated by taking the difference between the voltage at which the current density changes gradient (injection) and the voltage at which the luminance reaches 1 cd m^{-2} (recombination). A smaller offset implies a shorter delay between charge injection and radiative recombination, which essentially relates to how effective the carrier confinement is within the perovskite emitter layer. As compared to the 3D CsPbBr₃ device which shows an offset of close to 2 V, all naphthyl-based mixed-dimensional PeLEDs show offsets below 1 V. The smallest offset is recorded at 0.2 V for the 60% 1-NMA sample, which demonstrates its strong carrier confinement effect and further explains its high efficiencies.

By plotting the efficiencies against ligand concentration for each of the naphthyl molecules (Figure 7.30), a better comparison of the samples can be made at each concentration.

Figure 7.30 Comparison of (a) current efficiency and (b) EQE of mixed-dimensional CsPbBr₃ PeLEDs with the different naphthyl ligand molecules against concentration.

By examining the efficiency trends in Figure 7.29, at 40 mol% excess ligand molecule, the performance can be ranked as such: 1-NMA > 2-NEA > 2-NMA and 1-NEA. Interestingly, this trend almost exactly corresponds to the amount of 3D phase as seen from the absorption spectra (Figure 7.22a), where the 40% 1-NMA sample retains the most amount of 3D absorption followed by 2-NEA and the rest. At 60 mol% excess ligand molecule, the 1-NEA device has overtaken 2-NEA such that the device performance is now ranked as such: 1-NMA > 1-NEA > 2-NEA > 2-NMA. By comparing this with the absorption spectra of the 60 mol% samples (Figure 7.22b), this correlation is again observed where the 1-NEA sample has more 3D absorption component than 2-NEA. At 100 mol% excess ligand molecule, all three naphthyl molecules (2-NMA, 1-NEA and 2-NEA) have seen their efficiencies plummet to lower than 1 cd A⁻¹, whereas the 1-NMA sample is still able to achieve more than 5 cd A⁻¹. By looking closely at the absorption spectra for the 100 mol% samples (Figure 7.22c), only the 1-NMA sample still retains a significant amount of 3D absorption component while the other three samples seem to have their 3D absorption almost completely diminished. From this comparison, the proportion of the 3D phase seems to have a direct impact on the device performance, which is likely because it determines the amount of emitting area in the film. Here, the importance of the 3D component is once again underlined as a critical factor contributing to the effective choice of ligand molecule.

The EL spectra of the 40 and 60 mol% devices are plotted in Figure 7.31. The shift in peak position with increasing ligand concentration is consistent with that observed in the PL spectra (Figure 7.23). All samples undergo a blueshift with increasing ligand concentration, although 1-NMA shows the smallest shift, likewise to its PL. The FWHM of each EL spectrum is measured and shown in Table 7.3, along with the trend plotted in Figure 7.32.

Figure 7.31 EL spectra of mixed-dimensional CsPbBr₃ PeLEDs with 40 and 60 mol% excess of naphthyl ligand molecules: (a) 1-NMA, (b) 2-NMA, (c) 1-NEA, and (d) 2-NEA.

Figure 7.32 Full width at half maximum (FWHM) of the EL spectrum of each naphthyl-based mixed-dimensional CsPbBr₃ PeLED plotted against the concentration of ligand molecule (in excess mol%).

The increase in FWHM of the PL spectra (Figure 7.26) with increasing ligand concentration is again reflected in the FWHM of the EL spectra (Figure 7.32). While pure CsPbBr₃ shows the lowest FWHM of 19 nm, increasing concentration of 1-NMA to 60 mol% does not drastically change its FWHM, keeping it at 20 nm, which allows the colour purity to be retained. Further increase to 100 mol% gradually increases its FWHM to 22 nm. On the other hand, all three other naphthyl systems (2-NMA, 1-NEA and 2-NEA) undergo accelerated peak broadening, with FWHM_{EL} reaching more than 25 nm at 60 mol%, and close to 30 nm at 100 mol%. This is again due to the increase in quasi-2D states and suppression of 3D component (Figure 7.22), resulting in poorer colour purity in the emission. Based on the EL spectra, the CIE coordinates of the 40 and 60 mol% devices are shown in Figure 7.33. While the 1-NMA devices (both 40 and 60 mol%) show CIE coordinates close to the highest green region, all three other devices saw a rapid drop to the blue region at 60 mol% (Figure 7.33b).

Figure 7.33 Corresponding CIE coordinate based on EL spectra for (a) 40 mol% and (b) 60 mol% excess ligand additive.

The EL peak position is lastly plotted against applied bias (Figure 7.34), showing that the blueshift is independent of the voltage, implying that the blueshift is from the mixed-dimensional perovskite material itself.

Figure 7.34 Plot of EL peak position versus voltage, showing negligible change in emission wavelength with increasing bias.

7.3 Conclusion

Chapter 7 warrants being the longest chapter due to the systematic study of various families of ligand molecules, comparing a total of 10 different molecules. The effect of the size of the ligands is tested by increasing the size of the spacer structure, from alkyl to phenyl to naphthyl groups, the main objective being aimed at modulating the formation of lower dimensional quasi-2D states and maximizing the formation of the 3D phase. While some amount of ligand molecules is required to achieve a compact film morphology and efficient energy cascade, too much of it will suppress the 3D phase and a consequential reduction in the amount of emissive domains. In order to form mixed-dimensional perovskites without forming excessive quasi-2D states, using larger spacer cations is speculated to restrict the incorporation of these ligand molecules. This chapter starts by screening the octyl and phenyl alkyl spacer groups and confirms the suppression of quasi-2D states with larger spacer structures. However, the long spacer group of the alkyl chains concomitantly brought along problems with charge transport due to the insulating carbon chains. To overcome this, the naphthyl family of acene molecules is proposed, which consists of linearly fused benzene rings in a fully conjugated structure. Due to the asymmetry of the naphthyl structure, a total of four different naphthyl ligand molecules were studied, half of which are regioisomers. Although the naphthyl-based mixed-dimensional system again proves that the larger molecules successfully suppressed the quasi-2D absorption and emission states, another important factor is realized that the 3D absorption component should not be overlooked. While all four naphthyl ligand molecules show that the quasi-2D states are largely modulated, only 1-NMA shows retention of its 3D component even at high ligand concentration. This particular characteristic becomes an even more crucial factor when comparing the performances of PeLED devices, showing that both the suppression of the quasi-2D states and maximizing the 3D component are vital elements that determine how efficient the devices are. With this, the 1-NMA device at 60 mol% ligand concentration shows the highest current efficiency and EQE of 20.2 cd A^{-1} and 6.01% respectively, much higher compared to the other three naphthyl devices. The efficiency trend of the devices is directly in line with the 3D absorption component of the thin film samples, emphasizing the importance of the balance between 3D and quasi-2D phases, which is often overlooked when figuring out ways to suppress the quasi-2D components.

