Low dimensional organic metal-halide hybrids : molecular design & optoelectronic properties

Febriansyah, Benny

2019

Febriansyah, B. (2019). Low dimensional organic metal-halide hybrids : molecular design & optoelectronic properties. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/137083>

<https://doi.org/10.32657/10356/137083>

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

Downloaded on 26 Apr 2023 22:42:13 SGT

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**LOW DIMENSIONAL ORGANIC METAL-HALIDE HYBRIDS:
MOLECULAR DESIGN & OPTOELECTRONIC PROPERTIES**

BENNY FEBRIANSYAH

**Interdisciplinary Graduate School
Energy Research Institute @ NTU (ERI@N)**

2019

LOW DIMENSIONAL ORGANIC METAL-HALIDE HYBRIDS: MOLECULAR DESIGN & OPTOELECTRONIC PROPERTIES

BENNY FEBRIANSYAH

INTERDISCIPLINARY GRADUATE SCHOOL
ENERGY RESEARCH INSTITUTE @ NTU (ERI@N)

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.

08-08-2019

.....

Date

.....

Benny Febriansyah

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.

08-08-2019

.....

Date

.....

Asst. Prof. Dr. Jason England

Authorship Attribution Statement

This thesis contains material from two papers that are published in peer-reviewed journal where I was the first author.

Chapter 4 is published as Febriansyah, B.; Koh, T. M.; John, R. A.; Ganguly, R.; Li, Y.; Bruno, A.; Mhaisalkar, S. G.; England, J.* Inducing Panchromatic Absorption and Photoconductivity in Polycrystalline Molecular 1D Lead-Iodide Perovskites through π -Stacked Viologens. *Chem. Mater.* **2018**, 30 (17), 5827-5830.

DOI: 10.1021/acs.chemmater.8b02038.

The contributions of the co-authors are as follows:

- Asst. Prof. England, J. provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts.
- I co-designed the study with Asst. Prof. England, J. and performed the synthesis and material preparation work at the School of Physical and Mathematical Sciences (SPMS) and optical and structural characterizations at Energy Research Institute @ NTU (ERI@N).
- I interpreted and analyzed the overall data.
- Dr. Koh, T. M. and Prof. Mhaisalkar, S. G. provided guidance and insightful suggestions during manuscript preparations.
- Dr. John, R. A. was involved in the (photo)conductivity measurements.
- Drs. Ganguly, R. and Li, Y. were instrumental in the X-ray single crystallography.
- Dr. Bruno, A. assisted in the collection of the time-resolved photoluminescence data.

Chapter 6 is published as Febriansyah, B.; Koh, T. M.; Lekina, Y.; Jamaludin, N. F.; Bruno, A.; Ganguly, R.; Shen, Z. X.; Mhaisalkar, S. G.; England, J.* Improved Photovoltaic Efficiency and Amplified Photocurrent Generation in Mesoporous $n = 1$ Two-Dimensional Lead–Iodide Perovskite Solar Cells. *Chem. Mater.* **2019**, *31* (3), 890-898.

DOI: 10.1021/acs.chemmater.8b04064.

The contributions of the co-authors are as follows:

- Asst. Prof. England, J. provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts.
- I co-designed the study with Asst. Prof. England, J. and performed the synthesis and material preparation work at the School of Physical and Mathematical Sciences (SPMS) and optical characterizations, device fabrications and measurements, scanning electron microscopy, glancing angle and powder XRD at Energy Research Institute @ NTU (ERI@N).
- I interpreted and analyzed the overall data.
- Dr. Koh, T. M. and Prof. Mhaisalkar, S. G. provided guidance and insightful suggestions during manuscript preparations.
- Ms. Lekina, Y. and Prof. Shen, Z. X. were involved in the Raman spectroscopy data collection and interpretation.
- Ms. Jamaludin, N. F. and Dr. Bruno, A. assisted in the collection of the time-resolved photoluminescence data.
- Dr. Ganguly, R. was instrumental in the X-ray single crystallography.

Chapter 8 is published as Febriansyah, B.; Giovanni, D.; Sankaran, R.; Koh, T. M.; Li, Y.; Sum, T. C.; Mathews, N.; England, J.* Inducing formation of a corrugated, white-light emitting 2D lead-bromide perovskite via subtle changes in templating cation. *J. Mater. Chem. C*, 2020, Advance Article.

DOI: 10.1039/C9TC05357C.

The contributions of the co-authors are as follows:

- Asst. Prof. England, J. provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts.
- I co-designed the study with Asst. Prof. England, J. and performed the synthesis and material preparation work at the School of Physical and Mathematical Sciences (SPMS) and basic optical and structural characterizations at Energy Research Institute @ NTU (ERI@N).
- I interpreted and analyzed the overall data.
- Dr. Koh, T. M. and A/Prof. Mathews, N. provided guidance and insightful suggestions during manuscript preparations.
- Dr. Giovanni, D., Mr. Sankaran, R. and Prof. Sum, T. C. were involved in the time-resolved and temperature-dependent photoluminescence data collection and interpretation.
- Dr. Li, Y. was instrumental in the X-ray single crystallography.

In addition, the thesis also contains materials that will be published in the peer-reviewed journal where I am the first author (Chapters 5, 7, and 10) and co-author (Chapter 9). The submission of this thesis precedes the submission of the manuscripts.

Chapter 5 will be published as Febriansyah, B.; Lekina, Y.; Ghosh, B.; Harikesh, P. C.; Koh, T. M.; Li, Y.; Shen, Z. X.; Mathews, N.; England, J.* Tuning Pyridinium Cations to Selectively Template Formation of Pure 2D Lead-Iodide Perovskite Solar Absorbers Displaying Reduced Band Gaps and Relaxed Dielectric Confinement. *chemsuschem*, under review.

The contributions of the co-authors are as follows:

- Asst. Prof. England, J. provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts.

- I co-designed the study with Asst. Prof. England, J. and performed the synthesis and material preparation work at the School of Physical and Mathematical Sciences (SPMS) and basic optical characterizations as well as thin film fabrications at Energy Research Institute @ NTU (ERI@N).
- I interpreted and analyzed the overall data.
- Dr. Koh, T. M. and A/Prof. Mathews, N. provided guidance and insightful suggestions during manuscript preparations.
- Ms. Lekina, Y. and Prof. Shen, Z. X. were involved in the temperature-dependent photoluminescence and UV-vis absorbance data collection and interpretation.
- Dr. Ghosh, B. assisted in the collection of the DFT calculation data.
- Mr. Harikesh, P. C. was involved in the (photo)conductivity measurements.
- Dr. Li, Y. was instrumental in the X-ray single crystallography.

Chapter 7 will be published as Febriansyah, B.; Lekina, Y.; Hooper, T. J. N.; Harikesh, P. C.; Lim, M. H.; Koh, T. M.; Li, Y.; Shen, Z. X.; Mathews, N.; England, J.* Structural and optoelectronic properties of a 3×3 corrugated 2D tin-iodide perovskite. *In preparation*.

The contributions of the co-authors are as follows:

- Asst. Prof. England, J. provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts.
- I co-designed the study with Asst. Prof. England, J. and performed the synthesis and material preparation work at the School of Physical and Mathematical Sciences (SPMS) and basic optical characterizations as well as thin film fabrications at Energy Research Institute @ NTU (ERI@N).
- I interpreted and analyzed the overall data.
- Dr. Koh, T. M. and A/Prof. Mathews, N. provided guidance and insightful suggestions during manuscript preparations.
- Ms. Lekina, Y. and Prof. Shen, Z. X. were involved in the temperature-dependent photoluminescence data collection and interpretation.
- Dr. Hooper, T. J. N. assisted in the collection of the solid-state NMR data.

- Mr. Harikesh, P. C. was involved in the (photo)conductivity measurements.
- Dr. Li, Y. and Mr. Lim, M. H. were instrumental in the X-ray single crystallography.

Chapter 9 will be published as Febriansyah, B.;[†] Borzda, T.;[†] Cortecchia, D.; Neutzner, S.; Folpini, G.; Koh, T. M.; Li, Y.; Mathews, N.; Petrozza, A.;^{*} England, J.^{*} Two-dimensional hybrid lead-bromide perovskite broadband emitters with highly deformed metal coordination spheres. *Angew. Chem. Int. Ed.*, in revision.

The contributions of the co-authors are as follows:

- Asst. Prof. England, J. provided the initial project direction and edited the manuscript drafts.
- Prof. Petrozza, A. edited the manuscript drafts and provided guidance and insightful suggestions.
- I and Dr. Borzda, T. prepared the manuscript drafts.
- I and Dr. Borzda, T. interpreted and analyzed the overall data.
- I co-designed the study with Asst. Prof. England, J. and performed the synthesis and material preparation work at the School of Physical and Mathematical Sciences (SPMS) and basic optical and structural characterizations at Energy Research Institute @ NTU (ERI@N).
- Dr. Borzda, T. performed the photophysics characterizations (temperature-, power-dependent and time-resolved photoluminescences) at Center for Nanoscience and Technology at Istituto Italiano di Tecnologia.
- Dr. Cortecchia, D., Dr. Neutzner, S., and Folpini, G. assisted in collection and interpretation of photophysics data.
- Dr. Cortecchia, D., Dr. Koh, T. M. and A/Prof. Mathews, N. provided insightful suggestions during manuscript preparations.
- Dr. Li, Y. was instrumental in the X-ray single crystallography.

Chapter 10 will be published as Febriansyah, B.; Neo, D. C. S.; Giovanni, D.; Lekina, Y.; Koh, T. M.; Li, Y.; Shen, Z. X.; Sum, T. C.; Mathews, N.; England, J.^{*} Selective generation

of trimeric organic-bromoplumbate hybrids that display intrinsic, highly Stokes-shifted, efficient broadband emission. *Chem. Mater.*, in revision.

The contributions of the co-authors are as follows:

- Asst. Prof. England, J. provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts.
- I co-designed the study with Asst. Prof. England, J. and performed the synthesis and material preparation work at the School of Physical and Mathematical Sciences (SPMS) and basic optical and structural characterizations at Energy Research Institute @ NTU (ERI@N).
- I interpreted and analyzed the overall data.
- Mr. Neo, D. C. S. assisted with the synthesis of a few of the compounds.
- Dr. Koh, T. M. and A/Prof. Mathews, N. provided guidance and insightful suggestions during manuscript preparations.
- Dr. Giovanni, D. and Prof. Sum, T. C. were involved in the time-resolved and temperature-dependent photoluminescence data collection and interpretation.
- Ms. Lekina, Y. and Prof. Shen, Z. X. were involved in the Raman spectroscopy data collection and interpretation.
- Dr. Li, Y. was instrumental in the X-ray single crystallography.

08 – 08 – 2019

.....
Date

.....
Benny Febriansyah

Abstract

Low-dimensional (LD) hybrid metal-halide (perovskite) materials can be induced through incorporation of more hydrophobic, moderately-sized organic cations. This not only provides improved stability against degradation by moisture and oxygen relative to their three-dimensional (3D) counterparts, but also affords significant room for materials exploration and engineering. Although the number of reports on LD hybrids in the literature is numerous, systematic studies on the effect of cation structure towards the materials' final structures are still relatively scarce. LD hybrids are, generally, considered ill-suited for photovoltaic applications due to their reduced dimensionality manifests in compromised visible light absorption and poor charge transport. Furthermore, the strengthened binding energy and oscillator strength of the electron-hole pairs (excitons) in the LD system concomitantly result in increased radiative decay rates, which lead to typical narrow emissions. Motivated by these circumstances, this dissertation uses *targeted molecular approach* as a strategy to modulate the physical properties of such extended solid materials. Specifically, organic cations are rationally designed to target desired metal-halide structures at molecular level. As a result, the formability of such structures can be systematically investigated. More importantly, the resulting “molecularly-engineered” materials can be notably endowed with optoelectronic properties suitable for photovoltaic and solid-state lighting applications.

Firstly, using pyridinium core as the framework, empirical understanding of molecular features that induce formation of two-dimensional (2D), one-dimensional (1D), and trimeric lead-halide hybrid materials formation can be gleaned. Primary ammonium groups ($-\text{NH}_3^+$) are found to be a prerequisite for formation of 2D perovskites, presumably due to the highly localized charge density and limited steric bulk of this functionality. In the absence of $-\text{NH}_3^+$, 1D iodoplumbate inorganic architectures are obtained with comparatively short and flexible *N*-alkyl substituents (e.g. ethyl, propyl, and pentyl). The presence of *N*-alkyl substituents containing neutral hydrogen bond donors (e.g. alcohol, carboxylic acid, and primary amide functionality) did not change this outcome and the 1D structures were retained. When more rigid substituents are employed (e.g. benzyl, acetamidyl, and cyanomethyl), hybrids composed of very rare face-sharing inorganic trimers can be afforded. Secondly, systematic tuning of the aromatic ring size and position of $-\text{NH}$ functionalities lead to the discovery of the unprecedented corrugated “ 3×3 ” (110)-oriented 2D lead-iodide and tin-iodide perovskites (where “ $n \times n$ ” refers to the

number (n) of contiguous metal-halide octahedra comprising each ridge). The main driving force to formation of the unusual structure is attributed to the presence of a coulombic interaction that occurs perpendicular to the plane of the heterocyclic ring. With similar approach, a rare white-light emitting “2 × 2” (110)-oriented 2D lead-bromide perovskite (CIE coordinates of (0.32, 0.41), correlated colour temperature (CCT) of 5824 K and colour rendering index (CRI) of 73) with significance in solid-state lighting applications can also be obtained.

From photovoltaic application point of view, we demonstrate for the first time that 1D lead-iodide materials can be endowed with extended light absorption (up to 800 nm), reduced band gaps (1.74 eV to 1.77 eV) and enhanced photoconductivity. This is achieved by employing viologen cations endowed with hydrogen bonding functionalities that are capable of inducing π - π stacking, such that charge transfer interaction between the organic and inorganic lattices are reinforced. In addition, we also show new 2D perovskites exhibiting reduced band gaps (2.35 – 2.46 eV), relaxed dielectric confinement (excitonic binding energies of 130 – 200 meV), and improved electrical and photoconductivities (more than 10-fold) relative to conventional 2D lead-iodide perovskites. Such features can be realized by reducing their inorganic inter-octahedral distortions (largest Pb-(μ -I)-Pb bond angles of 170 – 179°) and inorganic layers separation (shortest I...I contacts $\leq$ 4.278 – 4.447 Å). At the time it was published, these features eventually afforded the world-record power conversion efficiencies for pure 2D perovskite solar cells of 1.43 and 1.83%.

From solid-state lighting application point of view, in addition to the discovery of a rare “2 × 2” (110)-oriented 2D lead-bromide perovskite, we demonstrate for the first time that white-light emission can be also be induced from (100)-oriented 2D compound with deformed lead-bromide coordination geometry (i.e. high degree of intra-octahedral distortion), while featuring mild inter-octahedral tilting. This is achieved by incorporating sterically-demanding organic cations, such as that with piperidinium core, where the resulting compound is shown to exhibit emission with CIE coordinates of (0.38, 0.38), CCT of 4088 K and CRI of 96. Furthermore, we also report three new compounds containing very rare lead-bromide trimers templated by pyridinium cations functionalized with rigid substituents. The compounds feature intrinsic, highly stoke-shifted (ca. 1.39 eV), ultra-broadband (full width at half maximum of ca. 540 meV), and efficient photoluminescence properties (PLQY of at least 10%), all of which serve as a powerful proof of concept of inorganic lattice control by the organic molecular structure.

Acknowledgements

First and foremost, I would like to thank Professor Jason England for having supervised my dissertation. Your perspective and knowledge in coordination chemistry, as well as patience in managing me and my work during the course of my research are highly appreciated. I am particularly grateful for your efforts in reviewing and editing numerous versions of my publications and this thesis, and also for your time in checking my progress despite your busy schedule with your teaching and other research commitments.

I would also like to extend my gratitude to Professor Nripan Mathews for being my advisor at ERI@N. My first two-and-half-year of research have been a rough and daunting patch to walk on, but your constant encouragement, ideas and energy have helped me get through, which culminated in the completion of this thesis. I am very thankful that you voluntarily invested so much of your valuable time guiding and motivating me. I have learnt so much through interacting with you and I will remember your advices on “getting the things done.”

Another person who has been instrumental to my work and my Ph.D. life whom I am very much grateful to, is my ERI@N mentor, Daymond. You have constantly served as an inspirational figure to me whenever I am faced with stress, failures, and hardships. Thanks for teaching me how to manage my time and capacities and also for providing me with the utmost backing to ensure that all proceed as planned. We shall finish what we started.

In addition, I would also like to thank Professor Subodh Mhaisalkar for the opportunity to link-up and work with ERI@N during my Ph.D. study. My sincere gratitude shall also go to Professors Chen Zhong and Soo Han Sen for serving on my qualifying examination and thesis committees as my co-supervisor and mentor, respectively. The inputs I received from all of them during the weekly ERI@N group meetings and/or TAC meetings have helped me tighten the loose ends. Not to forget, I also need to acknowledge IGS-ERI@N for providing the graduate scholarship, as well as Professor Claude Guet and Min Ying for their administrative assistances concerning the submission of this thesis.

Besides that, being an interdisciplinary researcher, I have interacted with people from diverse field of backgrounds. Thus, I would also like to acknowledge the support, assistance and inputs provided to me by my friends and colleagues at ERI@N (both PV and LED groups), CBC, MSE, PAP, and CREATE. My heartfelt appreciation in particular go to Japheth, Herlina, Biplap, Annalisa, Wang Hao, Riyas, Bening, Riyas, Bhumika, Thambi, Natalia, Xin Yu, Thiru, Alasdair, Tom, Bahu, Gede, Sneha, Rohit, Mohit, Stener, Yulia, David, Daniel, Sebastian, Suman, Zhi Zhong, Ming Hui, Hiro, Eric, Alan Ong, Alan Cheong, Shu Hui, Li Jia, Mathilde, Jia Haur, Prem, Zi Qiu and Meng Ru. My collaborators at Italy, Daniele and Tania should be mentioned for their valuable time and help too.

A separate note of thanks further goes to Yan Fong, Fadilah, Harikesh, and Xin Tong, my fellow IGS friends who started Ph.D. on the very same day as me. Thank you for your sympathetic ears and technical helps. Spending four years of doing intensive research has been a wonderful and fun experience because of all you. I definitely will not forget the outings we had and I wish all the best for whatever you do after this.

I am also deeply grateful to all my other close friends. My Ph.D. days would have been a lot more colorless without all of them. First, I would like to show gratitude to Rizky, Diego, and Shienny who have been unquestioningly helpful and fun to talk to. *Terima kasih!* I also appreciate Little Bodhi Student Care Centre committee, of which I have channeled my spare time volunteering, in particular Chun Hee, Neilson, Diego, Soon Sheng, Bro. Alan, Bro. Hong Seng, and Bro. Seng Yip, for the enjoyable time managing the center. 感謝! In addition, my friends and teachers at Goethe-Institut Singapore should be thanked. *Es ist schon verrückt, wie schnell zwei Jahre mit euch vergeht. Danke für alles!* At last, 31st main committee of NTU Buddhist Society will always remain in my heart: Ze Yong, Xin Wen, Rizky, Chun Hee, Andy, Shienny, Ivan, Si Hui, Martin, Freddy, Quan Lung, Jefferson, Josephine, and Aryani. I want to thank all of you for all the gatherings we had. They have served as timely reminiscent of the memorable moments of our vibrant undergraduate time. Finally, Dr. Benny says thank you!

To this end, a special mention goes to Charlynn who has been dear to me. I am grateful to have known you. The amount of time that we spent together, however limited it is, means a lot to me. 加油 for the rest of your Ph.D.!

A further note of gratitude should be extended to Uncle Seng Oh Eng, Auntie Neo Swan Chew, and their family for the great care and moral support. I am thankful to be considered as part of the family member and will always remember the warmth I received during my stay in Singapore. May God's blessings always be with all of you!

Last, but definitely not the least, I would like to thank my family members: my father, Bu Cun Min, my mother, Bong Lie Fun, and my sisters, Bella Nastasia and Bellen Mouretta for just being there. Your continuous understanding, patience and devotion to my cause, which I am deeply indebted towards, have been the strong pillars that sustain my momentum throughout my eight years of studies. 承蒙你等!

Table of contents

Abstract.....	i
Acknowledgements	iii
Table of contents	vii
Figure captions	xv
Scheme captions	xxxix
Table captions	xli
Abbreviations	xlvi
 Chapter 1 Introduction.....	 1
1.1 Energy crisis, solar to electricity conversion, and lightings	2
1.2 Objectives and scope of work	4
1.3 Thesis overview	7
1.4 Findings and originality	10
1.5 Bibliography	11
 Chapter 2 Literature review	 15
2.1 3D halide perovskites and their structural properties	16
2.1.1 Optoelectronic properties suitable for photovoltaics	17
2.1.2 Basics of perovskite solar cells (PSCs).....	20

2.1.3	Other optoelectronic applications	22
2.1.4	Chemical instability and limitation for exploration	23
2.2	Hybrids of lower-dimensionalities and their structural properties	25
2.2.1	Improvement in stability and greater room for improvisation.....	29
2.2.2	Optoelectronic drawbacks of hybrids of lower-dimensionalities and this thesis in the context of literature	30
2.3	Bibliography	34
Chapter 3 Experimental methodology		43
3.1	Materials fabrication	44
3.1.1	General design and synthesis of organic cations	44
3.1.1.1	Alkylation of pyridines and 4,4'-bipyridines.....	45
3.1.1.2	Hydrohalogenation of amines	45
3.1.2	Preparation of organic metal-halide hybrids (perovskites).....	46
3.1.2.1	Single crystals	46
3.1.2.2	Thin films	47
3.2	Device fabrication.....	48
3.2.1	Solar cell devices based on mesoporous architectures	48
3.2.2	Photodetector devices with lateral electrodes configuration	50
3.2.3	Photodetector devices with lateral interdigitated electrodes.....	51
3.3	Characterization techniques	51
3.3.1	Nuclear magnetic resonance (NMR) spectroscopy.....	52
3.3.2	X-ray single crystallography.....	53
3.3.3	Powder and glancing angle X-ray diffractometry.....	54
3.3.4	UV-vis spectroscopy	55

3.3.4.1	Linear absorption spectroscopy	55
3.3.4.2	Diffuse reflectance spectroscopy (DRS)	56
3.3.5	Photoluminescence (PL) spectroscopy	56
3.3.6	Field- emission scanning electron microscopy (FE-SEM)	57
3.3.7	Atomic force microscopy (AFM)	58
3.3.8	Raman spectroscopy	59
3.3.9	Solar cells current density-voltage (I - V) measurement	60
3.3.10	Incident photon-to-current efficiencies (IPCE) or external quantum efficiencies (EQE) measurement	61
3.4	Bibliography	62
 Chapter 4 Inducing panchromatic absorption and photoconductivity in polycrystalline molecular 1D lead-iodide perovskites through π-stacked viologens.....63		
4.1	Background	64
4.2	Results and discussions	65
4.2.1	π - π stacking and induced charge transfer interaction	65
4.2.2	Optoelectronic properties improvement due to π - π stacking	72
4.2.3	Solvent-dependent formation and processability issues	78
4.3	Summary	82
4.4	Bibliography	83
4.5	Instrumentations and additional data	85
 Chapter 5 Pyridinium-templated 2D lead-iodide perovskites: specific formability, reduced band gap, and relaxed dielectric confinement.....95		
5.1	Background	96

5.2	Results and discussions	98
5.2.1	Role of ammonium group in 2D iodoplumbate formation	98
5.2.2	Reduced band-gap and relaxed dielectric confinement	105
5.2.3	Improved (photo)conductivity properties and electronic structure calculations	111
5.3	Summary	117
5.4	Bibliography	118
5.5	Instrumentations and additional data	122
 Chapter 6 Improved photovoltaic efficiency & amplified photocurrent generation in mesoporous $n = 1$ 2D lead-iodide perovskite solar cells		
6.1	Background	134
6.2	Results and discussions	135
6.2.1	Structural features of (100)- and (110)-type 2D perovskites	135
6.2.2	Optical characteristics of 2D perovskite thin films	141
6.2.3	Application in solar cells, crystallization behavior, and electrical properties	150
6.3	Summary	161
6.4	Bibliography	163
6.5	Instrumentations and additional data	166
 Chapter 7 Structural and optoelectronic properties of a 3×3 corrugated 2D tin-iodide perovskite		
7.1	Background	174
7.2	Results and discussions	175
7.2.1	Formability and structure of (110)-lattice	175

7.2.2	Effects of corrugated structure to spectroscopic features	181
7.2.3	Low excitonic binding energy and application in photodetector.....	185
7.3	Summary	189
7.4	Bibliography	189
7.5	Instrumentations and additional data	192
 Chapter 8 Inducing formation of a corrugated, white-light emitting 2D lead-bromide perovskite via subtle changes in templating cation199		
8.1	Background	200
8.2	Results and discussions.....	201
8.2.1	Formability and structure of (110)-lattice.....	201
8.2.2	Effects of corrugated structure to optical properties.....	209
8.2.3	Self-trapped excitons and cold white-light emission	212
8.3	Summary	215
8.4	Bibliography	216
8.5	Instrumentations and additional data	218
 Chapter 9 Two-dimensional hybrid lead-bromide perovskite broadband emitters with highly deformed metal coordination spheres.....223		
9.1	Background	224
9.2	Results and discussions.....	226
9.2.1	(100)-2D perovskites based on sterically demanding organic cation	226
9.2.2	Generation of broadband emission	232
9.2.3	Formation of multiple photoinduced emissive colour centres.....	235
9.3	Summary	239
9.4	Bibliography	240

9.5	Instrumentations and additional data	243
Chapter 10	Selective generation of trimeric organic-bromoplumbate hybrids that display intrinsic, highly Stokes-shifted, efficient broadband emission	249
10.1	Background	250
10.2	Results and discussions	252
10.2.1	Lattice confinement by rigid organic cations	252
10.2.2	Distorted structures and broadband emission generations	255
10.2.3	Self-trapped excitons mechanism	261
10.3	Summary	265
10.4	Bibliography	266
10.5	Instrumentations and additional data	269
Chapter 11	Conclusions and future outlook	277
11.1	Conclusions of thesis	278
11.2	Outstanding questions	281
11.3	Implications and future outlook	283
11.3.1	Electron withdrawing group incorporation to enhance charge-transfer interaction	283
11.3.2	Halogen bonding for perovskite formability investigation and intermolecular electronic interaction enhancement	285
11.3.3	Inducing monomeric lead-halide hybrid with bulky organic cations	286
11.3.4	Broadband emitters based on Sn-Br lattices	287
11.4	Bibliography	288

Scientific portfolio	289
-----------------------------------	------------

Figure captions

Figure 1.1 Growth of world primary energy consumption (in million tonnes oil equivalent where 1 tonne of oil equivalent is ca. 1.163×10^{-5} TWh) by fuel since 1992. The figure is adapted from ref. 1.....	2
Figure 2.1 a) Representation of APbI_3 perovskite with cubic structure where monocationic A: green, Pb: blue, and I: red (not to scale). b) Alternative depiction of perovskite highlighting the iodoplumbate lattices ‘encapsulating’ A. c) The case of $[\text{PbI}_6]^{-4}$ octahedra tilting, normally because of too small A cation leading to strain on Pb-I bonds. The figure is adapted from ref. 16.....	16
Figure 2.2 Tolerance factors (t) of a series of different halide perovskites. The figure is adapted from ref. 23.....	17
Figure 2.3 a) Calculated density of states (DOS) of $\text{CH}_3\text{NH}_3\text{PbI}_3$, CsSnI_3 and GaAs. The VBMs (valence band maximums) are referred to as zero energy and CBMs (conduction band minimums) are marked as dashed lines. b) The optical absorptions of $\text{CH}_3\text{NH}_3\text{PbI}_3$, CsSnI_3 and GaAs. The figure is adapted from ref. 31..	18
Figure 2.4 a) UV-vis absorption spectra (top) and appearances (bottom) of $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ materials spincoated on top of FTO substrates coated with TiO_2 nanocomposite. The figure is adapted from ref. 38. b.) UV-vis absorption spectra of various 3D iodoplumbates. The figure is adapted from ref. 44.....	19
Figure 2.5 Schematic diagrams of perovskite solar cells in the (a) n-i-p mesoscopic, (b) n-i-p planar, (c) p-i-n planar, and (d) p-i-n mesoscopic structures where n, i, and p denote electron-transporting, light absorber (perovskites), and hole-transporting materials, respectively. The figure is adapted from ref. 45.....	20
Figure 2.6 a) Molecular structure of commonly used organic HTM, Spiro-OMeTAD. b) Schematic diagram of mesoscopic TiO_2 perovskite solar cell. The figure is adapted from ref. 51.....	21
Figure 2.7 Schematic of energy level diagram with charge transfer processes occurring in PSCs under light illumination.....	21

Figure 2.8 a) Light emitting diode (LED) made from $\text{CH}_3\text{NH}_3\text{PbX}_3$. The figure is adapted from ref. 59. b) Tunable amplified spontaneous emission (ASE) from $\text{CH}_3\text{NH}_3\text{PbX}_3$ thin film for laser applications. The figure is adapted from ref. 60.	22
Figure 2.9 a) UV-vis absorption spectra and b) XRD patterns of $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ before and after decomposition by moisture in air after 18 h of exposure. The figure is adapted from ref. 65..	23
Figure 2.10 Illustrations of hybrid organic-inorganic halometallates possessing inorganic lattices of a) 3D, b) 2D, c) 1D, and d) 0D structural features where ‘D’ refers to dimension. The blue octahedron represents the $[\text{MX}_6]^{n-}$ building unit with M being heavy main group metal cations (not shown) and X halide anions (orange spheres). The figure is adapted from ref. 68.	25
Figure 2.11 Structures of 2D perovskites, where the inorganic sublattices can be conceptually derived from (A) the (001) and (B) the (110) crystallographic planes of the cubic 3D perovskite structure. Insets show cubic 3D perovskites with these crystallographic planes highlighted. In these examples, the templating cations are N^1 -methylpropane-1,3-diammonium and N^1 -methylethane-1,2-diammonium, respectively. The figure is adapted from ref. 83.	26
Figure 2.12 Structures of the layered 2D lead-iodide perovskites, $(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ (BA and MA are butylammonium and methylammonium, respectively), extending from $n = 1$ to $n = \infty$ where n refers to the number of contiguous 2D inorganic layers; i.e., not separated by organic cations. The figure is adapted from ref. 84.	27
Figure 2.13 Examples of 1D lead-iodide hybrids that are templated by organic cations a) iodoformamidinium, b) imidazolium, and c) 1,4-dimethylpiperazine-1,4-dium where different connectivity modes (face, corner, or edge) can be observed. The figures are adapted from ref. 82, 67, and 88, respectively.	28
Figure 2.14 Examples of hybrid materials containing metal-halide monomers (i.e. ‘0D’) that are obtained from organic cations a) 1-butyl-1-methylpyrrolidinium, b) tetraphenylphosphonium, and c) N,N' -dimethylethylenediammonium. The figures are adapted from ref. 7, 89, and 90, respectively.	28
Figure 2.15 Comparison of dipping the 3D perovskite MAPbI_3 (left), lower dimensionality $n = 4$ perovskite $(\text{BA})_2(\text{MA})_2\text{Pb}_3\text{I}_{10}$ (center) (where BA is butylammonium and MA is	

methyammonium) and $n = 1$ (pyrene-O-propyl-NH₃)₂PbI₄ (right). The $n = 1$ compound remains intact even after several minutes of immersion. The figure is adapted from ref. 91.

.....29

Figure 2.16 Absorption spectra of a) lower dimensionality $n = 4$ perovskite (PEA)₂(MA)₂Pb₃I₁₀ (PEA is phenylethylammonium and MA is methyl-ammonium) and b) 3D perovskite MAPbI₃ upon exposure to 52% relative humidity, demonstrating the shelf stability of the former in comparison to the latter. The figure is adapted from ref. 76.30

Figure 2.17 UV-vis absorbance and PL spectra of various 2D lead-iodide perovskites. In contrast to the 3D congeners whose visible light absorption can span up to 780-810 nm, the absorption edges of the 2D materials occur at ca. 450-530 nm, indicating bandgaps of over 2.5 eVs. The figure is adapted from ref. 113.31

Figure 2.18 a) a) UV-vis absorbance spectra of 2D (PEA)₂PbI₄ at different temperatures (PEA is phenylethylammonium). b) temperature-dependent integrated photoluminescence intensity of (PEA)₂PbI₄. These two experiments are normally conducted to examine the excitonic binding energy (E_b) of the halide perovskite material. In this case, the E_b of (PEA)₂PbI₄ was determined to be ca. 220 meV, much higher than that of 3D MAPbI₃ (MA is methylammonium) whose E_b was reported to be ca. 30-45 meV. The figure is adapted from ref. 107.32

Figure 2.19 a) Photoluminescence (PL) spectra and b) photograph of solutions of (PEA)₂PbX₄ (PEA = phenylethylammonium and X = Br or I) nanosheets with different compositions under the irradiation of a 365 nm UV lamp showing color tuning from blue to green. The figures are adapted from ref. 125. c) Electroluminescence spectrum of a (PEA)₂SnI₄ device, registered by applying a 4 V bias to the device, demonstrating red color. The figure is adapted from ref. 97.33

Figure 3.1 General schematic of organic cations used throughout all studies in this thesis. Examples of the cyclic ring cores and functional groups acting as their substituents are shown.44

Figure 3.2 Illustration of growing single crystals with a) vapor diffusion and b) layering techniques. The figure is adapted from ref. 1.47

Figure 3.3 Illustration of growing single crystals with slow cooling method. The figure is adapted from ref. 1.47

Figure 3.4 Schematic of perovskite solar cell based on mesoscopic TiO ₂ architecture. The figure is adapted from ref. 2.....	48
Figure 3.5 Schematic of photodetector thin film devices with lateral electrodes configuration (i.e. ‘horizontal devices’).....	50
Figure 3.6 Schematic of photodetector devices with lateral electrodes configuration (i.e. ‘horizontal devices’) prepared from polycrystalline samples.	50
Figure 3.7 Schematic of photodetector devices with lateral interdigitated electrodes.....	51
Figure 3.8 The splitting of the degenerate nuclear energy levels (in this example, $I = 1/2$) under an applied magnetic field. The green spheres represent atomic nuclei which are either aligned with (low energy) or against (high energy) the magnetic field. E , m , γ , h , and B_0 represent energy level, magnetic quantum number, magnetogyric ratio, Planck constant, and external magnetic field, respectively. The figure is adapted from ref. 3.	52
Figure 3.9 Schematic illustration of Bragg reflection from a set of crystal planes with a spacing d_{hkl} . The figure is adapted from ref. 4.	53
Figure 3.10 Electron-specimen interaction volume illustration. The figure is adapted from ref. 6.	57
Figure 3.11 Spectral comparison of xenon arc lamp solar simulator utilized in this study and measured natural solar radiation. The figure is adapted from ref. 7.	61
Figure 4.1 Molecular structures and notation of dicationic viologens used in this chapter.	65
Figure 4.2 (a) UV-Vis spectra of polycrystalline powders of (HyEtV)Pb ₂ I ₆ (1 ; red solid line), (CaEtV)Pb ₂ I ₆ (2 ; blue solid line), (PrV)Pb ₂ I ₆ (3 ; orange solid line), and (BpbmA)Pb ₂ I ₆ (4 ; green solid line). The dashed lines obtained by extrapolation of the linear part of each spectrum correspond to the band gaps of each material. (b) Schematic energy diagram of the molecular 1D perovskites 1-4 . Valence band energies were obtained from photoelectron spectroscopy in air (PESA) measurements and optical band gaps from the UV-vis spectra.	66
Figure 4.3 UV-vis absorbance spectra of 1D perovskites (HyEtV)Pb ₂ I ₆ (1) and (CaEtV)Pb ₂ I ₆ (2), plus that of 3D methyl ammonium lead iodide (MA)PbI ₃ . Panchromatic visible light absorption of MAPbI ₃ is due to expanded orbital overlap of lead-iodide octahedra in three dimensions. Although the inorganic components of 1 and 2 are 1D in	

nature, absorption features similar to the 3D material are realized due to enhanced CT interactions of the inorganic chains with the viologen dications.....67

Figure 4.4 Photoelectron spectroscopy in air (PESA) measurements for (HyEtV)Pb₂I₆ (**1**; red), (CaEtV)Pb₂I₆ (**2**; blue), (PrV)Pb₂I₆ (**3**; orange), and (BpbmA)Pb₂I₆ (**4**; green). Solid lines are linear fittings of the points where the intersections between the linear fits of the two domains provides estimates of the valence bands energies of each 1D perovskite (5.79 eV, -5.68 eV, -5.70 eV, and -5.73 eV for **1**, **2**, **3**, and **4**, respectively).68

Figure 4.5 Schematic energy diagrams of (a) (HyEtV)Pb₂I₆, (b) (CaEtV)Pb₂I₆, (c) (PrV)Pb₂I₆, and (d) (BpbmA)Pb₂I₆. All valence bands are of similar energy and are localized on the iodoplumbate lattice. In the viologen containing materials, the cation-centred LUMOs act as the ‘conduction band’. As can be seen, the change in optical gap is dominated by lowering of the energy of the LUMOs of the organic component.68

Figure 4.6 Crystal structures of (a) (HyEtV)Pb₂I₆ (**1**), (b) (CaEtV)Pb₂I₆ (**2**), and (c) (PrV)Pb₂I₆ (**3**). Left insets indicate the relative orientation of organic viologens in the crystal lattice. Right insets show the visual appearances of the polycrystalline 1D perovskites. Gray, purple, brown, red, blue, and yellow spheres represent Pb, I, C, O, N, and S atoms, respectively. H atoms are omitted for clarity.69

Figure 4.7 Crystal structures of (a) (HyEtV)I₂ and (b) (CaEtV)I₂ showing random orientation and no significant π - π stacking of viologen cations, while (c) (PrV)I₂ shows the presence of π - π stacking to give PrV²⁺ dimers. Brown, red, blue, and yellow spheres represent C, O, N, and S atoms, respectively. H atoms are omitted for clarity. Crystallography and refinement data for each of the structures is summarized in **Section 4.5**.70

Figure 4.8 (a) UV-Vis absorbance spectra of polycrystalline viologen iodides (HyEtV)I₂, (CaEtV)I₂, and (PrV)I₂ (solid lines), plus their hybrid perovskite counterparts (dash lines). (b) Visual appearances of (HyEtV)I₂, (CaEtV)I₂, and (PrV)I₂, alongside the corresponding 1D lead-iodide perovskites (HyEtV)Pb₂I₆ (**1**), (CaEtV)Pb₂I₆ (**2**), and (PrV)Pb₂I₆ (**3**). See **Table 4.1** for a summary of the observed optical features.70

Figure 4.9 Single crystal X-ray structures of alternative structures (HyEtV)Pb₂I₆ (**1a**; (a) & (c)) and (CaEtV)Pb₂I₆ (**2a**; (b) & (d)), for which there is no π - π stacking of the viologen dications. **1a** was obtained by slow diffusion of benzene into vials containing DMF

precursor solutions, while **2a** was achieved using DMSO-benzene solvent combinations. Grey, purple, brown, red, blue, and yellow spheres represent Pb, I, C, O, N, and S atoms, respectively. H atoms are omitted for clarity. Crystallographic and refinement data for these structures is summarized in **Section 4.5**. Lack of π - π stacking leads to compromised light absorption capabilities (**Figure 4.10**) and an absence of photoconductivity (**Figure 4.11**).71

Figure 4.10 UV-Vis absorbance spectra of alternative structures (HyEtV)Pb₂I₆ (**1a**) and (CaEtV)Pb₂I₆ (**2a**). The spectrum of (PrV)Pb₂I₆ (**3**) is included for comparison. Absorption onsets for **1a** and **2a** occur at ~550 nm and ~650 nm, respectively. Charge transfer maxima are observed at 435 nm (**1a**) and 442 nm (**2a**).72

Figure 4.11 Current-voltage (*I-V*) curves of alternative structures (a) (HyEtV)Pb₂I₆ (**1a**) and (b) (CaEtV)Pb₂I₆ (**2a**), showing no significant current generated upon white light irradiation. Average dark conductivities are $2.243 \times 10^{-11} \text{ S cm}^{-1}$ for **1a** and $2.005 \times 10^{-11} \text{ S cm}^{-1}$ for **2a**, while their respective average conductivities in the presence of light (1 sun illumination) are $2.385 \times 10^{-11} \text{ S cm}^{-1}$ and $2.244 \times 10^{-11} \text{ S cm}^{-1}$72

Figure 4.12 Photoluminescence (PL) spectra (a) and time-resolved PL decay curves (b) of (HyEtV)Pb₂I₆ (**1**) (red circle and triangle), (CaEtV)Pb₂I₆ (**2**) (blue circle and triangle), and (PrV)Pb₂I₆ (**3**) (orange circle and triangle), obtained using an excitation wavelength at 405 nm.73

Figure 4.13 (a) Schematic diagram of the four-probe electrical conductivity measurements performed upon the polycrystalline samples. (b) Current-voltage (*I-V*) characteristics of (HyEtV)Pb₂I₆ (**1**; red line), (CaEtV)Pb₂I₆ (**2**; blue line), (PrV)Pb₂I₆ (**3**; orange line), and (BpbmA)Pb₂I₆ (**4**; green line) under white light irradiation (1 sun illumination). (c) Time-dependent photoresponses of the 1D perovskites at 2.0 V bias, upon repetitive on and off white light (1 sun AM1.5G) illumination (interval 10 s), measured for 300 s.75