By comparing to the phenyl alkyl study, the efficiency of the 1-NMA device is more than twice that of the best PEA device, showing not only the importance of a larger spacer structure for reducing quasi-2D states, but also the importance of conjugation for better charge transport. All in all, this study confidently concludes, with the vast supporting experimental observations, several important factors that should be taken into consideration while judiciously selecting a ligand molecule for mixed-dimensional perovskites:

- I. The formation of quasi-2D states can be modulated with the correct choice of spacer structures. Ligand molecules with larger spacer structures should be used for suppression of the quasi-2D states.
- II. The 3D phase formation should not be overlooked while trying to control the quasi-2D phase formation as this phase is where majority of the radiative recombination takes place. As much as the quasi-2D phase should be suppressed, the 3D phase should, at the same time, be monitored such that it is not compromised and still retains the majority of its absorption feature.
- III. While exploring larger ligand molecules, choosing longer alkyl spacer structures is not the way to go as issues with charge transport come into play. To eliminate this limitation, a more conjugated structure is recommended.

The conclusions may not necessarily apply to the inorganic perovskite system alone, but also to the organic-inorganic hybrid counterparts such as MA and FA perovskite systems. From here, future work will entail exploration into various families of ligand molecules for mixed-dimensional perovskites that satisfy the criteria set above. The acene class of organic spacer groups represents a promising route to progress research on, including the anthracene and tetracene ligand molecules, as well as other non-linear variants such as pyrenes. Furthermore, additional functionalities can be explored for these ligand molecules, such as a carboxylic or phosphonic acid end group for passivation of defect sites.¹⁹⁻²¹

References

1. Xiao, Z.; Kerner, R. A.; Zhao, L.; Tran, N. L.; Lee, K. M.; Koh, T.-W.; Scholes, G.

- D.; Rand, B. P., Efficient Perovskite Light-Emitting Diodes Featuring Nanometre-Sized Crystallites. *Nature Photonics* **2017**, *11* (2), 108-115.
2. Cho, J.; Choi, Y.-H.; O'Loughlin, T. E.; De Jesus, L.; Banerjee, S., Ligand-Mediated Modulation of Layer Thicknesses of Perovskite Methylammonium Lead Bromide Nanoplatelets. *Chemistry of Materials* **2016**, *28* (19), 6909-6916.
3. Gan, L.; Li, J.; Fang, Z.; He, H.; Ye, Z., Effects of Organic Cation Length on Exciton Recombination in Two-Dimensional Layered Lead Iodide Hybrid Perovskite Crystals. *The Journal of Physical Chemistry Letters* **2017**, *8* (20), 5177-5183.
4. Zhu, F.; Men, L.; Guo, Y.; Zhu, Q.; Bhattacharjee, U.; Goodwin, P. M.; Petrich, J. W.; Smith, E. A.; Vela, J., Shape Evolution and Single Particle Luminescence of Organometal Halide Perovskite Nanocrystals. *ACS Nano* **2015**, *9* (3), 2948-2959.
5. Bai, S.; Yuan, Z.; Gao, F., Colloidal Metal Halide Perovskite Nanocrystals: Synthesis, Characterization, and Applications. *Journal of Materials Chemistry C* **2016**, *4* (18), 3898-3904.
6. Huang, H.; Polavarapu, L.; Sichert, J. A.; Susha, A. S.; Urban, A. S.; Rogach, A. L., Colloidal Lead Halide Perovskite Nanocrystals: Synthesis, Optical Properties and Applications. *Npg Asia Materials* **2016**, *8*, e328.
7. Bhaumik, S.; Veldhuis, S. A.; Ng, Y. F.; Li, M.; Muduli, S. K.; Sum, T. C.; Damodaran, B.; Mhaisalkar, S.; Mathews, N., Highly Stable, Luminescent Core-Shell Type Methylammonium-Octylammonium Lead Bromide Layered Perovskite Nanoparticles. *Chemical Communications* **2016**, *52* (44), 7118-7121.
8. Fu, P.; Shan, Q.; Shang, Y.; Song, J.; Zeng, H.; Ning, Z.; Gong, J., Perovskite Nanocrystals: Synthesis, Properties and Applications. *Science Bulletin* **2017**, *62* (5), 369-380.
9. Huang, H.; Bodnarchuk, M. I.; Kershaw, S. V.; Kovalenko, M. V.; Rogach, A. L., Lead Halide Perovskite Nanocrystals in the Research Spotlight: Stability and Defect Tolerance. *ACS Energy Letters* **2017**, *2* (9), 2071-2083.
10. Chin, X. Y.; Perumal, A.; Bruno, A.; Yantara, N.; Veldhuis, S. A.; Martínez-Sarti, L.; Chandran, B.; Chirvony, V.; Lo, A. S.-Z.; So, J.; Soci, C.; Grätzel, M.; Bolink, H. J.; Mathews, N.; Mhaisalkar, S. G., Self-Assembled Hierarchical Nanostructured Perovskites Enable Highly Efficient LEDs via an Energy Cascade. *Energy & Environmental Science*

2018, *11* (7), 1770-1778.