Figure 4.14 Current-voltage (*I-V*) curves of polycrystalline samples of (a) (PrV)Pb₂I₆ (**3**) and (b) (BpbmA)Pb₂I₆ (**4**) showing no significant current generated upon white light irradiation. Average dark conductivities are $1.530 \times 10^{-11} \text{ S cm}^{-1}$ for **3** and $9.598 \times 10^{-12} \text{ S cm}^{-1}$ for **4**, while average conductivities in the presence of light (1 sun illumination) are $1.871 \times 10^{-11} \text{ S cm}^{-1}$ for **3** and $9.906 \times 10^{-12} \text{ S cm}^{-1}$ for **4**. The on/off current generation ratio at 3.0V for **3** and **4** are 1.08 and 1.02, respectively.76

Figure 4.15 Current-voltage (I - V) curves of polycrystalline samples of (a) (HyEtV)Pb₂I₆ (1) and (b) (CaEtV)Pb₂I₆ (2) showing significant current generated upon white light irradiation. Average dark conductivities are 1.754×10^{-11} S cm⁻¹ for **1** and 5.793×10^{-11} S cm⁻¹ for **2**, while average photoconductivities (1 sun illumination) are 1.245×10^{-10} S cm⁻¹ for **1** and 1.232×10^{-9} S cm⁻¹ for **2**.76

Figure 4.16 Current-voltage (I - V) curve of 2D perovskite based on 4,4'-bis(ammonium-ethyl)-1,1'-biphenyl diiodide ((BpbeA)PbI₄) (see **Figure 4.17** for structure of BpbeA and UV-vis absorption feature of the corresponding 2D perovskite). Average dark conductivity is 7.735×10^{-11} S cm⁻¹, while average conductivity in the presence of light (1 sun illumination) is 2.558×10^{-9} S cm⁻¹. At 2.0 V, the on/off ratio of current generation is ~ 33.177

Figure 4.17 (a) BpbmA and BpbeA are typical ammonium-based organic cations used in low-dimension perovskite formation. They are both electronically inert organics, despite the presence of biphenyl rings, where no charge transfer interaction can be induced with the 1D inorganic lattices. While BpbmA templates the formation of 1D perovskite, BpbeA is able to form a 2D hybrid structure, resulting in distinct light harvesting capabilities. Reorganization of BpbeA on a molecular level leads to its structural isomer, PrV²⁺, which is a potent electron acceptor. (b) The UV-vis absorbance spectrum of 1D (PrV)Pb₂I₆ shows that it has an extended absorption profile compared with inert 1D perovskites. Indeed, its absorptivity is comparable to that of 2D counterparts. 2D (BpbeA)PbI₄ (PbI₄²⁻ denotes molecular formula of 2D inorganic layer) has an excitonic peak at 513 nm and an inorganic band-gap of 2.41 eV, both of which are significantly red-shifted relative to those of 1D (BpbmA)Pb₂I₆ (410 nm and 2.94 eV) due to relaxation of quantum confinement effects. As a consequence of CT interactions, the optical features of 1D (PrV)Pb₂I₆ (intermolecular electronic gap of 2.21 eV) are not limited by quantum confinement effects of the lead-iodide lattices.78

Figure 4.18 Experimental glancing-angle XRD (GAXRD) and simulated powder XRD (pXRD) of thin films (a) (HyEtV)Pb₂I₆ (1) and (b) (CaEtV)Pb₂I₆ (2).79

Figure 4.19 Glancing angle-XRD patterns of thin films (HyEtV)Pb₂I₆ (1), (CaEtV)Pb₂I₆ (2), and (PrV)Pb₂I₆ (3).79

- Figure 4.20** UV-vis absorbance spectra of thin films (HyEtV)Pb₂I₆ (**1**) and (CaEtV)Pb₂I₆ (**2**). The thicknesses of thin and thick samples are ca. 200 and 400 nm, respectively.....80
- Figure 4.21** Images of a) 1D (HyEtV)Pb₂I₆ and b) 2D perovskite (PEA)₂PbI₄ thin films where gold electrodes with distances of 200 μm each are evaporated on top of them.81
- Figure 4.22** Current-voltage (*I-V*) curves of devices based on (a) (HyEtV)Pb₂I₆ (**1**) and (b) (CaEtV)Pb₂I₆ (**2**) in the dark and in the presence of light (1 sun illumination).81
- Figure 4.23** a) Current-voltage (*I-V*) curves of device based on 2D perovskite (PEA)₂PbI₄ in the dark and in the presence of light (1 sun illumination). b) UV-vis absorbance of 2D perovskite (PEA)₂PbI₄ thin film.82
- Figure 5.1** Molecular structures of the pyridinium-based organic cations used in this study.97
- Figure 5.2** X-ray crystal structures of 1D lead-iodide hybrids (a) **1**[PbI₄], (b) **2**[PbI₄], (c) **3**[PbI₄], (d) **4**[PbI₄], and (e) **5**[PbI₄]. Ellipsoids are shown at 50% probability and H atoms are omitted for clarity. Gray, purple, brown, red, and blue spheroids represent Pb, I, C, O, and N atoms, respectively.99
- Figure 5.3** X-ray crystal structures of 2D perovskites (a) **6**[PbI₄], (b) **7**[PbI₄], (c) **8**[PbI₄], and (d) **9**[PbI₄]. The inorganic layer separations denoted in the figure (red text) are defined as the distances between mean equatorial planes, of adjacent inorganic sheets. Ellipsoids are shown at 50% probability. H atoms are omitted for clarity. Gray, purple, brown, red, and blue spheroids represent Pb, I, C, O, and N atoms, respectively.101
- Figure 5.4** Depicted as red and green dashed lines are shortest distances between N atoms of primary ammonium group and aromatic ring's -NH⁺ functionalities of **6-9** and bridging or terminal Br atoms in cuboctahedral cavity of bromoplumbate lattice in a) **6**[PbI₄], b) **7**[PbI₄], c) **8**[PbI₄] and d) **9**[PbI₄]. Ellipsoids are shown at 50% probability. H atoms are omitted for clarity. Grey, purple, light brown and blue spheres represent Pb, I, C and N atoms, respectively.....102
- Figure 5.5** Penetration of the pyridinium rings and primary 2-ethylammonium pendant groups into the cuboctahedral cavities, which are built from the axial Pb-I bonds of four nearest neighbor [PbI₆]⁴⁻ octahedra, in (a) **6**[PbI₄], (b) **7**[PbI₄], (c) **8**[PbI₄], and (d) **9**[PbI₄]. The N-atom to axial I⁻ mean plane distances are provided in the figure. Ellipsoids are shown

at 50% probability. H atoms are omitted for clarity. Gray, purple, brown, red, and blue spheroids represent Pb, I, C, O, and N atoms, respectively.	103
Figure 5.6 Plan views of limited portions of single iodoplumbate layers, intended to show inter-octahedral distortions, in the 2D perovskites (a) $6[\text{PbI}_4]$, (b) $7[\text{PbI}_4]$, (c) $8[\text{PbI}_4]$, and (d) $9[\text{PbI}_4]$. Pb-I-Pb bond angles along the two equatorial axes are included. Gray and purple spheroids represent Pb and I atoms, respectively. Ellipsoids are shown at 50% probability.	104
Figure 5.7 Room temperature Ultra Violet-visible light (UV-vis) absorbance and photoluminescence (PL) spectra of 1D organic lead-iodide hybrids $1[\text{PbI}_3] - 5[\text{PbI}_3]$...	105
Figure 5.8 Images of 1D organic lead-iodide hybrids a) – b) $1[\text{PbI}_3]$, c) – d) $2[\text{PbI}_3]$, e) – f) $3[\text{PbI}_3]$, g) – h) $4[\text{PbI}_3]$ and i) – j) $5[\text{PbI}_3]$ under ambient light and UV lamp irradiation (365 nm).	106
Figure 5.9 a) Room temperature UV-vis and photoluminescence (PL) spectra of 2D hybrid perovskites $6[\text{PbI}_4] - 9[\text{PbI}_4]$ represented using solid and dashed lines, respectively. The PL spectra were obtained using 457nm continuous-wave laser excitation. b) Photographs of polycrystalline samples of $6[\text{PbI}_4] - 9[\text{PbI}_4]$ and a representative conventional 2D perovskite, $(\text{NEA})_2[\text{PbI}_4]$, where NEA = 2-(1-naphthyl)ethylammonium.	107
Figure 5.10 Temperature-dependent UV-vis spectra of thin films a) $6[\text{PbI}_4]$, b) $7[\text{PbI}_4]$, c) $8[\text{PbI}_4]$, and d) $9[\text{PbI}_4]$	108
Figure 5.11 UV-vis spectrum of a) $6[\text{PbI}_4]$, b) $7[\text{PbI}_4]$, c) $8[\text{PbI}_4]$, and d) $9[\text{PbI}_4]$ thin film at 80 K. E_g , E_x , and E_b denote optical band-gap, excitonic peak, and excitonic binding energy, respectively. E_g is obtained by extrapolation of the linear part of the bandgap onset in the spectrum.	109
Figure 5.12 Temperature-dependent PL spectra of single crystals a) $6[\text{PbI}_4]$, b) $7[\text{PbI}_4]$, c) $8[\text{PbI}_4]$, and d) $9[\text{PbI}_4]$ under excitation of a 457nm continuous-wave laser beam.	110
Figure 5.13 Temperature-dependent integrated PL intensity of single crystals a) $6[\text{PbI}_4]$, b) $7[\text{PbI}_4]$, c) $8[\text{PbI}_4]$, and d) $9[\text{PbI}_4]$ under excitation of a 457nm continuous-wave laser beam where the solid line is the best fit based on the Arrhenius equation.	111
Figure 5.14 a) Schematic diagram of the four-probe electrical conductivity measurements performed upon the polycrystalline samples. b) Plots of current density versus electric field strength ($J-E$ curves) for $6[\text{PbI}_4] - 9[\text{PbI}_4]$ at 297 K with $(\text{NEA})_2[\text{PbI}_4]$ serving as the	

control. c) Current versus voltage (I – V) characteristics of **6**[PbI₄]–**9**[PbI₄] and (NEA)₂[PbI₄] under white light irradiation (1 sun illumination). d) Time-dependent photoresponses of the 2D perovskites at 2.0 V bias, upon repetitive on and off white light (1 sun AM1.5G) illumination (interval 2.5 s), measured for around 20 s.....112

Figure 5.15 Single crystal structures of 2D perovskites (NEA)₂[PbI₄] where NEA is 2-naphthyl ethyl ammonium. The crystal structure is obtained from ref. 47. The inorganic layer separations shown in the figure are defined as the distances between successive mean equatorial planes built by neighbouring four lead atoms of the lead-iodide octahedra within an inorganic sheet. Ellipsoids are shown at 50% probability. H atoms are omitted for clarity. Gray, purple, brown, red, and blue spheres represent Pb, I, C, O, and N atoms, respectively.113

Figure 5.16 a) Room temperature UV-vis spectrum of conventional 2D perovskite (NEA)₂[PbI₄] where NEA is 2-naphthylethylammonium showing bandgap larger than **6**[PbI₄]–**9**[PbI₄] (ca. 2.58 eV). b) Pb–I–Pb bond angles shown on particular axes of (NEA)₂[PbI₄]. The higher bandgap can be attributed to the more ‘crumpled’ Pb–(μ-I)–Pb bond angles. The crystal structure is obtained from ref. 47. Ellipsoids are shown at 50% probability. Gray and purple spheres represent Pb and I atoms, respectively.114

Figure 5.17 Calculated total and partial density of states (DOS) of 2D perovskites a) **6**[PbI₄], b) **7**[PbI₄], c) **8**[PbI₄] and d) **9**[PbI₄].....115

Figure 5.18 Band structures of 2D perovskites a) **6**[PbI₄], b) **7**[PbI₄], c) **8**[PbI₄] and d) **9**[PbI₄] as functions of K-space paths calculated with density functional theory (DFT). Red arrows indicate the band gaps of the materials.116

Figure 6.1 Molecular structures of the dications PyrEA, ImEA, and PEA.....135

Figure 6.2 Single crystal X-ray structures of 2D perovskites (a) (PyrEA)[PbI₄] (**1**), (b) (ImEA)[PbI₄] (**2**), and (c) (PEA)₂[PbI₄] (**3**). Inorganic layer separations, defined as the distances between successive mean equatorial planes within an inorganic sheet, are 9.899, 9.537, and 16.073 Å for **1**, **2**, and **3**, respectively. Gray, purple, brown, and blue spheres represent Pb, I, C, and N atoms, respectively. H atoms are omitted for clarity.....136

Figure 6.3 Hydrogen bonding interactions between -NH functionality of the imidazolium cores and proximal bridging iodide ligands of the inorganic lattice (depicted as dashed lines) are believed to be the main driving force for corrugation of the lead-iodide sheets.137

- Figure 6.4** (a) Molecular structure of pyrazolium ethyl ammonium (PyrzEA) dication. (b) Single crystal X-ray structure of 1D inorganic-organic hybrid (PyrzEA)Pb₂I₆, where Pb₂I₆²⁻ corresponds to the molecular formula of 1D lead-iodide chains. Gray, purple, brown, red, and blue spheres represent Pb, I, C, O, and N atoms, respectively. H atoms are omitted for clarity. (c) UV-Vis absorption spectra of (PyrzEA)Pb₂I₆, spin coated onto a glass substrate. As is typical of a 1D lead-iodide hybrid material, it exhibits an excitonic peak at around 430nm. Inset is a photograph (i.e., visual appearance) of the corresponding thin film. ...138
- Figure 6.5** (a) Molecular structure of histammonium dication (HA). (b) Single crystal X-ray structure of 2D perovskite (HA)PbI₄, where PbI₄²⁻ corresponds to the molecular formula of 2D lead-iodide sheets. Gray, purple, brown, and blue spheres represent Pb, I, C, and N atoms, respectively. H atoms are omitted for clarity.139
- Figure 6.6** Low wavenumber Raman spectra of (PyrEA)PbI₄ (**1**), (ImEA)PbI₄ (**2**), and (PEA)₂PbI₄ (**3**), recorded at room temperature. Circles represent experimental data; red, blue, and green lines are the respective fitting components; and pink lines correspond to the resulting cumulative fits. Spectra are normalised and labels b_1 and b_2 correspond to the most intense vibrational modes.....140
- Figure 6.7** Low wavenumber Raman spectra of the 2D perovskites (PyrEA)PbI₄ (**1**), (ImEA)PbI₄ (**2**), and (PEA)₂PbI₄ (**3**), recorded at 80 K.140
- Figure 6.8** Field emission scanning electron micrographs of the surface morphologies of thin films of (a) (PyrEA)[PbI₄] (**1**), (b) (ImEA)[PbI₄] (**2**), and (c) (PEA)₂[PbI₄] (**3**) with insets showing the visual appearances of spin-coated thin films of the materials. Thin films of the 2D perovskites were created by spin coating onto glass substrates.....142
- Figure 6.9** (a) UV-vis absorption spectra of (PyrEA)PbI₄ (**1**), (ImEA)PbI₄ (**2**), and (PEA)₂PbI₄ (**3**). (b) Photoluminescence (PL) spectra of **1-3**, plus Gaussian fittings, recorded at RT, using excitation at 405 nm. (c) Time-resolved photoluminescence (TRPL) decays and fits for **1-3**. (d) Temperature-dependent integrated PL intensity for **1-3**. Excitonic binding energies (values given) were extracted by fitting to the Arrhenius equation.....143
- Figure 6.10** Top and side views of 2D inorganic lattices of (a) (PyrEA)[PbI₄] (**1**), (b) (ImEA)[PbI₄] (**2**) and (c) (PEA)₂[PbI₄] (**3**). Crystallographic axes are provided and the red lines denote particular Pb-I-Pb bond angles. The Pb-I-Pb bond angles between conjoined

$[\text{PbI}_6]^{4-}$ octahedra in **1** (159° to 174°), **2** (146° to 166°), and **3** (151° to 153°) are obtained from Mercury, where the smallest angles are measured without considering the exact planes in which in-plane and out-of-plane distortions occur. Thus, the values obtained are contributed to by both types of distortion and, in this report, there is no attempt to deconvolute the individual components. Schematic diagrams depict the (d) in-plane and (e) (complementary) out-of-plane distortion angles within the inorganic lattices. The blue line in (e) represents the mean plane of lead atoms within the 2D sheets.144

Figure 6.11 (a) Molecular structure of piperidinium ethyl ammonium (PipEA) dication. (b) Single crystal X-ray structure of 2D perovskite (PipEA) PbI_4 , where PbI_4^{2-} corresponds to the molecular formula of 2D lead-iodide sheets. Gray, purple, brown, and blue spheres represent Pb, I, C, and N atoms, respectively. H atoms are omitted for clarity. (c) UV-Vis absorption and photoluminescence (PL) spectra of (PipEA) PbI_4 spin coated onto a glass substrate. As is typical of a 2D lead-iodide perovskite, it exhibits excitonic absorption and PL peaks at about 540 and 575 nm, respectively. Inset is a photograph (i.e., visual appearance) of the corresponding thin film.146

Figure 6.12 (a) Time-resolved photoluminescence (TRPL) decays and fits for **1-3** along with the instrument response function (IRF). Residuals for the lifetime decay fittings of 2D perovskites **1** (b), **2** (c), and **3** (d).147

Figure 6.13 Temperature-dependent PL spectra, recorded in the range 77 to 298K, using an excitation wavelength (λ_{ex}) of 405 nm, of (a) (PyrEA) PbI_4 (**1**), (b) (ImEA) PbI_4 (**2**), and (c) (PEA) $_2\text{PbI}_4$ (**3**). For clarity, the PL intensities have been *normalized*.148

Figure 6.14 Temperature-dependent photoluminescence (PL) spectra of thin films of (a) (PyrEA)[PbI_4] (**1**), (b) (ImEA)[PbI_4] (**2**), and (c) (PEA) $_2$ [PbI_4] (**3**) with the relative intensity of each spectrum is shown. The samples were measured in the range 77 – 298K, using an excitation wavelength (λ_{ex}) of 405 nm.149

Figure 6.15 Peak deconvolution, using Gaussian fitting, of temperature-dependent photoluminescence (PL) spectra of thin films of (a) (PyrEA)[PbI_4] (**1**), (b) (ImEA)[PbI_4] (**2**), and (c) (PEA) $_2$ [PbI_4] (**3**). Gaussians 1 and 2 in (a) correspond to the P1a and P1b PL peaks of **1** at RT. Gaussians 1 and 2 in (b) could be P2a peak of **2** at RT, while Gaussian 3 is related to P2b. In agreement with the previous report,¹¹⁻¹² only 1 Gaussian is needed to deconvolute the PL peaks of **3** in the range of temperatures 77K – 298K. (Please note, the

assignments of each of the PL peaks are speculative and verification of their origins is beyond the scope of this study.) Integrated intensity of Gaussian 1 in both (a) and (b) were used to estimate the excitonic activation energy in **1** and **2**, respectively.150

Figure 6.16 (a) Typical cross-sectional scanning electron micrograph of 2D perovskite solar cells, with mesoporous architecture, employed in this study. (b) Photovoltaic current density-voltage ($J-V$) characteristics of best performing solar cells fabricated using (PyrEA)PbI₄ (**1**), (ImEA)PbI₄ (**2**), and (PEA)₂PbI₄ (**3**) as the solar absorbers. Dotted and solid lines represent measurements in the absence and presence of white light irradiation (1 sun; AM 1.5G), respectively. (c) External quantum efficiency (EQE) spectra of the best performing solar cells containing **1-3** (standard, vertical device configuration). Statistical representations of (d) Short-circuit current density (J_{sc}) and (e) power conversion efficiency (PCE) measured for 6 photovoltaic devices each for **1**, **2**, and **3**.153

Figure 6.17 Band energy diagrams of (PyrEA)[PbI₄] (**1**), (ImEA)[PbI₄] (**2**), (PEA)₂[PbI₄] (**3**), with the energies of the charge transport materials and electrodes comprising the solar cells included for reference. Valence band energies were estimated using photoelectron spectroscopy in air (PESA) measurements (**Figure 6.25**) and the band gaps were extracted from UV-Vis absorbance spectra (**Figure 6.26**).154

Figure 6.18 Cross-sectional view of field emission scanning electron microscope (FESEM) images of different solar cells containing the 2D perovskites (a) (PyrEA)[PbI₄] (**1**), (b) (ImEA)[PbI₄] (**2**), and (c) (PEA)₂[PbI₄] (**3**). Insets show prototypes of the solar cells fabricated.154

Figure 6.19 Glancing angle X-ray diffraction (GAXRD) patterns of thin layers of (a) (PyrEA)PbI₄ (**1**), (b) (ImEA)PbI₄ (**2**), and (c) (PEA)₂PbI₄ (**3**) deposited on glass (blue lines) and mesoporous titania-coated fluorinated tin oxide (TiO₂/FTO; red lines). For comparison, powder XRD patterns simulated using single crystal X-ray structures of **1**, **2**, and **3** are also included. Star symbols (*) denote peaks associated with the TiO₂/FTO substrate.155

Figure 6.20 (a) Schematic diagrams of ‘vertical’ and ‘horizontal’ device configurations used to assess the charge transport properties of the 2D perovskites. I-V curves of ‘horizontal devices’ based on (b) (PyrEA)[PbI₄] (**1**), (c) (ImEA)[PbI₄] (**2**), and (d) (PEA)₂[PbI₄] (**3**). Straight and dotted lines correspond to conductivity in absence and presence of white light (1 sun), respectively. At 2.0V, the on/off ratio of current generation

is ~89, 68, and 4286 for **1**, **2**, and **3**, respectively. (e) Time-dependent photoresponses of **1**, **2**, and **3** in devices fabricated with a horizontal configuration at 2.0V bias, upon repeated on and off white light irradiation (1 sun, interval 20s, measured for 250s).....156

Figure 6.21 UV-Vis absorption coefficients of thin films of (PyrEA)PbI₄ (**1**), (ImEA)PbI₄ (**2**), (PEA)₂PbI₄ (**3**). The values at each wavelength were extracted using the following equation, which takes into account the reflectance and transmittance of the films:

$$\alpha_{film}(\lambda) = \frac{1}{d_{film}} \ln \left(\frac{1 - R_{film}(\lambda)}{T_{film}(\lambda)} \right).^{13}$$

The films of **1**, **2**, and **3** used for measurement were 293, 278, and 338 nm thick, respectively.157

Figure 6.22 (a) Photoexcited carrier density (n_c) vs. integrated PL density (I_{PL}) for **1-3**. Dashed lines are numerical fits that take into account film thickness and relative absorbance at the excitation wavelength.¹⁴ Laser fluence-dependent photoluminescence (PL) spectra of thin films (b) (PyrEA)[PbI₄] (**1**) and (c) (ImEA)[PbI₄] (**2**). The samples were measured in the range of fluence set between 2.0 – 13.7 $\mu\text{J}.\text{cm}^{-2}$ at respective emission wavelengths of 558nm and 529 nm.158

Figure 6.23 Topological images of the surfaces of (a) (PyrEA)[PbI₄] (**1**) and (b) (ImEA)[PbI₄] (**2**) films. Average films roughness for **1** and **2** are 43 nm and 17 nm, respectively. The size of the atomic force microscopy (AFM) images is 20 x 20 μm^2 ...159

Figure 6.24 Statistical representations of 6 devices based on (PyrEA)PbI₄ (**1**), (ImEA)PbI₄ (**2**), and (PEA)₂PbI₄ (**3**) for parameters a) open-circuit voltage (V_{oc}) and b) fill-factor (FF).159

Figure 6.25 Photoelectron spectroscopy in air (PESA) measurements for (PyrEA)[PbI₄] (**1**), (ImEA)[PbI₄] (**2**), and (PEA)₂[PbI₄] (**3**). Solid lines represent linear fits of the two distinct domains in each data set, and the intersection between them provides an estimate of the valence band energy of the 2D perovskites (-5.54, -5.54 and -5.61 eV for **1**, **2** and **3**, respectively).....160

Figure 6.26 Absorption spectra of thin films of (PyrEA)[PbI₄] (**1**), (ImEA)[PbI₄] (**2**), and (PEA)₂[PbI₄] (**3**). Solid lines are from extrapolation of the rising edge of the absorbance plots (i.e. the linear parts of the curves) and correspond to the band gaps of the 2D perovskites.160

Figure 6.27 Summary of progress in efficiency of solar cells based upon pure $n = 1$ 2D lead-iodide perovskites as a function of templating organic cations.161

- Figure 7.1** Schematic representations of the structures of 2D metal-halide perovskites featuring a) (100)-orientation, b) '2 × 2' (110)-orientation, c) '3 × 3' (110)-orientation, and d) '4 × 4' (110)-orientation.175
- Figure 7.2** X-ray crystal structure of '3 × 3' (110)-oriented 2D perovskite ImEA[SnI₄]. Gray, purple, brown, and blue spheres represent Pb, I, C, and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.177
- Figure 7.3** Crystal structure of different organic conformations ImEA⁺² in corrugated 2D perovskite ImEA[SnI₄]. Grey and blue spheres represent C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.177
- Figure 7.4** Depicted as red dashed lines are shortest distances between N atoms of primary ammonium group and imidazolium ring of ImEA⁺² and bridging or terminal I atoms in cuboctahedral cavity of bromoplumbate lattice in ImEA[SnI₄]. Green dashed line, on another hand, depict the shortest distances between alkylated endocyclic N atom of imidazolium ring with terminally bound iodide ion. Light purple, purple, light brown and blue spheres represent Sn, I, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.179
- Figure 7.5** Single crystal structures of histamonium-based 2D (100) tin-iodide perovskite 2[SnI₄]. Light purple, purple, light brown and blue spheres represent Sn, I, C and N atoms, respectively. H atoms are omitted for clarity. In the insets are the molecular structures of **2**. The structure is obtained from ref. 19.180
- Figure 7.6** Single crystal structures of pyridinium-based 2D (100) tin-iodide perovskites a) **3**[SnI₄], b) **4**[SnI₄], c) **5**[SnI₄], and d) **6**[SnI₄]. Light purple, purple, light brown and blue spheres represent Sn, I, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability. In the insets are the molecular structures of **3-6**.180
- Figure 7.7** Depicted as red dashed lines are shortest distances between N atoms of primary ammonium group and aromatic ring's -NH⁺ functionalities of **4-6** and bridging or terminal Br atoms in cuboctahedral cavity of bromoplumbate lattice in **4**[SnI₄]-**6**[SnI₄]. Light purple, purple, light brown and blue spheres represent Sn, I, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability. As shown in the figures, unlike in ImEA[SnI₄], the intermolecular interaction between the organic hydrogen

functionalities of **4-6** and $[\text{SnI}_6]^{4-}$ cuboactahedral cavity are not capable of yielding ‘*cis* two vacant vertexes’, thus preventing the (110) inorganic lattices to form.181

Figure 7.8 Room temperature, static ^{119}Sn solid-state NMR spectra of (a) ImEA[SnI₄] and (b) 3-PyrEA[SnI₄]. Experimental data, total simulated line-shapes, and deconvoluted simulated resonances are depicted using black, red and blue lines, respectively.182

Figure 7.9 Room temperature magic angle spinning (MAS) ^{13}C solid state (SS)-NMR spectra of 3-PyrEA[SnI₄] (top) and ImEA[SnI₄] (bottom).183

Figure 7.10 Single crystal structures of a) (110)-type ImEA[SnI₄] and b) (100)-type 3-PyrEA[SnI₄] showing different number conformations of organic dications within the two-dimensional inorganic lattices. Light purple, purple, light brown and blue spheres represent Sn, I, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.183

Figure 7.11 a) Room temperature UV-visible absorbance and photoluminescence (PL) spectra of ImEA[SnI₄]. b) Temperature-dependent PL spectra of single crystal ImEA[SnI₄] (normalized intensity), recorded using a 573 nm excitation wavelength continuous-wave laser beam. c) Temperature-dependent integrated PL intensity of single crystal ImEA[SnI₄]. The solid line is a best fit of the experimental data (red circles) to the Arrhenius equation, where I_0 corresponds to the intensity at 0 K, E_a to the activation energy, and k_B to the Boltzmann constant.184

Figure 7.12 Chromaticity coordinates (0.64, 0.36) for the photoluminescence (PL) emission of ImEA[SnI₄] at room temperature (black circle).185

Figure 7.13 Images of ImEA[SnI₄] single crystal a) without and b) with exposure of laser of 573 nm excitation wavelength at room temperature. The laser spot size is around 2 μm185

Figure 7.14 Temperature-dependent photoluminescence (PL) spectra of single crystal ImEA[SnI₄] under excitation of a 573 nm continuous-wave laser beam.186

Figure 7.15 Schematic of the device configuration used for photoresponse study of ImEA[SnI₄].187

Figure 7.16 a) Current-voltage (I - V) curves for the lateral devices with interdigitated electrodes containing ImEA[SnI₄] (film on 100 μm spaced FTO electrodes; see SI for device configuration), before poling, measured in the dark (black circles) and upon

illumination by a 445 nm LED light, with a power of 1.4 mW mm ⁻² (red circles). b) <i>I-V</i> curve of the device after 2 V/μm poling, under illumination of light. c) Current-time (<i>I-t</i>) characteristic of the device after poling at 2 V/μm under pulsed light.	187
Figure 7.17 Current-voltage (<i>I-V</i>) curves for the lateral devices with interdigitated electrodes containing ImEA[PbI ₄]. Currents generated at 1.0 V in the absence and presence of light illumination are 0.013 nA and 1.183 nA, respectively.....	188
Figure 7.18 Response of the material during application of a field of pulsed 2 V/μm.....	188
Figure 8.1 The organic dications used in this study.....	201
Figure 8.2 Single crystal X-ray structures of the 2D perovskites a) 1 [PbBr ₄], b) 2 [PbBr ₄], c) 3 [PbBr ₄], d) 4 [PbBr ₄] and e) 5 [PbBr ₄]. Black, maroon, brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.	202
Figure 8.3 Depicted as dashed lines are shortest distances between N atoms of primary ammonium group (red) and, NH ⁺ functional group (group), and endocyclic N-atoms (blue) of the imidazolium ring of 1 and bridging or terminal Br atoms in cuboctahedral cavity of bromoplumbate lattice in 1 [PbBr ₄]. Grey, brown, light brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.	203
Figure 8.4 Depicted as dashed lines are shortest distances between N atoms of primary ammonium group (red) and, NH ⁺ functional group (group), and endocyclic N-atoms (blue) of the imidazolium ring of 1 and terminal Br atoms, leading to ‘ <i>cis</i> two vacant vertices’ in the inorganic lattice. Grey, brown, light brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.....	204
Figure 8.5 Depicted as dashed lines are shortest distances between N atoms of primary ammonium group (red) and imidazolium ring (green) of 2 and surrounding bridging or terminal Br atoms of (100) oriented bromoplumbate lattice in 2 [PbBr ₄]. Grey, brown, light brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.....	204

- Figure 8.6** Depicted as dashed lines are shortest distances between N atoms of primary ammonium group (red) and imidazolium ring (green) of **2** and terminal Br atoms, leading to ‘*trans* two vacant vertices’ in the inorganic lattice. Grey, brown, light brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.205
- Figure 8.7** Depicted as dashed lines are shortest distances between N atoms of primary ammonium group (red) and imidazolium ring (green) of **3** and surrounding bridging or terminal Br atoms of (100) oriented bromoplumbate lattice in **3**[PbBr₄]. Grey, brown, light brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.....205
- Figure 8.8** Depicted as dashed lines are shortest distances between N atoms of primary ammonium group (red) and imidazolium ring (green) of **3** and terminal Br atoms, leading to ‘*trans* two vacant vertices’ in the inorganic lattice. Grey, brown, light brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.206
- Figure 8.9** Depicted as dashed lines are shortest distances between N atoms of primary ammonium group (red) and imidazolium ring (green) of **4** and surrounding bridging or terminal Br atoms of (100) oriented bromoplumbate lattice in **4**[PbBr₄]. Grey, brown, light brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.....207
- Figure 8.10** Depicted as dashed lines are shortest distances between N atoms of primary ammonium group (red) and imidazolium ring (green) of **4** and terminal Br atoms, leading to ‘*trans* two vacant vertices’ in the inorganic lattice. Grey, brown, light brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.207
- Figure 8.11** Depicted as dashed lines are shortest distances between N atoms of primary ammonium group (red) and imidazolium ring (green) of **5** and surrounding bridging or terminal Br atoms of (100) oriented bromoplumbate lattice in **5**[PbBr₄]. Grey, brown, light brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.....208

Figure 8.12 Depicted as dashed lines are shortest distances between N atoms of primary ammonium group (red) of 4 and terminal Br atoms, leading to ‘ <i>trans</i> two vacant vertices’ in the inorganic lattice. Grey, brown, light brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.	208
Figure 8.13 Room temperature (RT) a) UV-vis absorption and b) photoluminescence (PL) spectra of 1 [PbBr ₄] – 5 [PbBr ₄]. c) Plot and linear fit of the dependence of PL intensity upon laser fluence for 1 [PbBr ₄], measured at 293 K, in the range 5 - 50 $\mu\text{J}/\text{cm}^2$. d) PL spectrum of 1 [PbBr ₄] at RT (red line) and 77 K (black line). e) Chromaticity coordinates for the PL emission of 1 [PbBr ₄], compared with reported values for previously reported 2 × 2 (110) 2D perovskites.	211
Figure 8.14 Photoluminescence (PL) evolution of 1 [PbBr ₄] as a function of excitation fluence.	213
Figure 8.15 Photoluminescence (PL) evolution of 1 [PbBr ₄] as a function of temperature.	213
Figure 8.16 Time-resolved photoluminescence (PL) spectra of 1 [PbBr ₄] recorded at emission wavelength 550 nm at 293 K and 77 K. PL lifetimes of approximately 1.43 ns and 3.31 ns at 293 K and 77 K, respectively, are obtained by monoexponential fittings.	214
Figure 8.17 Chromaticity coordinates of the emission of 1 [PbBr ₄] – 5 [PbBr ₄].	214
Figure 9.1 The organic dications, 1 and 2 , used in this study.	225
Figure 9.2 Powder X-ray diffraction (PXRD) patterns of powdered 2D hybrid perovskites 1 [PbBr ₄] (a) and 2 [PbBr ₄] (b). The simulated room temperature (RT) PXRD patterns are also provided for comparison.	226
Figure 9.3 Single crystal X-ray structures of a) 1 [PbBr ₄] and b) 2 [PbBr ₄] at room temperature. Penetration of the organic dications into the ‘bay regions’ of the 2D perovskites, built from four neighbouring [PbBr ₆] ⁴⁻ octahedra, are depicted in c) 1 [PbBr ₄] and d) 2 [PbBr ₄]. The approximate degree of penetration of the ethylammonium groups, (illustrated by a dotted orange line) are given in the figure. ‘Top view’ of (e) 1 [PbBr ₄] and (f) 2 [PbBr ₄], presented with their respective crystallographic axes. Pb-(μ -Br)-Pb bond angles are included. Black, brown, grey, and blue spheres represent Pb, Br, C, and N atoms,	

respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.....	227
Figure 9.4 Single crystal X-ray structures of a) 1 [PbBr ₄] and b) 2 [PbBr ₄] at 100 K. Penetration of the organic dications into the ‘bay regions’ of the 2D perovskites, built from four neighbouring [PbBr ₆] ⁴⁻ octahedra, are depicted in c) 1 [PbBr ₄] and d) 2 [PbBr ₄]. The approximate degree of penetration of the ethylammonium groups, (illustrated by a dotted orange line) are given in the figure. ‘Top view’ of (e) 1 [PbBr ₄] and (f) 2 [PbBr ₄], presented with their respective crystallographic axes. Pb-(μ-Br)-Pb bond angles are included. Black, brown, grey, and blue spheres represent Pb, Br, C, and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.	228
Figure 9.5 Raman spectra of (PipEA)PbBr ₄ (upper panel) and (PyrEA)PbBr ₄ (lower panel).	231
Figure 9.6 Absorption (blue line) and luminescence (red line) spectra of (a) 1 [PbBr ₄] and (b) 2 [PbBr ₄], at room temperature. Temperature-dependent photoluminescence of (c) 1 [PbBr ₄] and (d) 2 [PbBr ₄]. PL spectra were recorded on single crystals using an excitation wavelength (λ_{exc}) of 405 nm.	233
Figure 9.7 Absorption (blue line) and photoluminescence (red line) spectra of a) 1 [PbBr ₄] and b) 2 [PbBr ₄] measured on perovskite thin films.....	233
Figure 9.8 CIE chromaticity diagram and coordinates for the room temperature emission of 1 [PbBr ₄] (0.19;0.17) and 2 [PbBr ₄] (0.38;0.38) under excitation wavelength $\lambda_{\text{exc}} = 405$ nm.	234
Figure 9.9 Temperature dependent photoluminescence ($\lambda_{\text{exc}} = 405$ nm) of a) 1 [PbBr ₄] and b) 2 [PbBr ₄].	235
Figure 9.10 Temperature dependence of a) full width at half maximum (FWHM) and b) peak maximum of broadband emission.	236
Figure 9.11 Arrhenius plots of the integrated PL intensity (I) as a function of temperature. The fitting was done with the Arrhenius formula including two competitive nonradiative recombination channels $I = I_0 / [1 + C_1 \exp(-Ea_1/kT) + C_2 \exp(-Ea_2/kT)]$, where Ea_1 , Ea_2 are the activation energies for the thermal de-trapping process, k is the Boltzmann constant, I_0 is the zero-temperature PL intensity and C_1 , C_2 represent the strength of the quenching processes. The fitting results are summarized in Table 9.4	236

- Figure 9.12** Integrated PL intensity, at 77 K, as function of excitation fluence. a) **1**[PbBr₄] (integration range 428 nm – 435 nm); b) **1**[PbBr₄] (integration range 435 nm – 460 nm); c) broadband emission of **1**[PbBr₄] (red line) and **2**[PbBr₄] (blue line) with integration range of 460 - 900 nm for both. PL spectra were recorded for single crystals, using an excitation wavelength (λ_{exc}) of 405 nm.237
- Figure 9.13** Time-resolved photoluminescence (TRPL) of **1**[PbBr₄] and **2**[PbBr₄]. a) Excitonic emission of **1**[PbBr₄] (in the range 420 - 435 nm) and broadband emission of **2**[PbBr₄] (in the range 450 nm - 750 nm) at 298 K; b) broadband emission of **1**[PbBr₄] and **2**[PbBr₄] (in the range 470 - 750 nm) at 77 K. Data was recorded for single crystals, using an excitation wavelength (λ_{exc}) of 368 nm.238
- Figure 10.1** The *N*-alkyl pyridinium cations used in this work.251
- Figure 10.2** Single crystal X-ray structures of the one-dimensional (1D) lead-bromide hybrids a) **4**[PbBr₃], b) **5**[PbBr₃] and c) **6**[PbBr₃]. Dark gray, brown, gray, blue and red spheres represent Pb, Br, C, N and O atoms, respectively. H atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability.....253
- Figure 10.3** Single crystal X-ray structures of trimeric lead-bromide hybrids a) (**1**)₂[PbBr₄], b) (**2**)₂[PbBr₄] and c) (**3**)₂[PbBr₄]. Dark gray, brown, gray, blue, red, and yellow spheres represent Pb, Br, C, N, O and S atoms, respectively. H atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability.....253
- Figure 10.4** Single crystal X-ray structures of a) (**1**)₂[PbCl₄] and b) (**1**)[PbI₃] containing trimeric and one-dimensional chain of inorganic bromoplumbate lattice, respectively. Dark gray, green, purple, brown and blue spheres represent Pb, Cl, I, C, and N atoms, respectively. H atoms are omitted for clarity.....254
- Figure 10.5** Low-frequency Raman spectra of hybrid **4**[PbBr₃] and (**1**)₂[PbBr₄] single crystals showing a shift in Pb–Br stretching to lower wavenumber from one-dimensional bromoplumbate chain (142 cm⁻¹) to the trimeric structure (132 cm⁻¹).255
- Figure 10.6** Photoluminescence spectra of (**1**)₂[PbBr₄], (**2**)₂[PbBr₄], and (**3**)₂[PbBr₄] at room temperature with an excitation wavelength of 350 nm.257
- Figure 10.7** a) Room temperature UV-vis diffuse reflectance (DRS), transformed using Kubelka-Munk (K-M) function, and photoluminescence (PL, λ_{ex} = 350 nm) spectra of (**1**)₂[PbBr₄]. b) Laser fluence-dependent integrated PL intensity of (**1**)₂[PbBr₄], recorded in

the range 0.08 – 1.43 $\mu\text{J}/\text{cm}^2$ at 293 K, plus a linear fit of the data. c) Integrated PL intensity as a function of temperature (red triangles), and a fit of the data to equation 4 (black line). The experiment was conducted using 350 nm excitation and 0.08 $\mu\text{J}/\text{cm}^2$ laser fluence. d) Time-resolved PL spectra of $(\mathbf{1})_2[\text{PbBr}_4]$, recorded at an emission wavelength of 570 nm, at temperatures of 77 and 293 K. e) Full-width at half-maxima (FWHM, blue circles) and PL lifetime (red squares) as a function of temperature. Similarly coloured solid lines correspond to fits of the experimental data to equations 3 and 4, respectively.258

Figure 10.8 Excitation line of reference and emission spectrum of $(\mathbf{1})_2[\text{PbBr}_4]$ collected by an integrating sphere. The photoluminescence quantum efficiency (PLQE) is calculated using the equation: $\eta_{QE} = \frac{I_S}{(E_R - E_S)}$259

Figure 10.9 Photoluminescence spectrum of $\mathbf{4}[\text{PbBr}_3]$, $\mathbf{5}[\text{PbBr}_3]$, and $\mathbf{6}[\text{PbBr}_3]$ at room temperature with an excitation wavelength of 350 nm.259

Figure 10.10 Excitation-wavelength-dependent photoluminescence (PL) spectra of $(\mathbf{1})_2[\text{PbBr}_4]$ at room temperature.260

Figure 10.11 Emission-wavelength-dependent photoluminescence excitation (PLE) spectra of $(\mathbf{1})_2[\text{PbBr}_4]$ at room temperature.261

Figure 10.12 Photoluminescence (PL) evolution of $(\mathbf{1})_2[\text{PbBr}_4]$ as a function of excitation power at room temperature.261