11. Akkerman, Q. A.; Rainò, G.; Kovalenko, M. V.; Manna, L., Genesis, Challenges and Opportunities for Colloidal Lead Halide Perovskite Nanocrystals. *Nature Materials* **2018**, *17* (5), 394-405.
12. Li, J.; Xu, L.; Wang, T.; Song, J.; Chen, J.; Xue, J.; Dong, Y.; Cai, B.; Shan, Q.; Han, B.; Zeng, H., 50-Fold EQE Improvement up to 6.27% of Solution-Processed All-Inorganic Perovskite CsPbBr₃ QLEDs via Surface Ligand Density Control. *Advanced Materials* **2017**, *29* (5), 1603885.
13. Chiba, T.; Hoshi, K.; Pu, Y.-J.; Takeda, Y.; Hayashi, Y.; Ohisa, S.; Kawata, S.; Kido, J., High-Efficiency Perovskite Quantum-Dot Light-Emitting Devices by Effective Washing Process and Interfacial Energy Level Alignment. *ACS Applied Materials & Interfaces* **2017**, *9* (21), 18054-18060.
14. Kim, Y.-H.; Lee, G.-H.; Kim, Y.-T.; Wolf, C.; Yun, H. J.; Kwon, W.; Park, C. G.; Lee, T. W., High Efficiency Perovskite Light-Emitting Diodes of Ligand-Engineered Colloidal Formamidinium Lead Bromide Nanoparticles. *Nano Energy* **2017**, *38*, 51-58.
15. Zhang, Q.; Yin, Y., All-Inorganic Metal Halide Perovskite Nanocrystals: Opportunities and Challenges. *ACS Central Science* **2018**, *4* (6), 668-679.
16. Gao, F., *Advanced Nanomaterials for Solar Cells and Light Emitting Diodes*. Elsevier: 2019.
17. Cohen, B.-E.; Wierzbowska, M.; Etgar, L., High Efficiency Quasi 2D Lead Bromide Perovskite Solar Cells Using Various Barrier Molecules. *Sustainable Energy & Fuels* **2017**, *1* (9), 1935-1943.
18. Du, K.-z.; Tu, Q.; Zhang, X.; Han, Q.; Liu, J.; Zauscher, S.; Mitzi, D. B., Two-Dimensional Lead(II) Halide-Based Hybrid Perovskites Templated by Acene Alkylamines: Crystal Structures, Optical Properties, and Piezoelectricity. *Inorganic Chemistry* **2017**, *56* (15), 9291-9302.
19. Brown, A. A. M.; Hooper, T. J. N.; Veldhuis, S. A.; Chin, X. Y.; Bruno, A.; Vashishtha, P.; Tey, J. N.; Jiang, L.; Damodaran, B.; Pu, S. H.; Mhaisalkar, S. G.; Mathews, N., Self-Assembly of a Robust Hydrogen-Bonded Octylphosphonate Network on Cesium Lead Bromide Perovskite Nanocrystals for Light-Emitting Diodes. *Nanoscale* **2019**, *11* (25), 12370-12380.

20. Xu, K.; Vickers, E. T.; Rao, L.; Lindley, S. A.; Allen, A. L. C.; Luo, B.; Li, X.; Zhang, J. Z., Synergistic Surface Passivation of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Perovskite Quantum Dots with Phosphonic Acid and (3-Aminopropyl)triethoxysilane. *Chemistry – A European Journal* **2019**, 25 (19), 5014-5021.
21. Li, N.; Xu, F.; Qiu, Z.; Liu, J.; Wan, X.; Zhu, X.; Yu, H.; Li, C.; Liu, Y.; Cao, B., Sealing the Domain Boundaries and Defects Passivation by Poly(Acrylic Acid) for Scalable Blading of Efficient Perovskite Solar Cells. *Journal of Power Sources* **2019**, 426, 188-196.

Chapter 8

Conclusion and Outlook

This chapter summarizes the work reported in this thesis and links them towards the original motivation and objective, which is aimed towards addressing and overcoming the limitation of carrier confinement of CsPbBr₃ as a perovskite emitter material. The confinement effect is explored through a geometrical (spatial) and dimensional (electronic) approach. The geometrical approach involves tuning of the morphological structures via a rapid crystallization (Chapter 4) or a sequential deposition (Chapter 5) process, whereas the dimensional approach entails the combinatory effect of energy cascading and morphological improvement through the use of a mixed-dimensional CsPbBr₃ perovskite (Chapter 6). The dimensional approach is explored further in Chapter 7 through systematic studies of various families of ligand molecules and rigorous comparisons of each characterization to conclusively derive a set of crucial criteria in designing effective spacer structures for mixed-dimensional perovskites. In every chapter, the films were extensively studied along with device comparison to assess the role of charge confinement in influencing the optoelectronic properties of the perovskite emitter. The implications along with the scientific outlook based on conclusive evidence from this entire work will be discussed in broader context of this research field, while possible future work is proposed based on the insights derived.

8.1 Summary of Thesis

This thesis focuses on the inorganic class of halide perovskite material, more specifically, CsPbBr₃, due to its better thermal and ambient stability as compared to the organic-inorganic hybrid counterparts like MAPbBr₃ or FAPbBr₃. However, the conclusions made from each study does not necessarily apply only to the inorganic system, but likely to any halide perovskite systems used for light-emitting applications. The inherent problems of pristine CsPbBr₃ such as low exciton binding energy and poor morphology of the solution-processed film brings about issues such as poor carrier confinement, but this limitation also presents opportunities to research ways to overcome it. While the strength of the confinement effect is determined by intrinsic properties of the material itself, extrinsic factors can be employed to influence it to a significant extent. In this thesis, the confinement effect is studied through two main routes: geometrical control and dimensional modulation, with each route expanded to two separate chapters.

8.1.1 Geometrical Confinement

The first study of geometrical confinement is aimed towards using grain size to increase the radiative recombination of CsPbBr₃. Although it has been widely known that larger grains are better for PV devices, the opposite appears to be true for LED applications. This can be explained by the fact that solar cells require charge carriers to be separated and extracted while LEDs require them to recombine, thus charge confinement is desired for PeLEDs but not for PSCs. The work in Chapter 4 uses a N₂-facilitated process to rapidly crystallize the CsPbBr₃ film and pin the nucleated crystals to obtain smaller grains with less percolated microstructures. As compared to the pristine film by conventional spin-coating, the N₂-facilitated sample shows better optical and EL properties, in terms of higher PLQY and device performance. PeLEDs fabricated with this process achieved a luminance of more than 8k cd m⁻² along with a current efficiency of more than 0.7 cd A⁻¹, which is more than six times that of the control device. Along with various experiments done to eliminate contribution from other factors such as film thickness, this work conclusively

proves that indeed smaller grain sizes are required for better confinement of charge carriers and more efficient devices.