Figure 10.13 Photoluminescence (PL) evolution of $(\mathbf{1})_2[\text{PbBr}_4]$ as a function of temperature.262

Figure 10.14 Room temperature time-resolved photoluminescence (PL) spectra of $(\mathbf{1})_2[\text{PbBr}_4]$ at emission wavelengths 500 nm, 570 nm, and 600 nm.263

Figure 10.15 Temperature-dependent time-resolved photoluminescence (PL) spectra of $(\mathbf{1})_2[\text{PbBr}_4]$ (see **Table 10.2** for the summary of the PL lifetime at each temperature).263

Figure 11.1 Molecular structures of proposed organic cations containing electron withdrawing functionalities.284

Figure 11.2 Molecular structures of proposed organic cations containing electron diazines and triazines as the aromatic cores.284

Figure 11.3 Molecular structures of proposed organic cations containing heavy atoms iodine and bromine to induce halogen bonding interaction with the inorganic lattices.	285
Figure 11.4 Molecular structures of proposed organic cations where the cyclic core is expanded.	286
Figure 11.5 Molecular structures of proposed organic cations where the substituents are endowed with bulky functionalities.	287

Scheme captions

Scheme 2.1 Possible moisture degradation route of 3D MAPbI ₃ iodoplumbates. The scheme is adapted from ref. 65.	24
Scheme 3.1 General synthetic route to pyridinium halides used in this thesis.....	45
Scheme 3.2 General synthetic route to viologen dihalides used in this thesis.	45
Scheme 3.3 General synthetic route to ammonium halides used in this thesis.	46
Scheme 4.1 Synthetic route to 4,4'-bis(aminomethyl)-1,1'-biphenyl.....	88
Scheme 4.2 Synthetic route to 4,4'-bis(2-aminoethyl)-1,1'-biphenyl.....	88

Table captions

Table 2.1 Calculated effective radii of several small molecular cations. ¹⁷⁻¹⁸	25
Table 4.1 UV-Vis DRS spectral parameters of iodide salts and perovskite hybrids.	67
Table 4.2 Semiconducting parameters of the 1D perovskites.....	74
Table 4.3 Crystallographic and refinement data for (HyEtV)Pb ₂ I ₆ , (CaEtV)Pb ₂ I ₆ , (PrV)Pb ₂ I ₆ , and (BpbmA)Pb ₂ I ₆	91
Table 4.4 Crystallographic and refinement data for (HyEtV)I ₂ , (CaEtV)I ₂ , and (PrV)I ₂	92
Table 4.5 Crystallographic and refinement data for alternative structures (HyEtV)Pb ₂ I ₆ and (CaEtV)Pb ₂ I ₆	93
Table 5.1 Selected structural parameters for the 1D iodoplumbates templated by 1 – 5 . ^a	100
Table 5.2 Iodoplumbate inter-layer separations (Å) and Pb-I-Pb angles (°) in 6 [PbI ₄], 7 [PbI ₄], 8 [PbI ₄], and 9 [PbI ₄], plus selected published 2D perovskites templated with aromatic ring-based dications.	103
Table 5.3 Summary of distortion parameters of 1 [PbI ₃] – 5 [PbI ₃].....	127
Table 5.4 Crystallographic and structure refinement data for 1 [PbI ₃], 2 [PbI ₃], and 3 [PbI ₃]. ^a	128
Table 5.5 Crystallographic and structure refinement data for 4 [PbI ₃] and 5 [PbI ₃]. ^a	129
Table 5.6 Crystallographic and structure refinement data for 6 [PbI ₄] and 7 [PbI ₄]. ^a	130
Table 5.7 Crystallographic and structure refinement data for 8 [PbI ₄] and 9 [PbI ₄]. ^a	131
Table 6.1 Distortion parameters derived from the single crystal X-ray structures of 2D perovskites 1-3 . ^a	139
Table 6.2 Summary of selected optical parameters for 1-3 ^a	145
Table 6.3 Summary of the time-resolved photoluminescence (TRPL) parameters of the 2D perovskites 1-3	146
Table 6.4 Photovoltaic performance of the best performing 2D perovskite solar cells fabricated with different concentration solutions of precursors. Thickness of the perovskite layers was measured by field-emission scanning electron microscopy (FE-SEM).....	151

Table 6.5 Photovoltaic performance of devices fabricated from 0.50 M (PyrEA)[PbI ₄] precursor solutions.	152
Table 6.6 Photovoltaic performance of devices fabricated from 0.50 M (ImEA)[PbI ₄] precursor solutions.	152
Table 6.7 Photovoltaic performance of devices fabricated from 0.50 M (PEA) ₂ [PbI ₄] precursor solutions.	152
Table 6.8 Average photovoltaic performance of devices fabricated from 0.50 M (PyrEA)[PbI ₄], (ImEA)[PbI ₄], and (PEA) ₂ [PbI ₄] precursor solutions.	153
Table 6.9 Summary of photovoltaic parameters from the best performing solar cells fabricated from 1-3 . ^a	161
Table 6.10 Crystallographic and structure refinement data for (PyrEA)[PbI ₄] (1), (ImEA)[PbI ₄] (2), and (PEA)[PbI ₄] (3). ^a	171
Table 6.11 Crystallographic and structure refinement data for (PyrzEA)[Pb ₂ I ₆], (HA)[PbI ₄], and (PipEA)[PbI ₄]. ^a	172
Table 7.1 Summary of distortion parameters of ImEA[SnI ₄] in comparison to other (100)- and (110)-Sn-I perovskites.	178
Table 7.2 Crystallographic and structure refinement data for ImEA[SnI ₄]. ^a	196
Table 7.3 Crystallographic and structure refinement data for 3 [SnI ₄] and 4 [SnI ₄]. ^a	197
Table 7.4 Crystallographic and structure refinement data for 5 [SnI ₄] and 6 [SnI ₄]. ^a	198
Table 8.1 Calculated intra-octahedral distortion (Δ_{oct}) of 1 [PbBr ₄]- 5 [PbBr ₄].	209
Table 8.2 Summary of distortion parameters comparison of 1 [PbBr ₄], with other 2 × 2 (110) 2D perovskites.	210
Table 8.3 Calculated Commission Internationale de l'Eclairage (CIE) chromaticity coordinates, Color Rendering Index (CRI) and Correlated Color Temperature (CCT) of 1 [PbBr ₄] – 5 [PbBr ₄].	215
Table 8.4 Crystallographic and structure refinement data for 1 [PbBr ₄], 2 [PbBr ₄], and 3 [PbBr ₄]. ^a	221
Table 8.5 Crystallographic and structure refinement data for 4 [PbBr ₄] and 5 [PbBr ₄]. ^a	222
Table 9.1 Summary of distortion parameters for 1 [PbBr ₄], 2 [PbBr ₄] and other selected 2D perovskites.	229

Table 9.2 Summary of distortion parameters of 2D perovskites 1 [PbBr ₄] and 2 [PbBr ₄] in comparison to (110) Pb-Br perovskites.	230
Table 9.3 Summary of distortion parameters for 1 [PbBr ₄] and 2 [PbBr ₄] at different temperatures.	230
Table 9.4 Fitting results for the Arrhenius plots in Figure 9.11	236
Table 9.5 Fitting results of TRPL decays.	239
Table 9.6 Crystallographic and structure refinement data for 1 [PbBr ₄] and 2 [PbBr ₄] at room temperature. ^a	246
Table 9.7 Crystallographic and structure refinement data for 1 [PbBr ₄] and 2 [PbBr ₄] at 100 K. ^a	247
Table 10.1 Distortion parameters derived from the single crystal X-ray structures of the trimeric bromoplumbates (1) ₂ [PbBr ₄], (2) ₂ [PbBr ₄] and (3) ₂ [PbBr ₄]. ^a	256
Table 10.2 Summary of photoluminescence lifetime of (1) ₂ [PbBr ₄] at different temperature.	264
Table 10.3 Crystallographic and structure refinement data for (1) ₂ [PbBr ₄], (2) ₂ [PbBr ₄] and (3) ₂ [PbBr ₄]. ^a	273
Table 10.4 Crystallographic and structure refinement data for 4 [PbBr ₃], 5 [PbBr ₃] and 6 [PbBr ₃]. ^a	274
Table 10.5 Crystallographic and structure refinement data for (1) ₂ [PbCl ₄] and (1)[PbI ₃]. ^a	275

Abbreviations

°C	Centigrade degree
Å	Angstrom
0D	Zero-dimensional
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
a.u.	Arbitrary unit
AFM	Atomic force microscopy
ATR	Attenuated total reflectance
aq.	Aqueous
CBM	Conduction band minimum
CCT	Correlated color temperature
CIE	Commission internationale de l'éclairage
CRI	Color rendering index
dmf	Dimethylformamide
dmso	Dimethylsulfoxide
E_g	Band gap
ETM	Electron-transporting material
eq.	Equivalent
eV	Electron volt
FE-SEM	Field emission scanning electron microscopy
FF	Fill factor
FTIR	Fourier transform infrared spectroscopy
FTO	Fluorine-doped tin oxide
FWHM	Full width half maximum
HOMO	Highest occupied molecular orbital
HTM	Hole-transporting material
ITO	Indium tin oxide
IPCE	Incident photo-to-current efficiency

J_{sc}	Short-circuit current density
LUMO	Lowest unoccupied molecular orbital
M	Molar
mol	Mole
NMR	Nuclear magnetic resonance spectroscopy
PCE	Power conversion efficiency
PL	Photoluminescence
PXRD	Powder x-ray diffraction
PV	Photovoltaics
rpm	Rotations per minute
RT	Room temperature
UV	Ultraviolet
VBM	Valence band maximum
V_{oc}	Open-circuit voltage
XRD	X-ray diffraction

Chapter 1

Introduction

This chapter presents the motivation for the research project (i.e. energy crisis, solar to electricity conversion, and lighting). Strategies to improve the optoelectronic properties of low-dimensional hybrid metal-halides as materials of interest are summarized in objectives and scopes of the work. The overall flow of the thesis is also presented in this chapter before it is concluded with a summary of the scientific contribution of this thesis to the field.

1.1 Energy crisis, solar to electricity conversion, and electrical lightings

Human civilization's reliance on fossil fuels is huge and it constitutes to more than 80% of the total world primary power consumption of 157,135 TWh as reported in 2017 (**Figure 1.1**).¹ Such a staggering rate of energy expenditure and associated lopsided fraction of fossil fuel consumption has been made possible thanks to immense population growth and worldwide technological development. This has happened particularly in the last three decades during which additional of over 2 billion people and an increase in energy demands of at least 6 TW have occurred.¹⁻³ Not only that, further rapid modernization of developing nations and cities is expected to double-up the figure in another 2-3 decades, opening-up an immense power supply gap of 14 TW by 2050.¹⁻³

Figure 1.1 Growth of world primary energy consumption (in million tonnes oil equivalent where 1 tonne of oil equivalent is ca. 1.163×10^{-5} TWh) by fuel since 1992. The figure is adapted from ref. 1.

In addition to being deleterious towards health and environment due to the generation of harmful and undesirable gases, fossil fuels by themselves are an energy source that are not renewable within human lifetimes.⁴⁻⁸ Despite extensive efforts in looking for new points of supply,⁹⁻¹⁰ debates on the size of its total reserves,¹¹⁻¹² and surprising declining global

prices,¹³⁻¹⁵ fossil fuels are inevitably vanishing at a remarkable rate. Meeting the world's energy demand, which is projected to step-up to the level of 17,000-18,000 million tonnes oil equivalent by 2035, is no longer a trivial matter¹⁻³ and an imminent global economic emergency is feared to follow in the near future.¹⁶⁻¹⁸ There is, therefore, a sense of urgency to find sustainable and yet affordable, accessible sources that can supply sufficient energy for human consumptions.^{4-5, 7, 19}

The amount of energy that the Earth receives from the Sun is not only sustainable, but also near unimaginable. Each year, the Sun provides the Earth with around 3,850,000 exajoules of energy (equivalent to around 1.1 billion TWh), dwarfing any other energy sources, renewable and non-renewable alike.^{8, 20-21} Assuming a 100% energy conversion, such enormous continuously supplied power would translate to meeting human's annual energy consumption (~142,754 TWh) within just 1.1 hour. Considering the ultimate known recoverable fossil fuels reserves, the dependency of humans towards fossil fuels can be fully replaced by the energy which the Sun supplies in only a few days.^{8, 20-21}

Widespread utilization of solar energy is therefore deemed to bring positive impacts to global energy security. This can be done through simultaneous reduction of fossil fuel reliance because not only abundant, it is also conveniently accessible and does not produce significant pollutants harmful to health and environment. To harness the solar energy, various methods and techniques have been developed, but generally solar photons can be harvested and converted into three forms of energy, namely electricity (photovoltaic),²¹⁻²³ chemical/fuel (photocatalysis or artificial photosynthesis),²⁴⁻²⁵ and heat (solar thermal & heating).²⁶⁻²⁷ To date, most attention has been paid to the first option because as an end-product, electricity is a form of energy that can be easily and cheaply transported with relatively small losses through an electric grid. More importantly, 17% of all the World's secondary energy has been used in the form of electricity.²⁸ It has been providing human civilization with energy to perform activities such as food cooking, washing and laundry, domestic and public illumination and access to electronic appliances. As such, access to electricity strongly determines humanity's living standard.

Furthermore, with regards to global electricity consumption, around one-fifth of its total share is attributed to lighting purposes where such fraction is higher in many developing countries.²⁹⁻³¹ This proportion is expected to increase by 80% by 2030 as a result of introduction of electric lighting to 1.6 billion people who have been using lamps based on combustible fuels like kerosene and biomass.²⁹⁻³¹ As one of the biggest electrical end-uses, lighting, represented more than 33 billion lamps currently operating worldwide, has consumed more than 2650 TWh of energy annually.²⁹ Since current electricity generation is highly dependent on fossil fuels,³² such consumption values translate to CO₂ emissions as high as 1.9 gigatonnes, dwarfing the yearly CO₂ emissions from global aviation activities by a factor of three.²⁹ Thus, improving the energy efficiency of lighting devices would potentially be one of the most effective solutions as it would not only save energy, but can also reduce the emissions of CO₂ by at least 5% over the next decade.³³ Even with a reduction in energy usage, enhanced performance can still be realized, rendering the technology even more attractive to consumers, policymakers, and company stakeholders.

Driven by the aforementioned problems, this thesis centers around the synthesis and exploration of novel alternative materials *via* systematic modification at a molecular level (i.e. molecular engineering). The materials will be made of Earth-abundant precursors, easy and cheap to process, reproducible with good quality and high throughput. More critically, they will be endowed with suitable semiconducting, electronic, and optical properties in such a way that they can be relevant to applications such as photovoltaics and solid-state lightings.

1.2 Objectives and scope of work

The studies in this thesis focus on the use of molecular engineering to induce desirable optoelectronic properties of low-dimensional organic metal-halide hybrid materials. For photovoltaic applications, we investigate the use of electron-withdrawing viologen (*N,N'*-dialkyl-4,4'-bipyridinium) cations endowed with hydrogen bonding functionalities and compact organic dications bearing pyridinium or imidazolium core. As for solid-state lighting applications, the templating effects of organic cations with imidazolium,

piperidinium, and pyridinium cores will be probed. In between, the studies also attempt to understand the formability of inorganic framework with different structures and dimensionalities *via* functional group variation. The detailed main objectives and scopes of this thesis are summarized as follows:

- a. Enhancing photoconductivity of one- and two-dimensional perovskites via modulation of a) charge transfer interaction between organic and inorganic moieties and/or b) inter-inorganic framework interaction in the lattices.*

Due to the high HOMO-LUMO gap, organic cations in low-dimensional perovskites do not typically exhibit electronic interaction with the metal-halide lattices, which results in optoelectronic properties that solely come from the latter.

To address this, we incorporated electron withdrawing viologens so that charge transfer interaction with the 1D inorganic chain could be realized. The effects of such interaction were mainly probed with UV-vis and photoelectron spectroscopies. Furthermore, in order to reinforce such interaction, viologens endowed with hydrogen bonding groups are deliberately chosen so as to induce π - π stacking of the organics in the crystal packing. The roles and effects of π - π stackings in the enhanced charge-transfer were revealed through thorough cross-characterizations between single X-ray crystallography, UV-vis, photoluminescence (PL) and photoelectron spectroscopies, as well as four-probe conductivity measurements.

In addition, organic dications with compact charge arrangement between the pyridinium (or imidazolium) core and alkylammonio pendant were also utilized. This resulted in formation of 2D perovskites with very short inorganic layer separation and relaxed inter-octahedra tilting (single X-ray crystallography). This leads to materials with reduced band gaps and decreased dielectric confinement, as ascertained from UV-vis, photoluminescence (PL) and photoelectron spectroscopies, four-probe conductivity measurements, as well as density functional theory calculations. The

materials ultimately result in photovoltaic devices with much higher efficiencies and photocurrent conversions in comparison to conventional 2D perovskites.

b. Inducing broadband emissions via reinforcement of the inorganic frameworks' structural distortion and dimensionality.

As 'soft' materials, ionic metal-halide lattices in low-dimensional perovskites are easily deformable. This implies that the behaviors of strongly bound excitons (that dominates the materials photophysical properties) can be engineered, depending on the inorganic structures and their interaction with the organic cations. For example, several studies have highlighted the formation of self-trapped excitons involving electrons and holes localization at specific crystal sites by their own lattice distortion field.³⁴⁻³⁹ Other studies also suggest that the trapping of excitons can be mediated by the presence of permanent color centers (e.g. positive and negative ion vacancies and atoms in interstitial sites).⁴⁰⁻⁴¹ Although the two mechanisms are still actively investigated, the resulting effect of such exciton trappings is the observation of broadband emission, which is attractive for solid lighting applications due to the possibility of it to be used as a single-source broadband white-light-emitting phosphor.

Here, by designing suitable organic cations, we introduced three ways to induce the broadband emissions: a.) formation of rare corrugated (110)-oriented 2D perovskites, b.) formation of flat (100)-oriented 2D perovskites with heavily deformed metal center coordination, and c.) formation of materials containing 1D and trimeric inorganic lattices. The structures of the metal-halide hybrids were discussed in details through single X-ray crystallography analysis, while the PL properties and mechanisms were probed with time resolve-, power- and temperature-dependent PL spectroscopies.

c. Understanding the inorganic lattice formability in low-dimensional perovskite.

As mentioned previously, systematic explorations on cation structure effect towards the hybrids' final structures are relatively limited. As a response, while inducing

desirable properties of the materials for photovoltaic and solid-state lightings, this thesis also concomitantly investigates the formability of different inorganic lattices dimensionality (e.g. 0D, 1D, and 2D) and architectures (e.g. (100)- and (110)-oriented 2D perovskites). This was achieved *via* systematic tuning of aromatic cores, functional groups, and substituents of the organic cations before the resulting materials structures were analyzed with single X-ray crystallography. The corresponding optoelectronic properties were then examined mainly with UV-vis, photoluminescence (PL), Raman, and solid-state NMR spectroscopies.

1.3 Thesis overview

This thesis consists of 10 chapters. Chapter 1 presents the motivation for doing research (i.e. energy crisis, solar to electricity conversion, and lightings). Strategies to improve the optoelectronic properties of low-dimensional hybrid metal-halides as materials of interest are summarized in objectives and scopes of the work. The chapter is concluded with scientific contribution of this thesis to the field.

Chapter 2 reviews relevant works reported in the literature. The structural and concomitant optoelectronic properties of 3D halide perovskites that make them suitable for photovoltaic applications are described, followed by a brief discussion on the basics of perovskite solar cells. Their limitations in terms of synthetic versatility and environmental stability are then highlighted, many of which are mitigated in the low-dimensional (LD) counterpart. Structural diversity and superior stability of LD hybrids are comprehensively discussed, before their drawbacks in the context of photovoltaic and solid-state lighting applications are being identified. Finally, proposition to use targeted molecular approach to improve the optoelectronic properties of the aforementioned LD hybrids is put forward.

Chapter 3 explains the design and preparation of organic halide precursors, followed by the synthesis of low-dimensional organic metal-halide hybrids (both in single crystal and thin film forms). In addition, fabrication of devices with different configuration will be presented in details. Lastly, principles of the characterization techniques employed in this

thesis are also qualitatively elaborated, which is essential for data interpretation and analysis.

Chapter 4 describes the incorporation of electron-accepting viologen cations to a 1D lead-iodide framework to induce a charge-transfer interaction with the inorganic chain. The role and effect of π - π stacking in enhancing such interaction are discussed along with the presentation of concomitant improvement in optoelectronic properties of the overall materials. The solvent-dependent formation and solution-processability of the materials are also examined to assess their potential for photovoltaic device fabrications.

Chapter 5 presents the investigation results of the role of ammonium group in 2D lead-iodide perovskite formation, where a pyridinium ring is used as the cation core. The optoelectronic properties difference between 1D and 2D materials are highlighted. As a consequence of cations' compact and diffuse charge arrangement, 2D perovskites endowed with reduced band gap and relaxed dielectric confinement are demonstrated. The resulting materials along with their comprehensive experimental and theoretical optoelectronic characterizations are also discussed.

Chapter 6 discusses the structural feature differences between (100)- and (110)-oriented 2D lead-iodide perovskites that are obtained from organic dications with pyridinium and imidazolium cores, respectively. Thorough characterizations of the optoelectronic properties of the 2D perovskites in thin film forms are also presented. This is followed by demonstration of high efficiency 2D perovskite solar cells where improvement in photocurrents are notably highlighted and compared with that of conventional 2D perovskite.

Chapter 7 details the formability of a very rare corrugated (110)-oriented 2D tin-iodide perovskite templated by imidazolium-based organic dication. The spectroscopic features of the material are then compared with those of more common (100)-oriented congener. The charge carrier generation in the material is further investigated, followed by its

electrical and photoresponsivity behaviors where the potential of the material to be doped *via* electrical bias is revealed.

Chapter 8 describes the formation of a rare white-light emitting corrugated (110)-oriented 2D lead-bromide perovskite as a function of subtle differences in organic molecular structure. This is facilitated by systematic tuning of the cation's aromatic core. Specifically, the role of the coulombic interaction between the organic and inorganic lattice is highlighted. The broadband-emitting properties of the corrugated compound are then comprehensively studied *via* diverse PL spectroscopy methods and compared with those of (100)-type compounds.

Chapter 9 presents a strategy to reinforce high deformation on the lead-bromide octahedra coordination geometry by incorporating sterically demanding organic dications into the 2D perovskite. As a result, white-light emitting (100)-oriented lead-bromide compound is demonstrated, which otherwise would exhibit narrow photoluminescence. The mechanism in which the broadband emission occurs is further investigated with time-resolve, power- and temperature-dependent PL spectroscopy techniques.

Chapter 10 describes the effect of endowing pyridinium ring with rigid substituents to selectively generate trimeric lead-bromide hybrid materials from the 1D counterpart. The broadband-emitting behaviors are then presented, pointing in particular, the high inorganic lattice structural distortion relative to the conventional 2D perovskite. Higher photoluminescence quantum yield (PLQY) in comparison to the 1D material is also highlighted, before the mechanism in which the broadband emission occurs is further discussed with the help of different PL spectroscopy techniques.

Chapter 11 summarizes the findings and provides insights about the implication and novelty of the research. It reiterates the extent to which the thesis objectives have been met. Finally, opportunities and strategies for future work are suggested.

1.4 Findings and originality

Scientific contributions achieved in this Ph.D. project include:

1. Empirical understanding of 2D, 1D, and trimeric lead-halide hybrid material based on pyridinium cation which is achieved *via* systematic tuning of organic substituents. In addition, detailed optoelectronic characterizations were also carried out towards the new series of compounds.
2. For the first time, 1D lead-iodide materials are endowed with panchromatic absorption and enhanced photoconductivity. This is achieved by employing viologen cations endowed with hydrogen bonding functionalities that are capable of inducing π - π stackings in the crystal packing, such that charge transfer interaction between the organic and inorganic lattices are reinforced.
3. Incorporation of compact organic cations containing diffuse pyridinium or imidazolium core leads to formation of rare 2D perovskites with reduced band gap and relaxed dielectric confinement properties. As a result, enhanced electrical and photoconductivity of the overall materials can be realized, which leads to the world-record efficiencies (at the time it was published) for pure 2D perovskite solar cells.
4. Through systematic exploration of organic cations, the first corrugated ' 3×3 ' (110)-oriented 2D lead-iodide and tin-iodide perovskites can be synthesized (where ' $n \times n$ ' refers to the number (n) of contiguous Pb octahedra comprising each ridge). The spectroscopic features and optoelectronic properties of the compounds were then examined and compared with the conventional (100)-oriented 2D perovskites. In addition, using the same cation, a rare white-light emitting ' 2×2 ' (110)-oriented 2D lead-bromide perovskite is also obtained.
5. For the first time, the idea to reinforce lead-bromide coordination geometry (i.e. intra-octahedral distortion) is presented. This has an important implication as the resulting (110)-oriented 2D compound is endowed with white-light emitting behavior.

Previously, broadband emission in 2D perovskites are realized with corrugated structures or flat structure with huge inter-octahedral tiltings. Thus, the study opens an alternative pathway of designing white-light emitting material for solid-state lighting purpose.

6. Three new compounds containing very rare lead-bromide trimers through incorporation of pyridinium cations functionalized with rigid substituents. The materials emit intrinsic and efficient broadband photoluminescence (PLQY of at least 10%) which serves as a powerful proof of concept of inorganic lattice control by the organic molecular structure.

1.5 Bibliography

1. British Petroleum in British Petroleum Statistical Review of World Energy, June 2018 <http://bp.com/statisticalreview>.
2. International Energy Agency in World Energy Outlook, 2018 www.iea.org.
3. U.S. Energy Information Administration in Annual Energy Outlook, January 2019 <http://www.eia.gov/aeo>.
4. Hoffert, M. I.; Caldeira, K.; Jain A. K.; Haites, E. F.; Danny Harvey, L. D.; Potter, S. D.; Schlesinger, M. E.; Schneider. S. H.; Watts, R. G.; Wigley, T. M. L.; Wuebbles, D. J. *Nature* **1998**, *395*, 881-884.
5. Caldeira, K.; Jain, A. K.; Hoffert, M. I. *Science* **2003**, *299* (5615), 2052-2054
6. Feeling the heat. *Nature Climate Change* **2018**, *8* (5), 347-347.
7. Goeppert, A.; Czaun, M.; Jones, J. P.; Surya Prakash, G. K.; Olah, G. A. *Chem. Soc. Rev.* **2014**, *43* (23), 7995-8048.
8. Jäger, K.; Isabella, O.; Smets, A. H. M.; van Swaaij, R. A. C. M. M.; Zeman, M. *Solar Energy - Fundamentals, Technology, and Systems*; Delft University of Technology, 2014.
9. Wang, X.; Economides, M. *Natural Gas Supply, Alternative Energy Sources, and the Environment in Advanced Natural Gas Engineering*; Elsevier Inc., 2010; 303-331
10. Lazarus, M.; van Asselt, H. *Climate Change* **2018**, *150* (1-2), 1-13.

11. ourworldindata.org/fossil-fuels (accessed 27 Jul 2019).
12. unfccc.int/news/most-fossil-fuels-must-stay-in-the-ground-new-study (accessed 27 Jul 2019).
13. www.wsj.com/articles/oil-prices-stumble-on-fears-of-falling-demand-11560337016 (accessed 27 Jul 2019).
14. www.bbc.com/news/topics/cmjppj223708t/oil (accessed 27 Jul 2019).
15. oilprice.com/Energy/Oil-Prices/Oil-Set-For-Worst-Monthly-Drop-Since-November.html (accessed 27 Jul 2019).
16. Mercure, J. F.; Pollitt, H.; Viñuales, J. E.; Edwards, N. R.; Holden, P. B.; Chewpreecha, U.; Salas, P.; Sognnaes, I.; Lam, A.; Knobloch, F. *Nat. Clim. Change* **2018**, 8 (7), 588-593.
17. www.theguardian.com/news/2015/apr/08/can-world-economy-survive-without-fossil-fuels (accessed 27 Jul 2019).
18. www.theguardian.com/environment/2018/jun/04/carbon-bubble-could-spark-global-financial-crisis-study-warns (accessed 27 Jul 2019).
19. De Luna, P.; Hahn, C.; Higgins, D.; Jaffer, S. A.; Jaramillo, T. F.; Sargent, E. H. *Science* **2019**, 364 (6438).
20. Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci.* **2006**, 103 (43), 15729-15735.
21. Gratzel, M. *Acc. Chem. Res.* **2009**, 42 (11), 1788-1798.
22. Gratzel, M. *Nat. Mater.* **2014**, 13 (9), 838-842.
23. Battaglia, C.; Cuevas, A.; De Wolf, S. *Energy Environ. Sci.* **2016**, 9 (5), 1552-1576.
24. Barber, J.; Tran, P. D. *J. R. Soc. Interface* **2013**, 10 (81), 20120984.
25. Ravelli, D.; Dondi, D.; Fagnoni, M.; Albini, A. *Chem. Soc. Rev.* **2009**, 38 (7).
26. Tian, Y.; Zhao, C. Y. *Appl. Energy* **2013**, 104, 538-553.
27. Thirugnanasambandam, M.; Iniyan, S.; Goic, R. *Renew. and Sust. Energy Rev.* **2010**, 14 (1), 312-322.
28. International Energy Agency in Policies for Renewable Heat – an Integrated Approach, 2012 www.iea.org.
29. International Energy Agency in Light's Labour's Lost – Policies for Energy-Efficient Lighting, 2006 www.iea.org.

30. Schwartz, L. C.; Wei, M.; Morrow III, W. R.; Deason, J.; Schiller, S. R.; Leventis, G.; Smith, S. J.; Leow, W. L.; Levin, T.; Plotkin, S.; Zhou, Y.; Teng, J. Electricity End Uses, Energy Efficiency, and Distributed Energy Resources Baseline; Lawrence Berkeley National Laboratory, 2017.
31. Sun, Y.; Giebink, N. C.; Kanno, H.; Ma, B.; Thompson, M. E.; Forrest, S. R. *Nature* **2006**, *440* (7086), 908-912.
32. U. S. Department of Energy in 2015 Renewable Energy Data Book, 2015 www.nrel.gov.
33. Moram, M. A. *P. I. Civil Eng. - Energy* **2011**, *164* (1), 17-24.
34. Williams, R. T.; Song, K. S., *J. Phys. Chem. Solids* **1990**, *51* (7) 679-716.
35. Smith, M. D.; Karunadasa, H. I. *Acc. Chem. Res.* **2018**, *51* (3), 619-627.
36. Wang, X.; Meng, W.; Liao, W.; Wang, J.; Xiong, R. G.; Yan, Y. *J. Phys. Chem. Lett.* **2019**, *10* (3), 501-506.
37. Cortecchia, D.; Yin, J.; Bruno, A.; Lo, S.-Z. A.; Gurzadyan, G. G.; Mhaisalkar, S.; Brédas, J.-L.; Soci, C. *J. Mater. Chem. C* **2017**, *5* (11), 2771-2780.
38. Yin, J.; Li, H.; Cortecchia, D.; Soci, C.; Brédas, J.-L. *ACS Energy Lett.* **2017**, *2* (2), 417-423.
39. Katan, C.; Mercier, N.; Even, J. *Chem. Rev.* **2019**, *119* (5), 3140-3192.
40. Booker, E. P.; Thomas, T. H.; Quarti, C.; Stanton, M. R.; Dashwood, C. D.; Gillett, A. J.; Richter, J. M.; Pearson, A. J.; Davis, N. J. L. K.; Sirringhaus, H.; Price, M. B.; Greenham, N. C.; Beljonne, D.; Dutton, S. E.; Deschler, F. *J. Am. Chem. Soc.* **2017**, *139* (51), 18632-18639.
41. Paternò, G. M.; Mishra, N.; Barker, A. J.; Dang, Z.; Lanzani, G.; Manna, L.; Petrozza, A., *Adv. Funct. Mater.* **2019**, *29* (21), 1805299.

Chapter 2

Literature review

This chapter reviews relevant work reported in the literature. The structural and concomitant optoelectronic properties of 3D halide perovskites that make them suitable for photovoltaic applications are described, followed by a brief discussion of the basics of perovskite solar cells. Their limitations in terms of synthetic versatility and environmental stability are then highlighted, many of which are mitigated in the low-dimensional (LD) counterpart. Structural diversity and superior stability of LD hybrids are comprehensively discussed, before their drawbacks with respect to photovoltaic and solid-state lighting applications are identified. Finally, proposition to use targeted molecular approach to improve the optoelectronic properties of the aforementioned LD hybrids is put forward.

2.1 3D halide perovskites and their structural properties

The halometallate material MAPbI₃ (MA being methylammonium) that has had a major impact upon the world of photovoltaics (PV) research due to its stunning rise in device conversion efficiency has a perovskite crystal structure.¹⁻³ Therein, the 3D inorganic lattice is built from [PbI₆]⁻⁴ octahedra that corner-share with each other.¹⁻³ Having a general formula of APbI₃, the perovskite's structure is cubic with space group *Pm3m*. 'A' cation is located at the cuboctahedral cavity constructed of the four-neighboring lead-iodide octahedra, and thus is 12-fold coordinated crystallographically by the iodide anion (**Figures 2.1a & 2.1b**). 'A' should be monocationic and of certain sizes, otherwise the whole perovskite structure will experience various degrees of distortion due to the tilting of PbI₆⁻⁴ octahedra⁴⁻⁶ (**Figure 2.1c**). It can even fall apart and condense into lower dimensional material if the inorganic lattice is not capable of accommodating the cation species.⁷⁻¹⁵

Figure 2.1 a) Representation of APbI₃ perovskite with cubic structure where monocationic A: green, Pb: blue, and I: red (not to scale). b) Alternative depiction of perovskite highlighting the iodoplumbate lattices 'encapsulating' A. c) The case of [PbI₆]⁻⁴ octahedra tilting, normally because of too small A cation leading to strain on Pb-I bonds. The figure is adapted from ref. 16.

$$t = \frac{R_A + R_{I^-}}{\sqrt{2}(R_{Pb^{2+}} + R_{I^-})} \quad (\text{Eqn. 2.1})$$

It is commonly accepted that Goldsmith's tolerance factor, a semiempirical geometrical parameter, in **Eqn. 2.1** can be used to predict the lower and upper limit size of 'A'.¹⁷⁻¹⁹ In

general, ‘A’ can be inorganic, such as Cs^+ , but much of the focus in PV field has been dedicated to those of hybrid counterparts (i.e. with the ‘A’ being small organic cation such as methylammonium (MA) and formamidinium (FA)) due to their better generated properties that leads to improved device performances.²⁰⁻²² Apart from ‘A’ cation, the Pb^{+2} and I^- constituents can also be replaced by other elements possessing same oxidation states, such as Sn^{+2} or Ge^{+2} for the former and Br^- or Cl^- for the latter. The combination of each of the component together forms variants of group-14-metal (M)-halide (X) AMX_3 perovskite family with tolerance factor ranging from 0.85 to 0.95 (**Figure 2.2**).^{16, 23} However, it has to be taken note that high performing devices have yet been resulted from Sn^{+2} - or Ge^{+2} -based compounds because of the smaller inert pair effect within those metal cations that leads them to be more prone towards oxidation to form +4 species.²⁴

Figure 2.2 Tolerance factors (t) of a series of different halide perovskites. The figure is adapted from ref. 23.

2.1.1 Optoelectronic properties suitable for photovoltaics

The desirable properties of hybrid lead-iodide perovskite arise mainly from the inorganic component rather than the organic counterpart because the latter has frontier molecular orbitals energetically far separated from those of the former (i.e. no interaction electronically).²⁵⁻²⁶ Firstly, it features suitable bandgaps (E_g s) of ca. 1.5 eV that are suitable for photovoltaics.²⁷ Larger E_g s typically leads to a large portion of non-absorbed photons in the solar spectrum, while smaller E_g s results in inefficient absorption of solar light as most of the energy will be dissipated as heat.²⁸ With that bandgap value, the theoretical limit for perovskite-based solar cells is calculated to be around 31%, which is close to the Shockley-Queisser (SQ) limit (33%).²⁸⁻²⁹ Additionally, the 3D iodoplumbate network does

not only absorb photons over a wide range of the visible light spectrum (i.e. panchromatic), but also it does it efficiently (i.e. absorbed photons can readily excite electrons into the conduction band) due to its high absorption coefficient (α).³⁰⁻³² Theoretical calculations suggest that such superior optical absorption is derived from high density of states (DOS) of Pb^{+2} p orbital in the lower conduction band of the hybrid perovskites. The calculated value is reported to be significantly higher than that of gallium arsenide (GaAs), one of the established solar cell materials (Figure 2.3).³¹

Figure 2.3 a) Calculated density of states (DOS) of CH₃NH₃PbI₃, CsSnI₃ and GaAs. The VBMs (valence band maximums) are referred to as zero energy and CBMs (conduction band minimums) are marked as dashed lines. b) The optical absorptions of CH₃NH₃PbI₃, CsSnI₃ and GaAs. The figure is adapted from ref. 31.

Upon photoexcitation, the generated charge carriers are also known to be capable of diffusing in reasonable rates within long distances over 100 nms in thin film and 150 μm in single crystal.³³⁻³⁵ Such excellent diffusion lengths have been attributed to small values of excitonic binding energy (30 – 45 meV) owing to good shielding of electron-hole interactions in 3D lattices. Additionally, this is also contributed by strong s - p anti-bonding coupling that leads to small effective masses of both electrons and holes.³⁶⁻³⁷ The observed high diffusion length implies that the photogenerated charge carriers can be transported to other layers in photovoltaic device stack and collected as useful current before they get recombined. As a result, efficient photocurrent generation can be expected, leading to good solar cells performance.

More interestingly, the band gap of the material is adjustable by alteration in both the inorganic and organic compositions (**Figure 2.4**). In principle, the electronegativity difference between the main group metal and the halide (i.e. covalency character of the inorganic bond) plays a major role in determining how large the band gap of the hybrid is. Retaining Pb^{+2} as the polyoctahedral metal center for example, one would obtain more blue shifted absorption edges upon substituting iodide with bromide or chloride (**Figure 2.4a**).^{32, 38-39} Meanwhile, going up from lead to tin and germanium, materials with even lower bandgap can be obtained if iodide is maintained as the halide of interest.⁴⁰⁻⁴²

The choice of small organics can also still bring about materials with different physical properties. However, this is achieved through indirect influence towards inorganic lattice *via* steric or hydrogen bonding interaction because as mentioned previously, organic cation in hybrid 3D iodoplumbates does not interact optoelectronically with the inorganic framework. For example, formamidinium-based iodoplumbate hybrid is found to feature band gap that is smaller than that of methylammonium congener due to the ability of the former bigger cation to minimize iodoplumbate octahedral tilting and lattice distortion that would otherwise lead to the widening of the band gap (**Figure 2.4b**).⁴³⁻⁴⁴

Figure 2.4 a) UV-vis absorption spectra (top) and appearances (bottom) of $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ materials spincoated on top of FTO substrates coated with TiO_2 nanocomposite. The figure is adapted from ref. 38. **b.)** UV-vis absorption spectra of various 3D iodoplumbates. The figure is adapted from ref. 44.

2.1.2 Basics of perovskite solar cells (PSCs)

In general, the configurations of PSC can be classified into four categories as shown in **Figure 2.5** where the perovskite acting as the solar absorber material (i) is sandwiched between electron- and hole-transporting materials (ETM and HTM, respectively).⁴⁵ Historically, PSC with n-type mesoporous TiO_2 (titania) was first employed by Kojima and co-worker in 2009 with the metal-oxide scaffolds serving as ETM, yielding solar cells of 3.8% power conversion efficiency (PCE).¹ Such configuration inherits the architecture of dye-sensitized solar cells (DSSCs) where multiple components are fabricated on top of transparent conductive oxide (TCO) substrates (e.g. fluorinated tin oxide (FTO) or indium tin oxide (ITO)) and liquid iodide/triiodide electrolyte system that acts as redox shuttle was employed.⁴⁶

Figure 2.5 Schematic diagrams of perovskite solar cells in the (a) n-i-p mesoscopic, (b) n-i-p planar, (c) p-i-n planar, and (d) p-i-n mesoscopic structures where n, i, and p denote electron-transporting, light absorber (perovskites), and hole-transporting materials, respectively. The figure is adapted from ref. 45.

However, the perovskite instability in organic solvent limited the operational lifetime of the devices at the time and thus, p-type solid state HTM, such as $\text{N}^2, \text{N}^2', \text{N}^{2'}, \text{N}^7, \text{N}^7', \text{N}^{7'}, \text{N}^{7'}$ -octakis(4-methoxyphenyl)-9,9'-spirobi[9H-fluorene]-2,2',7,7'-tetramine (Spiro-OMeTAD; **Figure 2.6a**) was subsequently developed to address the issue.⁴⁷⁻⁴⁸ Concomitantly, the inclusion of solid-state HTM brought about improvement in efficiency and upon optimization conducted on the materials in each of the layer as well

as the interfaces, within short period of time similar configuration has turned into one that is known for its reproducibility and capability of delivering high efficiency devices of over 20% PCE (**Figure 2.5a** and **Figure 2.6b**).⁴⁹⁻⁵⁰

Figure 2.6 a) Molecular structure of commonly used organic HTM, Spiro-OMeTAD. b) Schematic diagram of mesoscopic TiO_2 perovskite solar cell. The figure is adapted from ref. 51.

Unlike conventional inorganic solar cells, such as Si or GaAs, that rely on p-n junction as their working principles,⁵²⁻⁵³ the light absorption and electron/hole separation in PSC take place in specifically designed components. Therefore, electronic band energy alignment of each layer plays a critical role in PSC configuration, so that the transport of photogenerated charge carriers can be assisted and the undesirable recombination processes can be reduced.⁵⁴⁻⁵⁶ **Figure 2.7** depicts an energy level diagram of a typical PSC based on TiO_2 and Spiro-OMeTAD as ETM and HTM, respectively, along with the charge transfer processes that occur in the device stack.