While the first work conclusively determines that smaller grain sizes are more desirable due to the stronger spatial charge confinement, the poor coverage in film morphology still implies that the vast uncovered area remains unconfined. These exposed areas mean the injected charge carriers can easily leak through, resulting in non-radiative recombination losses, which could otherwise enhance the film emission have they been effectively confined within a fully covered emitter film. This coverage limitation intrinsically stems from the poor solubility of the ionic precursor CsBr. Chapter 5 then seeks to overcome this by using a sequential deposition method, where the deposition of the precursor solution is decoupled. PbBr₂ is first coated on the substrate before dipping in a dilute CsBr solution to convert to CsPbBr₃. This approach essentially nullifies the solubility limitation of CsBr since the conversion to CsPbBr₃ is now mainly dependent on the exposure time. Although this sequential process is more sophisticated and requires more steps than the single-step spin-coating method, it allows more control over the deposition and growth of the individual precursor compounds and therefore the final film morphology can be more precisely modulated. This work shows that by optimizing two key variables, the initial PbBr₂ concentration and the exposure duration to the CsBr solution, over 90% film coverage can be achieved, while the single-step spin-coating method can only obtain less than 70% coverage. Although the degree of conversion to CsPbBr₃ improves with longer exposure time, the film coverage starts to decrease, possibly due to the preferred vertical growth of the converted crystals. At a PbBr₂ concentration of 0.5 M and an exposure time of 5 min in the CsBr solution, the resultant CsPbBr₃ exhibits the best film coverage along with complete perovskite conversion. Fabrication of proof-of-concept devices shows the highest efficiency of 7.6×10^{-2} cd A⁻¹ for the optimized condition, while longer exposure times led to poorer device performances due to increase in thickness and grain size and reduction in film coverage.

The sequential deposition method appears to give better control over coverage and compactness of the CsPbBr₃ film, which leads to lesser leakage pathways and non-radiative

recombination losses and better confinement of charge carriers within the perovskite layer. However, several drawbacks were discovered from this method. Firstly, there is a lack of control over the converted grain size and thickness of the film. During the dipping and conversion process from PbBr_2 , the growth of the CsPbBr_3 crystals with exposure time means that it is difficult to reduce the grain size and thickness without sacrificing the degree of perovskite phase conversion. The larger grains and thicker film ultimately lead to poorer spatial confinement of charge carriers. Due to the non-uniform growth of the converted CsPbBr_3 crystals, the rougher film morphology also requires a thicker ETL to fully cover the perovskite EML, which gives rise to additional bulk resistance in electron transport. The disadvantages of this process eventually lead to poorer devices as compared to the single-step method in Chapter 4, albeit the improvement in coverage from $<70\%$ to $>90\%$.

Overall, Chapters 4 and 5 demonstrate the importance of geometrical confinement through modulation in film morphology. The methodologies used in both chapters focus on modulating the mechanism of film crystallization using physical approaches, without the use of any additives. Both sets of results conclude that an ideal film morphology requires the following traits: small grain size along with a compact and smooth film with minimum thickness. While physical approaches may not be able to achieve all the desired traits, chemical approaches through additive engineering may be able to overcome the physical limitations. Based on this, subsequent work is shifted to using ligand molecules to create multidimensional perovskites.

8.1.2 Electronic Confinement

Chapter 6 ventures out to explore the electronic confinement of charge carriers through a dimensional approach. In this work, carrier confinement is achieved through the concept of energy funnelling from a mixed-dimensional CsPbBr_3 perovskite. This multidimensional system is obtained by incorporating a large spacer cation, known as a ligand molecule, into the 3D perovskite framework of CsPbBr_3 , resulting in the formation of quasi-2D phases alongside the 3D phase. By optimizing the molar excess addition of a

commonly used ligand molecule, PEABr, an improved morphology based on the ideal traits concluded in the previous two chapters was achieved, with highly uniform, smooth, compact and nano-sized grains with a small thickness of ~ 80 nm. On top of the geometrical confinement contributed by the morphological enhancement, it is found that the energy cascade provided by the mixed phases allows efficient energy channelling from the higher band gap domains to the lowest band gap phase. This funnelling process greatly augments the charge carrier density within the emissive domains, resulting in higher radiative recombination probability. The importance of this energy landscape is highlighted through excitation and transient spectroscopic analyses, while the benefits are directly reflected in the device performances of the mixed-dimensional PeLEDs. With an optimized ligand concentration of 80 mol% PEABr, devices show current efficiencies of up to 6.16 cd A^{-1} (EQE of $\sim 2\%$) with close to 10k cd m^{-2} of luminance. The enhancement in efficiency values as compared to the pure 3D CsPbBr₃ device is more than 50-fold. In addition, the dimensional confinement shown in this work far outperforms the geometrical approach shown in Chapter 4 and 5, strongly emphasizing that more research should be focused on the mixed-dimensional perovskite system.

The promising results from Chapter 6 in turn inspired the work in Chapter 7. While the work done in Chapter 6, along with most published literatures, shows only one type of ligand molecule with differing concentrations and the effect on film properties and device performance, the question of how to choose or even design a good ligand molecule remains unestablished. Chapter 7 aims to tackle this unknown and bring to light the ideal traits that are desired for an efficient ligand molecule. In this chapter, it is hypothesized that the size of the ligand molecule will affect how much it gets incorporated into the final film. A more bulky ligand molecule will be harder to incorporate and thus the lower dimensional phases will become suppressed, although at the same time, sufficient ligand molecules should be present to achieve a compact morphology and efficient energy cascade. The initial part of this work focuses on increasing the size of the ligand molecule by using longer alkyl chains, such as OABr, as well as five different phenyl alkyl ligands with different lengths of carbon chain linking the benzene ring and the ammonium functional group. Although it is shown that the longer ligand molecules are able to suppress the quasi-2D states and lead to stronger

emission from the 3D phase, the increasing alkyl chains, which are insulating in nature, present another issue with charge transport, as confirmed by the low current density and poor device performances. To eliminate this factor, the focus shifts to the naphthyl family of ligand molecules, which consist of fully conjugated structures. Two naphthyl ligand molecules with short alkyl chains are selected, 1-NMA and 1-NEA, along with their regioisomers, 2-NMA and 2-NEA, totalling to four different ligand molecules. While the naphthyl ligand molecules also show suppression in the quasi-2D states in line with the previous observations, the 3D phase component, which is often overlooked, seems to change with different ligand molecule as well. This factor will later play a crucial role in determining the performance of the naphthyl-based mixed-dimensional PeLEDs. Eventually, 1-NMA (with 60 mol% excess ligand concentration) devices turn out to give the highest current efficiency of 20.2 cd A^{-1} (EQE of 6.01%), along with a high luminance of more than 13 k cd m^{-2} . The efficiency attained here is almost two orders of magnitude higher than the standard 3D CsPbBr_3 , and is the highest compared to all other chapters, reinforcing the importance of this study towards more efficient PeLEDs. Importantly, through a series of rigorous analysis and comparison of the different systems used in this study, it is finally concluded, with strong supporting evidence, three key traits required of a ligand molecule for mixed-dimensional perovskites: i) a larger ligand molecule is desired for suppression of quasi-2D phases, ii) the mixed-dimensional perovskite should retain majority of its 3D absorption component, and iii) a fully conjugated molecular structure is needed for charge transport within the mixed-dimensional perovskite.

The conclusions of Chapter 6 and 7 seem to suggest that the device performance of mixed-dimensional PeLEDs can be further improved with careful selection and optimization of ligand molecules based on the knowledge and insights learned from these works. The future of PeLEDs strongly points to the mixed-dimensional systems, which combine the effects of geometrical and electronic confinement, leading to brighter and more efficient devices that can rival OLEDs and QDLEDs.

8.2 Overall Contributions and Implications

- Using a modified gas-facilitated spin-coating technique, reduction in CsPbBr_3 grain size has been achieved through the effect of rapid crystallization. The use of an extremely facile and scalable technique has been shown here to highlight the importance of geometrical (spatial) confinement through modulation of perovskite grain size. Although the concept of smaller grain size for stronger spatial confinement has been debatable in several literatures showing high efficiencies in perovskite films with large grains, this work reasserts the concept and confirms that smaller grains are desired for PeLEDs.
- By decoupling the deposition of each precursor through a sequential process, the solubility limitation of CsBr can be overcome, resulting in a significant improvement in film coverage to more than 90%. The critical variables here are found to be the initial PbBr_2 concentration as well as the exposure time in the CsBr solution. A mono PbBr_2 base layer with sufficient coverage is required for optimal chemical reaction and conversion to CsPbBr_3 with the desired final morphology, while an optimum exposure time is necessary for diffusion and reaction to occur, but concomitantly, not excessively to cause significant grain growth. Although the sequential deposition procedure has been shown previously for solar cell applications, this work represents the first of such process used on CsPbBr_3 for LEDs.
- The study on multidimensional CsPbBr_3 perovskite shows the first of such work on inorganic perovskite for LED applications. The energy funnelling process is carefully investigated using time-resolved PL spectroscopy. By measuring the lifetime at each quasi-2D emission wavelengths, it is shown that the energy from the higher band gap domains is transferred all the way to the lowest band gap phase, indicating that this technique can be very useful in studying the funnelling mechanism in multidimensional perovskite systems. The mixed-dimensional perovskite shows remarkable enhancement in its device performance, ascribed to a combination of improved morphology as well as the energy cascading effect, strongly suggesting that this field holds high promise in achieving more efficient PeLEDs.

- Finally, a systematic and comprehensive study has been conducted to elucidate the ideal traits required of a ligand molecule, a research gap that still requires answers to. In this work, an extensive study on 10 different ligand molecules along with rigorous comparison of each characterization has shed light on how an effective ligand molecule should be designed and what properties the resultant mixed-dimensional perovskite should hold. Finally, a list of guidelines is established for the screening of ligand molecules for mixed-dimensional perovskites. The conclusions of this work do not necessarily apply to only the inorganic perovskite, but also to all halide perovskite systems.

8.3 Outlook and Future Directions

Based on the conclusions of this thesis, the future direction to achieve high efficiency PeLEDs seems to point towards the mixed-dimensional perovskites due to the strong geometrical and electronic confinement possessed by these systems.

8.3.1 Exploration into Functional Molecular Design

Using the selection criteria concluded at the end of Chapter 7 that clarified the ideal characteristics of a ligand molecule and its corresponding mixed-dimensional perovskite, it is now more straightforward to find better ligand molecules. The general guideline is to find larger but also conjugated ligand molecules that form mixed-dimensional perovskites with minimal quasi-2D states and maximal 3D absorption component. The most obvious choices will be polycyclic aromatic hydrocarbons (PAHs), fully conjugated molecules consisting of multiple benzene rings fused either linearly (acenes) or non-linearly. The linear class of PAHs include anthracene (3), tetracene (4) and pentacene (5) in increasing order of number of benzene rings assigned in brackets. The non-linear PAHs can consist of benzene rings fused in different manners, thus having several structural isomers that can

differ in steric hindrance. They include phenanthrene (3), phenalene (3), chrysene (4), triphenylene (4) and pyrene (4), with all the proposed molecular structures shown in Figure 8.1. The larger molecules will have even more different possible combinations of regioisomers, where the position of the alkyl ammonium functional group may lead to different properties of the ligand molecule. While larger and more bulky ligand molecules are being explored, there are also questions of how large they can go and what happens when too large a ligand molecule is used. Filling in these research gaps will then finally address the ideal size requirement of a ligand molecule.

Figure 8.1 Molecular structures of various proposed PAHs.