Figure 2.7 Schematic of energy level diagram with charge transfer processes occurring in PSCs under light illumination.

Upon light absorption, the photon energy absorbed in perovskite layer creates free charge carriers in the form of electrons and holes. Subsequently, the lower conduction band (CB) energy level of the TiO_2 layer allows the photogenerated electrons in perovskite layer to move downwards (i.e. ‘get injected’) easily and transport to the bottom electrode (FTO). The perovskite is then regenerated to its ground state by electron donation from Spiro-OMeTAD which at the same time transport the photogenerated holes to the top electrode (gold). Considering all the charge carriers dynamics in the system, much of the efforts in improving the devices efficiency have been dedicated in decreasing the recombination at TiO_2 /Spiro-OMeTAD interface.^{22, 57-58}

2.1.3 Other optoelectronic applications

In addition, halide perovskite materials have also been known for its excellent light-emitting properties. This has been attributed partly to the direct bandgap nature and high photoluminescence quantum yield (PLQY) of the materials upon electrons and holes recombination. As such, light emitting diodes (LEDs) have been made out of the 3D system with relatively high efficiency and especially narrow FWHM (full width at half-maximum) electroluminescence where the wavelength of emitted light is determined by the bandgap of perovskite materials. (Figure 2.5a).⁵⁹

Figure 2.8 a) Light emitting diode (LED) made from $\text{CH}_3\text{NH}_3\text{PbX}_3$. The figure is adapted from ref. 59. b) Tunable amplified spontaneous emission (ASE) from $\text{CH}_3\text{NH}_3\text{PbX}_3$ thin film for laser applications. The figure is adapted from ref. 60.

Taking advantage of its composition versatility, studies have further demonstrated laser devices based on $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with tunable, narrow and low threshold amplified spontaneous emission (**Figure 2.5b**),⁶⁰ photodetector,⁶¹ and even X-ray scintillators,⁶² all of which exemplify the potential of 3D iodoplumbates for optoelectronic applications.

2.1.4 Chemical instability and limitation for exploration

Despite all of the tremendous progress and hype surrounding iodoplumbate perovskites, the materials however are known to be intrinsically prone towards several chemical stressors that make them unstable even at ambient condition. Instability towards moisture, in particular, has been considered as a major problem and this can be boiled down to both the intrinsic weak bonding between Pb^{+2} metal center and I^- bridging ‘ligand’ in the 3D inorganic lattice and the propensity of hygroscopic small organic cation to attract moistures.⁶³⁻⁶⁴ For example, water sensitivity has been reported to result in complete degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskites thin film that can occur as fast as 18 h upon exposure to ambient condition (**Figure 2.9**),⁶⁵ precluding, as a consequence, any sustainable good device performance.

Figure 2.9 a) UV-vis absorption spectra and b) XRD patterns of $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ before and after decomposition by moisture in air after 18 h of exposure. The figure is adapted from ref. 65.

It is generally agreed that the decomposition pathway goes through a multi-step mechanism in which the first process involves hydration of lead iodide lattice to yield discrete $[\text{PbI}_6]^{-4}$

octahedra and this is supported by reported crystal structure of hydrated complex $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$ though there is a suggestion that monohydrated species could form initially before the second water molecule comes in.⁶³⁻⁶⁴ The hydration process is believed to be reversible and photovoltaic performance seems to be restorable upon undergoing some dehydration procedure, but if the moisture is much in excess, complete degradation of material *via* irreversible release of organic vapor and HI will be unavoidable (**Scheme 2.1**).

Scheme 2.1 Possible moisture degradation route of 3D MAPbI_3 iodoplumbates. The scheme is adapted from ref. 65.

Apart from stability, steric constraints imposed on the organic cations by Goldschmidt's tolerance factor means that 3D perovskites have a constrained space for structural exploration and compositional engineering. In addition to steric factor, other aspects of the cations, such as Coulombic and hydrogen bonding interactions with the halides in the cuboctahedral cavity have also been shown to affect the formation of the 3D lattices.^{19, 66-67} As such, only methylammonium and formamidinium have been reported to be capable of templating stable pure 3D metal-halide frameworks despite the fact that other relatively small organic cations also have similar ionic radii size **Table 2.1**. Consequently, modulation of the chemical and photophysical properties of this class of material *via* molecular approach becomes very limited.

Table 2.1 Calculated effective radii of several small molecular cations.¹⁷⁻¹⁸

No.	Cation	Effective radius r_{Aeff} (pm)
1.	Ammonium $[\text{NH}_4]^+$	146
2.	Hydroxylammonium $[\text{H}_3\text{NOH}]^+$	216
3.	Methylammonium $[(\text{CH}_3)\text{NH}_3]^+$	217
4.	Hydrazinium $[\text{H}_3\text{N}-\text{NH}_2]^+$	217
5.	Azetidinium $[(\text{CH}_2)_3\text{NH}_2]^+$	250
6.	Formamidinium $[\text{NH}_2(\text{CH})\text{NH}_2]^+$	253
7.	Imidazolium $[\text{C}_3\text{N}_2\text{H}_5]^+$	258
8.	Dimethylammonium $[(\text{CH}_3)_2\text{NH}_2]^+$	272
9.	Ethylammonium $[(\text{C}_2\text{H}_5)\text{NH}_3]^+$	274
10.	Guanidinium $[\text{C}(\text{NH}_2)_3]^+$	278
11.	Tetramethylammonium $[(\text{CH}_3)_4\text{N}]^+$	292

2.2 Hybrids of lower-dimensionalities and their structural properties

The use of organic cations ('A') with sizes relatively bulkier than those of methylammonium and formamidinium leads to dimensionality breakdown of the inorganic framework at molecular level to yield 2D, 1D or 0D hybrid materials (**Figure 2.10**).

Figure 2.10 Illustrations of hybrid organic-inorganic halometallates possessing inorganic lattices of a) 3D, b) 2D, c) 1D, and d) 0D structural features where 'D' refers to dimension. The blue octahedron represents the $[\text{MX}_6]^{n-}$ building unit with M being heavy main group metal cations (not shown) and X halide anions (orange spheres). The figure is adapted from ref. 68.

2D hybrid halide perovskites have a sheet-like structure of inorganic motif that consists of typically corner-sharing M-X octahedra sandwiched by the moderately-sized A cations. Though the organics could contain various functionalities such as normal-,⁶⁹⁻⁷⁰ heteroatom-endowed-aliphatic chain,⁷¹⁻⁷² cyclic aliphatic or aromatic⁷³⁻⁷⁵ moiety, they typically would have primary ammonium group attached to them to drive the 2D lattice formation. The most common examples found in the literature include phenylethylammonium (PEA)⁷⁶⁻⁷⁷ and 1-butylammonium (BA) ions.⁷⁸⁻⁷⁹ As shown in **Figure 2.11**, the structures are derived from specific cuts/slices of the corresponding cubic parent 3D framework along certain crystallographic directions (e.g., the (100)- or (110)-plane).⁸⁰⁻⁸²

Figure 2.11 Structures of 2D perovskites, where the inorganic sublattices can be conceptually derived from (A) the (001) and (B) the (110) crystallographic planes of the cubic 3D perovskite structure. Insets show cubic 3D perovskites with these crystallographic planes highlighted. In these examples, the templating cations are *N*¹-methylpropane-1,3-diammonium and *N*¹-methylethane-1,2-diammonium, respectively. The figure is adapted from ref. 83.

Alloying small cations (e.g. methylammonium) with that of bulky cations capable of forming 2D perovskites (e.g. butylammonium) yields hybrid materials with inorganic layers of multiple thickness (i.e. multiple '*n*' where *n* refers to the number of contiguous 2D inorganic layers; i.e., not separated by organic cations).⁸⁴⁻⁸⁵ The materials have sometimes been termed as quasi-, pseudo-, or higher dimensionality 2D perovskite (**Figure 2.12**). The structure can be seen as intermediates between 3D & 2D iodoplumbates in which the larger organic cations are now embedded between slabs of 3D material, which host small organic cations.

Figure 2.12 Structures of the layered 2D lead-iodide perovskites, $(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ (BA and MA are butylammonium and methylammonium, respectively), extending from $n = 1$ to $n = \infty$ where n refers to the number of contiguous 2D inorganic layers; i.e., not separated by organic cations. The figure is adapted from ref. 84.

Meanwhile, the 1D congeners have structures that consist of the $[\text{MX}_6]^{n-}$ octahedra arranged in chains *via* different connectivity modes (face, corner, or edge) and surrounded by the A cations (**Figure 2.13**). Relative to 2D materials, there are more examples documented for this class of compounds where diverse type of organic cations, regardless of the size and shape, can be employed to template the formation of this structure. However, the most common examples come from inclusion of organic cations containing sterically hindered charge center in character, such as pyridinium,⁸⁶ piperidinium⁸⁷ and imidazolium⁶⁷ cores.

Figure 2.13 Examples of 1D lead-iodide hybrids that are templated by organic cations a) iodoformamidinium, b) imidazolium, and c) 1,4-dimethylpiperazine-1,4-diium where different connectivity modes (face, corner, or edge) can be observed. The figures are adapted from ref. 82, 67, and 88, respectively.

Figure 2.14 Examples of hybrid materials containing metal-halide monomers (i.e. '0D') that are obtained from organic cations a) 1-butyl-1-methylpyrrolidinium, b) tetraphenylphosphonium, and c) *N,N'*-dimethylethylenediammonium. The figures are adapted from ref. 7, 89, and 90, respectively.

0D hybrids are materials that have a discrete molecular mono- (e.g. tetrahedron and octahedron structures) or oligometallate species isolated from each other by a matrix of organic cations. They are relatively rare compared to their 2D and 1D counterparts and thus, are still underexplored (especially in terms of formability). Nonetheless, organic cations that typically possess rigid and/or bulky substituents, such as 1-butyl-1-

methylpyrrolidinium, tetraphenylphosphonium, and N,N' -dimethyl-ethylenediammonium have been reported to be capable of yielding these type of structures (**Figure 2.14**).

2.2.1 Improvement in stability and greater room for improvisation

Having much larger cations that are hydrophobic in character can result in materials that are relatively more stable towards moisture and oxygen.²⁵ For example, Stupp and co-workers demonstrated that pure $n = 1$ 2D perovskite can withstand immersion in water for several minutes without any decomposition to lead(II) iodide (**Figures 2.15**).⁹¹ It epitomizes the materials' more stable properties in comparison to the higher dimensionality counterparts, such as prototypical 3D perovskite MAPbI_3 and even $n = 4$ layered perovskite $(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$. Similar notions were also reported by several other groups in the field where the inclusion of relatively bulky, more hydrophobic organic species have been shown to enhance the stability of the overall materials (**Figure 2.16**).^{76, 92-93}

Figure 2.15 Comparison of dipping the 3D perovskite MAPbI_3 (left), lower dimensionality $n = 4$ perovskite $(\text{BA})_2(\text{MA})_2\text{Pb}_3\text{I}_{10}$ (center) (where BA is butylammonium and MA is methylammonium) and $n = 1$ (pyrene-O-propyl- NH_3) $_2\text{PbI}_4$ (right). The $n = 1$ compound remains intact even after several minutes of immersion. The figure is adapted from ref. 91.

Semiconducting and optoelectronic features of the low-dimensional hybrids still mostly depend on the compositional constituents of their inorganic frameworks that typically possess higher dielectric constant than the organic constituents. However, in contrast to 3D iodoplumbate perovskites, much freedom can be made to improvise the aforementioned properties in the overall material. This can be achieved through incorporation of organics endowed with various physical traits and templating capability as the size of the iodoplumbate cuboctahedral cavity space is no longer relevant. Indeed, tuning of the

organic cations has, for instance, provided access to low dimensional hybrids with properties required for application in transistors,⁹⁴⁻⁹⁵ photovoltaics,^{75, 96} light emitting devices,⁹⁷⁻⁹⁸ chemisorption,⁹⁹⁻¹⁰⁰ and photocatalysis.¹⁰¹

Figure 2.16 Absorption spectra of a) lower dimensionality $n = 4$ perovskite $(\text{PEA})_2(\text{MA})_2\text{Pb}_3\text{I}_{10}$ (PEA is phenylethylammonium and MA is methyl-ammonium) and b) 3D perovskite MAPbI_3 upon exposure to 52% relative humidity, demonstrating the shelf stability of the former in comparison to the latter. The figure is adapted from ref. 76.

2.2.2 Optoelectronic drawbacks of hybrids of lower-dimensionalities and this thesis in the context of literature

Although they are more resistant towards moisture and synthetically more versatile, low dimensional perovskites are, normally not considered suitable for photovoltaic devices, owing to heavily compromised visible light absorption and poor charge transport originating from strongly-bound electron-hole pairs, or excitons.¹⁰²⁻¹⁰³ The quantum confinement of the dimensionally reduced structure is responsible for higher bandgap (E_g) and exciton binding energy (E_b) values relative to the 3D materials.^{26, 104-106} Additionally, the E_b in these materials is further enhanced by the dielectric mismatch between organic and inorganic components and the isolation between the two (i.e. no electronic interaction). This can be attributed to big gaps between highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of the organic species that are typically larger than the bandgaps of the inorganic components.^{103, 107-108} Here, the low dielectric constant of the adjacent organic layers provides poor shielding of the electrons

and holes in the inorganic lattices resulting in the exciton's dielectric confinement. Bandgaps of over 3.0 eV and 2.5 eV are, for examples, reported for hybrid 1D and 2D lead-iodide compounds, respectively (**Figure 2.17**),¹⁰⁹⁻¹¹³ with excitonic binding energies of above 200 meV have been observed in the materials (**Figure 2.18**).^{105, 107, 114-116} As a consequence, photovoltaic performances based upon these materials typically fall below 1% efficiency, far below that of their 3D congeners.^{75, 91, 117}

Figure 2.17 UV-vis absorbance and PL spectra of various 2D lead-iodide perovskites. In contrast to the 3D congeners whose visible light absorption can span up to 780-810 nm, the absorption edges of the 2D materials occur at ca. 450-530 nm, indicating bandgaps of over 2.5 eVs. The figure is adapted from ref. 113.

Figure 2.18 a) UV-vis absorbance spectra of 2D (PEA)₂PbI₄ at different temperatures (PEA is phenylethylammonium). b) temperature-dependent integrated photoluminescence intensity of (PEA)₂PbI₄. These two experiments are normally conducted to examine the excitonic binding energy (E_b) of the halide perovskite material. In this case, the E_b of (PEA)₂PbI₄ was determined to be ca. 220 meV, much higher than that of 3D MAPbI₃ (MA is methylammonium) whose E_b was reported to be ca. 30-45 meV. The figure is adapted from ref. 107.

Concomitantly, the strengthened binding energy and oscillator strength of the excitons in the low dimensional system would cause their radiative decay rates to increase, owing to breakdown in translational symmetry.^{108, 118-119} While this can lead to some unique features, such as second to third order optical linearity, high intensity emission and good quantum efficiencies, the resulting emissions are typically narrow, mimicking that of 3D counterpart (**Figure 2.19**).^{112-113, 118, 120-121} This is a result of close-to-ideal metal-halide octahedral coordination geometry in the inorganic network and negligible intermolecular interaction with the organic moiety, all of which lead to weak electron-phonon interaction in the lattice.^{83, 122} Typically, sharp blue, green, and red emissions can be obtained by simply tuning the composition of the inorganic framework (**Figure 2.19**). With such properties, the materials can act as phosphors in solid state lighting applications where white-light emission can be generated by combining each of the blue-, green-, and red-light emitters.¹²³⁻¹²⁴ However, mixing phosphors often results in efficiency losses due to self-absorption.¹²³⁻¹²⁴ Also, the different degradation rates of the individual phosphors lead to changes in emission color over time.¹²³⁻¹²⁴ This renders the materials to be a less attractive solution to the inefficiencies of traditional incandescent and fluorescent lighting sources.

Figure 2.19 a) Photoluminescence (PL) spectra and b) photograph of solutions of $(\text{PEA})_2\text{PbX}_4$ (PEA = phenylethylammonium and X = Br or I) nanosheets with different compositions under the irradiation of a 365 nm UV lamp showing color tuning from blue to green. The figures are adapted from ref. 125. c) Electroluminescence spectrum of a $(\text{PEA})_2\text{SnI}_4$ device, registered by applying a 4 V bias to the device, demonstrating red color. The figure is adapted from ref. 97.

The number of reports on low-dimensional perovskites in the literature is numerous and materials that are templated by organic cations containing a normal alkyl-,⁶⁹⁻⁷⁰ heteroatom-substituted-aliphatic chain,⁷¹⁻⁷² cyclic aliphatic or aromatic moiety,⁷³⁻⁷⁵ have been documented. Additionally, the photophysical features of certain class of compounds have also been intensively investigated. However, systematic studies on the effect of cation structure towards the materials' final structures are still relatively scarce.^{86-87, 126} The majority of the studies typically report compounds that are 'isolated' in nature, where wide-ranging, unrelated organic cations have been selected to template the formation of final materials. This is carried-out without a further probing on why and how the templating effect can come about. As such, the formability aspect of low-dimensional perovskites has been underexplored and thus, this renders directed design of materials impossible.

Motivated by the above circumstances, this Ph.D. thesis puts forward a proposition that targeted molecular design could mitigate many of the problems inherent to low-

dimensional materials. Based on that, the studies documented in this thesis aim to strategically design and employ organic cations such that certain inorganic halometallate structures in low-dimensional perovskites can be induced by the cations templating effect. Those ‘molecularly engineered’ structures would notably be endowed with optoelectronic properties suitable for photovoltaic and solid-state lighting applications. The studies also go one step further by attempting to explain the formability of the above structures, in the hope that they will open a pathway to a better targeted rational design of materials with desired optoelectronic properties.

2.3 Bibliography

1. Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. *J. Am. Chem. Soc.* **2009**, *131* (17), 6050-6051.
2. Gratzel, M. *Nat. Mater.* **2014**, *13* (9), 838-842.
3. Snaith, H. J. *Nat. Mater.* **2018**, *17* (5), 372-376.
4. Bechtel, J. S.; Van der Ven, A. *Phys. Rev. Mater.* **2018**, *2* (2).
5. Shojaei, F.; Yin, W.-J. *J. Phys. Chem. C* **2018**, *122* (27), 15214-15219.
6. Butler, K. T. *J. Mater. Chem. C* **2018**, *6* (44), 12045-12051.
7. Zhou, C.; Lin, H.; Shi, H.; Tian, Y.; Pak, C.; Shatruk, M.; Zhou, Y.; Djurovich, P.; Du, M.-H.; Ma, B. *Angew. Chem. Int. Ed.* **2018**, *57* (4), 1021-1024.
8. Zhou, C.; Lin, H.; Worku, M.; Neu, J.; Zhou, Y.; Tian, Y.; Lee, S.; Djurovich, P.; Siegrist, T.; Ma, B. *J. Am. Chem. Soc.* **2018**, *140* (41), 13181-13184.
9. Zhou, J.; Li, M.; Ning, L.; Zhang, R.; Molokeev, M. S.; Zhao, J.; Yang, S.; Han, K.; Xia, Z. *J. Phys. Chem. Lett.* **2019**, *10* (6), 1337-1341.
10. Devic, T.; Canadell, E.; Auban-Senzier, P.; Batail, P. *J. Mater. Chem.* **2004**, *14* (2), 135-137.
11. Liu, J. J.; Guan, Y. F.; Jiao, C.; Lin, M. J.; Huang, C. C.; Dai, W. X., *Dalton Trans.* **2015**, *44* (13), 5957-5960.
12. Duan, H. B.; Zhao, H. R.; Ren, X. M.; Zhou, H.; Tian, Z. F.; Jin, W. Q. *Dalton Trans.* **2011**, *40* (8), 1672-1683.