In addition, the ligand molecule can be further functionalized to give extra functionalities. For instance, carboxylic acids like amino valeric acid or poly(acrylic) acid have been used to passivate surface defect sites in perovskite solar cells,¹⁻² thus increasing the resistance against oxygen-induced degradation and increasing the PCE; phosphonic acids have also been shown to passivate Pb^{2+} and CH_3NH_3^+ surface defects¹ as well as CsPbBr_3 NCs surface through strong hydrogen bonds,³ leading to enhancement in PLQY and efficiency

of the passivated PeLEDs. Besides the ammonium group required for formation of mixed-dimensional perovskites, an additional carboxylic or phosphonic acid group can be attached to the ligand molecule, forming a zwitterion with dual functions. A mixed-dimensional perovskite that is well-passivated will be able to achieve even higher carrier confinement with minimization of non-radiative traps-related losses, leading to higher PLQY and device EQE.

Furthermore, the organic ligand molecule may have its own unique set of properties which may either compliment or have a negative effect on the final properties of the mixed-dimensional perovskite. For instance, anthracene, chrysene, triphenylene and pyrene core structures have been used for blue light emission in OLEDs,⁴⁻¹⁰ which may contribute an additional energy cascade pathway if the energy band levels align favourably. While comparing the size of the spacer structures, their inherent properties should also be taken into consideration as these characteristics can be exploited to achieve even more novel and better materials.

8.3.2 Assessment of Charge Injection Balance

Besides focusing on the perovskite emitter, the charge carrier injection balance should not be overlooked. Mixing a ligand additive to form mixed-dimensional perovskites may have altered some properties unknowingly. For instance, the delocalization of electrons in a benzene molecule makes it electron-rich. By having increasing number of fused conjugated rings, the electron and hole mobility of the resultant film may have shifted in favour of the electrons, which presents another challenge in charge injection balance.

In most of the efficiency curves shown in Chapters 4 – 7, the current efficiency (or EQE) rises with luminance (or current density) up to a certain point, before it rapidly descends, commonly known as the efficiency roll-off phenomenon. A device with balanced injection, however, should show a flat efficiency curve as depicted in Figure 8.2, where a highly balanced injection rate of charge carriers from both the positive and negative terminal leads

to a constant efficiency that is almost independent of current density.¹¹ Possible proposed reasons for this efficiency roll-off can be due to increasing Auger recombination at high current densities,¹² Joule heating that accelerates exciton dissociation,¹³ or the more commonly reported imbalance in charge injection in OLEDs,¹⁴ QDLEDs,¹⁵ and PeLEDs.¹¹

Figure 8.2 Schematic illustrating balanced injection of electrons and holes in a PeLED device, resulting in an almost flat EQE curve with current density from 0.1 to 200 mA cm⁻².¹¹ Reprinted with permission from Fakharuddin, A.; Qiu, W.; Croes, G.; Devižis, A.; Gegevičius, R.; Vakhnin, A.; Rolin, C.; Genoe, J.; Gehlhaar, R.; Kadashchuk, A., Reduced Efficiency Roll-Off and Improved Stability of Mixed 2D/3D Perovskite Light Emitting Diodes by Balancing Charge Injection. *Advanced Functional Materials* **2019**, 1904101. Copyright © 2019 John Wiley and Sons.

The balance between electron and hole injection is paramount to attain a high efficiency that is constant with increasing current density, which not only leads to lesser non-radiative losses at the interfaces, but also a longer operational lifetime of the device. The mobility of electrons and holes in the mixed-dimensional perovskite should be measured to unravel the effects of the ligand molecules on the electrical properties of the perovskite. This can be done through measuring the I-V characteristics of specific charge-only devices (electron- or hole-only devices). If the charge mobility is indeed scaled towards a specific charge, the injected carriers will get accumulated at the interface where the specific charge

injection is limiting. The charge injection then has to be rebalanced through engineering of the device architectures, for instance changing the interfacial layers to suit the change in charge mobility, tuning the thickness of one charge transport layer to modulate its injection rate, or doping of the transport layer to increase its conductivity.

8.3.3 Towards Large-Area PeLEDs

Apart from forming mixed-dimensional perovskites, the ligand molecule additives also act as surfactants which help to improve the film formation and final morphology, as demonstrated in Chapter 6. The presence of these surfactants also allows self-assembly of the film,¹⁶⁻¹⁷ forming extremely smooth and flat films, thus making uniform large-area devices more realizable. Through this mixed-dimensional system, scaling up of PeLED fabrication will be easier, which means that commercialization of such technology is more practicable. Several feasible large-scale deposition techniques are shown in Figure 8.3.

Figure 8.3 Schematic illustrations showing various large-scale solution deposition technologies.¹⁸ Reprinted with permission from Pasquarelli, R. M.; Ginley, D. S.; O'Hayre, R., Solution processing of transparent conductors: from flask to film. *Chemical Society Reviews* **2011**, 40 (11), 5406-5441. Copyright © 2019 Royal Society of Chemistry.

Doctor blading and slot-die casting will be the most efficient methods for large area film deposition, while screen and inkjet printing will be useful if specific patterns are required. These methods can also be used for flexible substrates, thereby adding the possibility of bendable and stretchable PeLEDs for flexible electronic displays.

8.3.3 Unveiling the Contributions from Energy and Carrier Funnelling

While the cascade / funnelling phenomenon of the mixed-dimensional perovskites proves to be an efficient way of electronically confining the charge carriers, it has not been

elucidated whether the energy or charge transfer is the dominant mechanism. Although it is widely accepted that the energy transfer is the main process in the cascade effect, it is also believed that both mechanisms are occurring simultaneously. The charge transfer process will involve less transition since the carrier is directly transferred to the lowest band gap domain. On the other hand, the energy transfer will require multiple transitions including relaxation of a carrier to release a photon, followed by absorption of the photon by a lower energy carrier, and excitation of the second carrier and so on until the energy is finally transferred to the carrier in the lowest band gap domain (Figure 8.4). The multiple transition is likely to involve more energetic losses. It will thus be interesting to deconvolve both processes and uncover the more dominant origin of funnelling and establish new insights to the dynamics involved.

Figure 8.4 Schematic illustrating the different possible funnelling mechanisms (charge transfer or energy transfer) in a quasi-2D perovskite.¹⁹ Reprinted with permission from Chen, P.; Meng, Y.; Ahmadi, M.; Peng, Q.; Gao, C.; Xu, L.; Shao, M.; Xiong, Z.; Hu, B., Charge-transfer versus energy-transfer in quasi-2D perovskite light-emitting diodes. *Nano energy* **2018**, 50, 615-622. Copyright © 2019 Elsevier.

The limiting process should be predicted based on certain properties of the mixed-dimensional perovskite, for example the dielectric constant. Thereafter, a combination of charge dynamics, electrical injection and excitation intensity-dependent PL measurements may be able to extract the contribution from each process. Revealing this will then give a better understanding of how the funnelling mechanism contributes to the device efficiency

and suggest possible approaches to influence the system in favour of the more efficient path of funnelling.

References

1. Xu, K.; Vickers, E. T.; Rao, L.; Lindley, S. A.; Allen, A. L. C.; Luo, B.; Li, X.; Zhang, J. Z., Synergistic Surface Passivation of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Perovskite Quantum Dots with Phosphonic Acid and (3-Aminopropyl)triethoxysilane. *Chemistry – A European Journal* **2019**, 25 (19), 5014-5021.
2. Li, N.; Xu, F.; Qiu, Z.; Liu, J.; Wan, X.; Zhu, X.; Yu, H.; Li, C.; Liu, Y.; Cao, B., Sealing the Domain Boundaries and Defects Passivation by Poly(Acrylic Acid) for Scalable Blading of Efficient Perovskite Solar Cells. *Journal of Power Sources* **2019**, 426, 188-196.
3. Brown, A. A. M.; Hooper, T. J. N.; Veldhuis, S. A.; Chin, X. Y.; Bruno, A.; Vashishtha, P.; Tey, J. N.; Jiang, L.; Damodaran, B.; Pu, S. H.; Mhaisalkar, S. G.; Mathews, N., Self-Assembly of a Robust Hydrogen-Bonded Octylphosphonate Network on Cesium Lead Bromide Perovskite Nanocrystals for Light-Emitting Diodes. *Nanoscale* **2019**, 11 (25), 12370-12380.
4. Chien, C.-H.; Chen, C.-K.; Hsu, F.-M.; Shu, C.-F.; Chou, P.-T.; Lai, C.-H., Multifunctional Deep-Blue Emitter Comprising an Anthracene Core and Terminal Triphenylphosphine Oxide Groups. *Advanced Functional Materials* **2009**, 19 (4), 560-566.
5. Lin, S.-H.; Wu, F.-I.; Liu, R.-S., Synthesis, Photophysical Properties and Color Tuning of Highly Fluorescent 9,10-Disubstituted-2,3,6,7-Tetraphenylanthracene. *Chemical Communications* **2009**, (45), 6961-6963.
6. Thomas, K. R. J.; Kapoor, N.; Bolisetty, M. N. K. P.; Jou, J.-H.; Chen, Y.-L.; Jou, Y.-C., Pyrene-Fluorene Hybrids Containing Acetylene Linkage as Color-Tunable Emitting Materials for Organic Light-Emitting Diodes. *The Journal of Organic Chemistry* **2012**, 77 (8), 3921-3932.
7. Figueira-Duarte, T. M.; Del Rosso, P. G.; Trattnig, R.; Sax, S.; List, E. J. W.; Müllen, K., Designed Suppression of Aggregation in Polypyrene: Toward High-Performance Blue-

Light-Emitting Diodes. *Advanced Materials* **2010**, 22 (9), 990-993.

8. Shin, H.; Jung, H.; Kim, B.; Lee, J.; Moon, J.; Kim, J.; Park, J., Highly Efficient Emitters of Ultra-Deep-Blue Light Made from Chrysene Chromophores. *Journal of Materials Chemistry C* **2016**, 4 (17), 3833-3842.
9. Park, S. N.; Lee, H. W.; Kim, Y. S.; Kim, J.; Lee, S. E.; Lee, H. W.; Kim, Y. K.; Yoon, S. S., Blue Organic Light-Emitting Diodes Based on Phenyl-Bridged Fluoranthene and Triphenylene Derivatives. *Synthetic Metals* **2015**, 206, 124-130.
10. Saleh, M.; Baumgarten, M.; Mavrinskiy, A.; Schäfer, T.; Müllen, K., Triphenylene-Based Polymers for Blue Polymeric Light Emitting Diodes. *Macromolecules* **2010**, 43 (1), 137-143.
11. Fakharuddin, A.; Qiu, W.; Croes, G.; Devižis, A.; Gegevičius, R.; Vakhnin, A.; Rolin, C.; Genoe, J.; Gehlhaar, R.; Kadashchuk, A.; Gulbinas, V.; Heremans, P., Reduced Efficiency Roll-Off and Improved Stability of Mixed 2D/3D Perovskite Light Emitting Diodes by Balancing Charge Injection. *Advanced Functional Materials* **2019**, 29 (37), 1904101.
12. Yang, M.; Wang, N.; Zhang, S.; Zou, W.; He, Y.; Wei, Y.; Xu, M.; Wang, J.; Huang, W., Reduced Efficiency Roll-Off and Enhanced Stability in Perovskite Light-Emitting Diodes with Multiple Quantum Wells. *The Journal of Physical Chemistry Letters* **2018**, 9 (8), 2038-2042.
13. Tyagi, P.; Indu Giri, L.; Tuli, S.; Srivastava, R., Elucidation on Joule Heating and Its Consequences on the Performance of Organic Light Emitting Diodes. *Journal of Applied Physics* **2014**, 115 (3), 034518.
14. Murawski, C.; Leo, K.; Gather, M. C., Efficiency Roll-Off in Organic Light-Emitting Diodes. *Advanced Materials* **2013**, 25 (47), 6801-6827.
15. Dai, X.; Zhang, Z.; Jin, Y.; Niu, Y.; Cao, H.; Liang, X.; Chen, L.; Wang, J.; Peng, X., Solution-Processed, High-Performance Light-Emitting Diodes Based on Quantum Dots. *Nature* **2014**, 515 (7525), 96.
16. Cao, D. H.; Stoumpos, C. C.; Farha, O. K.; Hupp, J. T.; Kanatzidis, M. G., 2D Homologous Perovskites as Light-Absorbing Materials for Solar Cell Applications. *Journal of the American Chemical Society* **2015**, 137 (24), 7843-7850.
17. Song, J.; Xu, L.; Li, J.; Xue, J.; Dong, Y.; Li, X.; Zeng, H., Monolayer and Few-

Layer All-Inorganic Perovskites as a New Family of Two-Dimensional Semiconductors for Printable Optoelectronic Devices. *Advanced materials* **2016**, 28 (24), 4861-4869.

18. Pasquarelli, R. M.; Ginley, D. S.; O'Hayre, R., Solution Processing of Transparent Conductors: From Flask to Film. *Chemical Society Reviews* **2011**, 40 (11), 5406-5441.

19. Chen, P.; Meng, Y.; Ahmadi, M.; Peng, Q.; Gao, C.; Xu, L.; Shao, M.; Xiong, Z.; Hu, B., Charge-Transfer Versus Energy-Transfer in Quasi-2D Perovskite Light-Emitting Diodes. *Nano energy* **2018**, 50, 615-622.

List of Publications

1. **Y. F. Ng**, N. F. Jamaludin, N. Yantara, M. Li, V. K. R. Irukuvarjula, H. V. Demir, T. C. Sum, S. Mhaisalkar, and N. Mathews, "Rapid Crystallization of All-Inorganic CsPbBr₃ Perovskite for High-Brightness Light-Emitting Diodes," *ACS Omega*, **2017**, 2 (6), 2757-2764.
2. **Y. F. Ng**, W. J. Neo, N. F. Jamaludin, N. Yantara, S. Mhaisalkar, and N. Mathews, "Enhanced Coverage of All-Inorganic Perovskite CsPbBr₃ through Sequential Deposition for Green Light-Emitting Diodes," *Energy Technology*, **2017**, 5 (10), 1859-1865.
3. **Y. F. Ng**, S. A. Kulkarni, S. Parida, N. F. Jamaludin, N. Yantara, A. Bruno, C. Soci, S. Mhaisalkar, and N. Mathews, "Highly efficient Cs-based perovskite light-emitting diodes enabled by energy funnelling," *Chemical Communications*, **2017**, 53 (88), 12004-12007.
4. **Y. F. Ng**, B. Febriansyah, N. F. Jamaludin, D. Giovanni, N. Yantara, T. C. Sum, S. Mhaisalkar, and N. Mathews, "Rational Design of Ligand Molecules for Mixed-Dimensional Perovskite Light-Emitting Diodes," **2019**, *In Preparation*.
5. S. Bhaumik, S. A. Veldhuis, **Y. F. Ng**, M. Li, S. K. Muduli, T. C. Sum, B. Damodaran, S. Mhaisalkar, and N. Mathews, "Highly stable, luminescent core-shell type methylammonium-octylammonium lead bromide layered perovskite nanoparticles," *Chemical Communications*, **2016**, 52 (44), 7118-7121.
6. N. F. Jamaludin, N. Yantara, **Y. F. Ng**, M. Li, T. W. Goh, K. Thirumal, T. C. Sum, N. Mathews, C. Soci, and S. Mhaisalkar, "Grain Size Modulation and Interfacial Engineering of CH₃NH₃PbBr₃ Emitter Films through Incorporation of Tetraethylammonium Bromide," *ChemPhysChem*, **2018**, 19 (9), 1075-1080.
7. S. A. Veldhuis, **Y. F. Ng**, R. Ahmad, A. Bruno, N. F. Jamaludin, B. Damodaran, N. Mathews, and S. G. Mhaisalkar, "Crown Ethers Enable Room-Temperature Synthesis of CsPbBr₃ Quantum Dots for Light-Emitting Diodes," *ACS Energy Letters*, **2018**, 3 (3), 526-531.
8. N. F. Jamaludin, N. Yantara, **Y. F. Ng**, A. Bruno, B. K. Chandran, X. Y. Chin, K. Thirumal, N. Mathews, C. Soci, and S. Mhaisalkar, "Perovskite templating via a

- bathophenanthroline additive for efficient light-emitting devices," *Journal of Materials Chemistry C*, **2018**, 6 (9), 2295-2302.
9. R. A. John, N. Yantara, **Y. F. Ng**, G. Narasimman, E. Mosconi, D. Meggiolaro, M. R. Kulkarni, P. K. Gopalakrishnan, C. A. Nguyen, F. De Angelis, S. G. Mhaisalkar, A. Basu, and N. Mathews, "Ionotronic Halide Perovskite Drift-Diffusive Synapses for Low-Power Neuromorphic Computation," *Advanced Materials*, **2018**, 30 (51), 1805454.
 10. B. Wu, H. Yuan, Q. Xu, J. A. Steele, D. Giovanni, P. Puech, J. Fu, **Y. F. Ng**, N. F. Jamaludin, A. Solanki, S. Mhaisalkar, N. Mathews, M. B. J. Roeffaers, M. Grätzel, J. Hofkens, and T. C. Sum, "Indirect tail states formation by thermal-induced polar fluctuations in halide perovskites," *Nature Communications*, **2019**, 10 (1), 484.
 11. J. Fu, N. F. Jamaludin, B. Wu, M. Li, A. Solanki, **Y. F. Ng**, S. Mhaisalkar, C. H. A. Huan, and T. C. Sum, "Localized Traps Limited Recombination in Lead Bromide Perovskites," *Advanced Energy Materials*, **2019**, 9 (12), 1803119.

Appendix

Figure A.1 (a) ^1H - and (b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 1-NMABr in DMSO-d_6 . Chemical shift values (δ in ppm) were referenced against residual protic solvent peaks. *Peak at 39.75 ppm overlaps with ^{13}C resonance of residual DMSO-d_6 solvent.

Figure A.2 (a) ^1H - and (b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 2-NMABr in DMSO-d_6 . Chemical shift values (δ in ppm) were referenced against residual protic solvent peaks.

Figure A.3 (a) ^1H - and (b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 1-NEABr in DMSO-d_6 . Chemical shift values (δ in ppm) were referenced against residual protic solvent peaks. *Peak at 39.56 ppm overlaps with ^{13}C resonance of residual DMSO-d_6 solvent.

Figure A.4 (a) ^1H - and (b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 2-NEABr in DMSO-d_6 . Chemical shift values (δ in ppm) were referenced against residual protic solvent peaks. *Peak at 39.80 ppm overlaps with ^{13}C resonance of residual DMSO-d_6 solvent.