13. Dohner, E. R.; Hoke, E. T.; Karunadasa, H. I. *J. Am. Chem. Soc.* **2014**, *136* (5), 1718-1721.
14. Dohner, E. R.; Jaffe, A.; Bradshaw, L. R.; Karunadasa, H. I. *J. Am. Chem. Soc.* **2014**, *136* (38), 13154-13157.
15. Du, K. Z.; Tu, Q.; Zhang, X.; Han, Q.; Liu, J.; Zauscher, S.; Mitzi, D. B. *Inorg. Chem.* **2017**, *56* (15), 9291-9302.
16. Chen, Q.; De Marco, N.; Yang, Y.; Song, T.-B.; Chen, C.-C.; Zhao, H.; Hong, Z.; Zhou, H.; Yang, Y. *Nano Today* **2015**, *10* (3), 355-396.
17. Kieslich, G.; Sun, S.; Cheetham, A. K. *Chem. Sci.* **2014**, *5* (12), 4712-4715.
18. Kieslich, G.; Sun, S.; Cheetham, A. K. *Chem. Sci.* **2015**, *6* (6), 3430-3433.
19. Gholipour, S.; Ali, A. M.; Correa-Baena, J. P.; Turren-Cruz, S. H.; Tajabadi, F.; Tress, W.; Taghavinia, N.; Gratzel, M.; Abate, A.; De Angelis, F.; Gaggioli, C. A.; Mosconi, E.; Hagfeldt, A.; Saliba, M. *Adv. Mater.* **2017**, *29* (38).
20. Liu, Z.; Qiu, L.; Juarez-Perez, E. J.; Hawash, Z.; Kim, T.; Jiang, Y.; Wu, Z.; Raga, S. R.; Ono, L. K.; Liu, S. F.; Qi, Y. *Nat. Commun.* **2018**, *9* (1), 3880.
21. Jiang, Q.; Zhao, Y.; Zhang, X.; Yang, X.; Chen, Y.; Chu, Z.; Ye, Q.; Li, X.; Yin, Z.; You, J. *Nat. Photon.* **2019**.
22. Stolterfoht, M.; Wolff, C. M.; Márquez, J. A.; Zhang, S.; Hages, C. J.; Rothhardt, D.; Albrecht, S.; Burn, P. L.; Meredith, P.; Unold, T.; Neher, D. *Nat. Energy* **2018**, *3* (10), 847-854.
23. Fan, Z.; Sun, K.; Wang, J. *J. Mater. Chem. A* **2015**, *3* (37), 18809-18828.
24. Drago, R. S. *J. Phys. Chem.* **1958**, *62* (3), 353-357.
25. Pedesseau, L.; Jancu, J.-M.; Rolland, A.; Deleporte, E.; Katan, C.; Even, J. *Opt. Quant. Electron.* **2013**, *46* (10), 1225-1232.
26. Umebayashi, T.; Asai, K.; Kondo, T.; Nakao, A. *Phys. Rev. B* **2003**, *67* (15).
27. Xiao, Z.; Zhou, Y.; Hosono, H.; Kamiya, T.; Padture, N. P. *Chem.: Eur. J.* **2018**, *24* (10), 2305-2316.
28. Shockley, W.; Queisser, H. J. *J. App. Phys.* **1961**, *32* (3), 510-519.
29. Sha, W. E. I.; Ren, X.; Chen, L.; Choy, W. C. H. *App. Phys. Lett.* **2015**, *106* (22).
30. De Wolf, S.; Holovsky, J.; Moon, S. J.; Loper, P.; Niesen, B.; Ledinsky, M.; Haug, F. J.; Yum, J. H.; Ballif, C. *J. Phys. Chem. Lett.* **2014**, *5* (6), 1035-1039.

31. Yin, W.-J.; Shi, T.; Yan, Y. *Adv. Mater.* **2014**, *26* (27), 4653-4658.
32. McMeekin, D. P.; Sadoughi, G.; Rehman, W.; Eperon, G. E.; Saliba, M.; Hörantner, M. T.; Haghighirad, A.; Sakai, N.; Korte, L.; Rech, B.; Johnston, M. B.; Herz, L. M.; Snaith, H. J. *Science* **2016**, *351*, 152-155.
33. Xing, G.; Mathews, N.; Sun, S.; Lim, S. S.; Lam, Y. M.; Grätzel, M.; Mhaisalkar, S.; Sum, T. C. *Science* **2013**, *342*, 344-347.
34. Stranks, S. D.; Eperon, G. E.; Grancini, G.; Menelaou, C.; Alcocer, M. J. P.; Leijtens, T.; Herz, L. M.; Petrozza, A.; Snaith, H. J. *Science* **2013**, *342*, 341-344.
35. Dong, Q.; Fang, Y.; Shao, Y.; Mulligan, P.; Qiu, J.; Cao, L.; Huang, J. *Science* **2015**, *347* (6225), 967-970.
36. Giorgi, G.; Fujisawa, J.; Segawa, H.; Yamashita, K. *J. Phys. Chem. Lett.* **2013**, *4* (24), 4213-4216.
37. Umari, P.; Mosconi, E.; De Angelis, F. *Sci. Rep.* **2014**, *4*, 4467.
38. Noh, J. H.; Im, S. H.; Heo, J. H.; Mandal, T. N.; Seok, S. I. *Nano Lett.* **2013**, *13* (4), 1764-1769.
39. Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. *Nano Lett.* **2015**, *15* (6), 3692-3696.
40. Koh, T. M.; Krishnamoorthy, T.; Yantara, N.; Shi, C.; Leong, W. L.; Boix, P. P.; Grimsdale, A. C.; Mhaisalkar, S. G.; Mathews, N. *J. Mater. Chem. A* **2015**, *3* (29), 14996-15000.
41. Tong, J.; Song, Z.; Kim, D. H.; Chen, X.; Chen, C.; Palmstrom, A. X.; Ndione, P. F.; Reese, M. O.; Dunfield, S. P.; Reid, O. G.; Liu, J.; Zhang, F.; Harvey, S. P.; Li, Z.; Christensen, S. T.; Teeter, G.; Zhao, D.; Al-Jassim, M. M.; van Hest, M. F. A. M.; Beard, M. C.; Shaheen, S. E.; Berry, J. J.; Yan, Y.; Zhu, K. *Science* **2019**, *364* (6439), 475-479.
42. Chen, M.; Ju, M. G.; Garces, H. F.; Carl, A. D.; Ono, L. K.; Hawash, Z.; Zhang, Y.; Shen, T.; Qi, Y.; Grimm, R. L.; Pacifici, D.; Zeng, X. C.; Zhou, Y.; Padture, N. P. *Nat. Commun.* **2019**, *10* (1), 16.
43. Koh, T. M.; Fu, K.; Fang, Y.; Chen, S.; Sum, T. C.; Mathews, N.; Mhaisalkar, S. G.; Boix, P. P.; Baikie, T. *J. Phys. Chem. C* **2013**, *118* (30), 16458-16462.

44. Eperon, G. E.; Stranks, S. D.; Menelaou, C.; Johnston, M. B.; Herz, L. M.; Snaith, H. *J. Energy Environ. Sci.* **2014**, *7* (3).
45. Song, Z.; Wathage, S. C.; Phillips, A. B.; Heben, M. J. *J. Photon. Energy* **2016**, *6* (2).
46. Grätzel, M. *Acc. Chem. Res.* **2009**, *42* (11), 1788-1798.
47. 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.; Gratzel, M.; Park, N. G. *Sci. Rep.* **2012**, *2*, 591.
48. Lee, M. M.; Teuscher, J.; Miyasaka, T.; Murakami, T. N.; Snaith, H. J. *Science* **2012**, *338* (6107), 643-647.
49. 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.; Gratzel, M. *Energy Environ. Sci.* **2016**, *9* (6), 1989-1997.
50. Bi, D.; Yi, C.; Luo, J.; Décoppet, J.-D.; Zhang, F.; Zakeeruddin, Shaik M.; Li, X.; Hagfeldt, A.; Grätzel, M. *Nat. Energy* **2016**, *1* (10).
51. Im, J.-H.; Lee, C.-R.; Lee, J.-W.; Park, S.-W.; Park, N.-G. *Nanoscale* **2011**, *3* (10), 4088-4093.
52. Jäger, K.; Isabella, O.; Smets, A. H. M.; van Swaaij, R. A. C. M. M.; Zeman, M. *Solar Energy - Fundamentals, Technology, and Systems*; Delft University of Technology, 2014.
53. Karzazil, Y.; Arbouch, I. *J. Mater. Environ. Sci.* **2014**, *5* (5), 1505-1515.
54. Johnston, M. B.; Herz, L. M. *Acc. Chem. Res.* **2016**, *49* (1), 146-154.
55. Sum, T. C.; Mathews, N.; Xing, G.; Lim, S. S.; Chong, W. K.; Giovanni, D.; Dewi, H. A. *Acc. Chem. Res.* **2016**, *49* (2), 294-302.
56. Haruyama, J.; Sodeyama, K.; Han, L.; Tateyama, Y. *Acc. Chem. Res.* **2016**, *49* (3), 554-61.
57. Yan, L.; Xue, Q.; Liu, M.; Zhu, Z.; Tian, J.; Li, Z.; Chen, Z.; Chen, Z.; Yan, H.; Yip, H. L.; Cao, Y. *Adv. Mater.* **2018**, e1802509.
58. Bai, Y.; Meng, X.; Yang, S. *Adv. Energy Mater.* **2018**, *8* (5).
59. Li, G.; Tan, Z. K.; Di, D.; Lai, M. L.; Jiang, L.; Lim, J. H.; Friend, R. H.; Greenham, N. C. *Nano Lett.* **2015**, *15* (4), 2640-2644.

60. Xing, G.; Mathews, N.; Lim, S. S.; Yantara, N.; Liu, X.; Sabba, D.; Gratzel, M.; Mhaisalkar, S.; Sum, T. C. *Nat. Mater.* **2014**, *13* (5), 476-480.
61. Zhang, M.; Zhang, F.; Wang, Y.; Zhu, L.; Hu, Y.; Lou, Z.; Hou, Y.; Teng, F. *Sci. Rep.* **2018**, *8* (1), 11157.
62. Wei, H.; Huang, J. *Nat. Commun.* **2019**, *10* (1), 1066.
63. 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. *Energy Environ. Sci.* **2016**, *9* (2), 323-356.
64. Niu, G.; Guo, X.; Wang, L. *J. Mater. Chem. A* **2015**, *3* (17), 8970-8980.
65. Niu, G.; Li, W.; Meng, F.; Wang, L.; Dong, H.; Qiu, Y. *J. Mater. Chem. A* **2014**, *2* (3), 705-710.
66. Pering, S. R.; Deng, W.; Troughton, J. R.; Kubiak, P. S.; Ghosh, D.; Niemann, R. G.; Brivio, F.; Jeffrey, F. E.; Walker, A. B.; Islam, M. S.; Watson, T. M.; Raithby, P. R.; Johnson, A. L.; Lewis, S. E. *J. Mater. Chem. A* **2017**, *5* (39), 20658-20665.
67. Weber, O. J.; Marshall, K. L.; Dyson, L. M.; Weller, M. T. *Acta Crystallogr. B Struct. Sci. Cryst. Eng. Mater.* **2015**, *71* (Pt 6), 668-78.
68. Sum, T. C.; Mathews, N. *Energy Environ. Sci.* **2014**, *7* (8), 2518-2534.
69. Lemmerer, A.; Billing, D. G. *CrystEngComm* **2012**, *14* (6).
70. Lemmerer, A.; Billing, D. G. *Dalton Trans.* **2012**, *41* (4), 1146-1157.
71. Lemmerer, A.; Billing, D. G. *CrystEngComm* **2010**, *12* (4), 1290-1301.
72. Sourisseau, S.; Louvain, N.; Bi, W.; Mercier, N.; Rondeau, D.; Boucher, F.; Buzaré, J.-Y.; Legein, C. *Chem. Mater.* **2007**, *19* (3), 600-607.
73. Billing, D. G.; Lemmerer, A. *CrystEngComm* **2007**, *9* (3), 236-244.
74. Billing, D. G.; Lemmerer, A. *CrystEngComm* **2006**, *8* (9), 686-695.
75. Mao, L.; Tsai, H.; Nie, W.; Ma, L.; Im, J.; Stoumpos, C. C.; Malliakas, C. D.; Hao, F.; Wasielewski, M. R.; Mohite, A. D.; Kanatzidis, M. G. *Chem. Mater.* **2016**, *28* (21), 7781-7792.
76. Smith, I. C.; Hoke, E. T.; Solis-Ibarra, D.; McGehee, M. D.; Karunadasa, H. I. *Angew. Chem. Int. Ed. Engl.* **2014**, *53* (42), 11232-11235.

77. 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. *J. Am. Chem. Soc.* **2016**, *138* (8), 2649-2655.
78. Cao, D. H.; Stoumpos, C. C.; Farha, O. K.; Hupp, J. T.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2015**, *137* (24), 7843-7850.
79. Tsai, H.; Nie, W.; Blancon, J. C.; Stoumpos, C. C.; Asadpour, R.; Harutyunyan, B.; Neukirch, A. J.; Verduzco, R.; Crochet, J. J.; Tretiak, S.; Pedesseau, L.; Even, J.; Alam, M. A.; Gupta, G.; Lou, J.; Ajayan, P. M.; Bedzyk, M. J.; Kanatzidis, M. G. *Nature* **2016**, *536* (7616), 312-316.
80. Saparov, B.; Mitzi, D. B. *Chem Rev* **2016**, *116* (7), 4558-4596.
81. Febriansyah, B.; Koh, T. M.; Lekina, Y.; Jamaludin, N. F.; Bruno, A.; Ganguly, R.; Shen, Z. X.; Mhaisalkar, S. G.; England, J. *Chem. Mater.* **2019**, *31* (3), 890-898.
82. Wang, S.; Mitzi, D. B.; Feild, C. A.; Guloy, A. *J. Am. Chem. Soc.* **1995**, *117* (19), 5297-5302.
83. Smith, M. D.; Jaffe, A.; Dohner, E. R.; Lindenberg, A. M.; Karunadasa, H. I. *Chem. Sci.* **2017**, *8* (6), 4497-4504.
84. Stoumpos, C. C.; Cao, D. H.; Clark, D. J.; Young, J.; Rondinelli, J. M.; Jang, J. I.; Hupp, J. T.; Kanatzidis, M. G. *Chem. Mater.* **2016**, *28* (8), 2852-2867.
85. Mao, L.; Ke, W.; Pedesseau, L.; Wu, Y.; Katan, C.; Even, J.; Wasielewski, M. R.; Stoumpos, C. C.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2018**, *140* (10), 3775-3783.
86. Gómez, V.; Fuhr, O.; Ruben, M. *CrystEngComm* **2016**, *18* (42), 8207-8219.
87. Mao, L.; Guo, P.; Kepenekian, M.; Hadar, I.; Katan, C.; Even, J.; Schaller, R. D.; Stoumpos, C. C.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2018**, *140* (40), 13078-13088.
88. Corradi, A. B.; Ferrari, A. M.; Righi, L.; Sgarabotto, P. *Inorg. Chem.* **2001**, *40* (2), 218-223.
89. Zhou, C.; Worku, M.; Neu, J.; Lin, H.; Tian, Y.; Lee, S.; Zhou, Y.; Han, D.; Chen, S.; Hao, A.; Djurovich, P. I.; Siegrist, T.; Du, M.-H.; Ma, B. *Chem. Mater.* **2018**, *30* (7), 2374-2378.
90. Zhou, C.; Tian, Y.; Wang, M.; Rose, A.; Besara, T.; Doyle, N. K.; Yuan, Z.; Wang, J. C.; Clark, R.; Hu, Y.; Siegrist, T.; Lin, S.; Ma, B. *Angew. Chem. Int. Ed.* **2017**, *56* (31), 9018-9022.

91. Passarelli, J. V.; Fairfield, D. J.; Sather, N. A.; Hendricks, M. P.; Sai, H.; Stern, C. L.; Stupp, S. I. *J. Am. Chem. Soc.* **2018**, *140* (23), 7313-7323.
92. Tsai, H.; Nie, W.; Blancon, J.-C.; Stoumpos, C. C.; Asadpour, R.; Harutyunyan, B.; Neukirch, A. J.; Verduzco, R.; Crochet, J. J.; Tretiak, S.; Pedesseau, L.; Even, J.; Alam, M. A.; Gupta, G.; Lou, J.; Ajayan, P. M.; Bedzyk, M. J.; Kanatzidis, M. G.; Mohite, A. D. *Nature* **2016**, *536* (7616), 312-316.
93. Koh, T. M.; Thirumal, K.; Soo, H. S.; Mathews, N. *ChemSusChem* **2016**, *9* (18), 2541-2558.
94. Mitzi, D. B.; Dimitrakopoulos, C. D.; Rosner, J.; Medeiros, D. R.; Xu, Z.; Noyan, C. *Adv. Mater.* **2002**, *14*, 1772-1776.
95. Mitzi, D. B.; Feild, C. A.; Harrison, W. T. A.; Guloy, A. M. *Nature* **1994**, *369*, 467-469.
96. Zimmermann, I.; Aghazada, S.; Nazeeruddin, M. K. *Angew. Chem. Int. Ed.* **2019**, *58* (4), 1072-1076.
97. Lanzetta, L.; Marin-Beloqui, J. M.; Sanchez-Molina, I.; Ding, D.; Haque, S. A., *ACS Energy Lett.* **2017**, *2* (7), 1662-1668.
98. Zhang, X.; Wang, C.; Zhang, Y.; Zhang, X.; Wang, S.; Lu, M.; Cui, H.; Kershaw, S. V.; Yu, W. W.; Rogach, A. L. *ACS Energy Lett.* **2018**, *4* (1), 242-248.
99. Xu, Z.; Mitzi, D. B. *Chem. Mater.* **2003**, *15*, 3632-3637.
100. Mitzi, D. B.; Medeiros, D. R.; Malenfant, P. R. L. *Inorg. Chem.* **2002**, *41*, 2134-2145.
101. Hong, Z.; Chong, W. K.; Ng, A. Y. R.; Li, M.; Ganguly, R.; Sum, T. C.; Soo, H. S. *Angew. Chem. Int. Ed.* **2019**, *58* (11), 3456-3460.
102. Chong, W. K.; Giovanni, D.; Sum, T. Excitonics in 2D Perovskites. In Halide Perovskites: Photovoltaics, Light Emitting Devices, and Beyond; Sum, T., Mathews, N.; Wiley-VCH Verlag GmbH & Co. KGaA, 2019; 55-79.
103. Muljarov, E. A.; Tikhodeev, S. G.; Gippius, N. A.; Ishihara, T. *Phys. Rev. B* **1995**, *51* (20), 14370-14378.
104. Kamminga, M. E.; Fang, H.-H.; Filip, M. R.; Giustino, F.; Baas, J.; Blake, G. R.; Loi, M. A.; Palstra, T. T. M. *Chem. Mater.* **2016**, *28* (13), 4554-4562.
105. Tanaka, K.; Kondo, T. *Sci. Tech. Adv. Mater.* **2004**, *4* (6), 599-604.

106. Kitazawa, N.; Aono, M.; Watanabe, Y. *J. Phys. Chem. Solids* **2011**, *72* (12), 1467-1471.
107. Hong, X.; Ishihara, T.; Nurmikko, A. V. *Phys. Rev. B* **1992**, *45* (12), 6961-6964.
108. Ishihara, T.; Takahashi, J.; Goto, T. *Phys. Rev. B Condens. Matter.* **1990**, *42* (17), 11099-11107.
109. Duan, H. B.; Yu, S. S.; Liu, S. X.; Zhang, H. *Dalton Trans.* **2017**, *46* (7), 2220-2227.
110. Duan, H.-B.; Yu, S.-S.; Liu, S.-X.; Zhang, H. *RSC Adv.* **2017**, *7* (37), 23234-23237.
111. Duan, H. B.; Yu, S. S.; Tong, Y. B.; Zhou, H.; Ren, X. M. *Dalton Trans.* **2016**, *45* (11), 4810-8.
112. Zhang, S.; Lanty, G.; Lauret, J.-S.; Deleporte, E.; Audebert, P.; Galmiche, L. *Acta Materialia* **2009**, *57* (11), 3301-3309.
113. Pradeesh, K.; Nageswara Rao, K.; Vijaya Prakash, G., *J. App. Phys.* **2013**, *113* (8).
114. Kitazawa, N.; Aono, M.; Watanabe, Y. *Thin Solid Films* **2010**, *518* (12), 3199-3203.
115. Kitazawa, N.; Aono, M.; Watanabe, Y. *Mater. Chem. Phys.* **2012**, *134* (2-3), 875-880.
116. Gauthron, K.; Lauret, J.-S.; Doyennette, L.; Lanty, G.; Al Choueiry, A.; Zhang, S. J.; Brehier, A.; Largeau, L.; Mauguin, O.; Bloch, J.; Deleporte, E. **2010**, *18*(6), 5912-5919.
117. Safdari, M.; Svensson, P. H.; Hoang, M. T.; Oh, I.; Kloo, L.; Gardner, J. M., *J. Mater. Chem. A* **2016**, *4* (40), 15638-15646.
118. Hanamura, E. *Phys. Rev. B Condens. Matter.* **1988**, *38* (2), 1228-1234.
119. Kataoka, T.; Kondo, T.; Ito, R.; Sasaki, S.; Uchida, K.; Miura, N. *Phys. Rev. B Condens. Matter.* **1993**, *47* (4), 2010-2018.
120. Era, M.; Morimoto, S.; Tsutsui, T.; Saito, S. *App. Phys. Lett.* **1994**, *65* (6), 676-678.
121. Booker, E. P.; Thomas, T. H.; Quarti, C.; Stanton, M. R.; Dashwood, C. D.; Gillett, A. J.; Richter, J. M.; Pearson, A. J.; Davis, N. J. L. K.; Sirringhaus, H.; Price, M. B.; Greenham, N. C.; Beljonne, D.; Dutton, S. E.; Deschler, F. *J. Am. Chem. Soc.* **2017**, *139* (51), 18632-18639.
122. Smith, M. D.; Karunadasa, H. I. *Acc. Chem. Res.* **2018**, *51* (3), 619-627.
123. Ye, S.; Xiao, F.; Pan, Y. X.; Ma, Y. Y.; Zhang, Q. Y. *Mater. Sci. Eng. R: Rep.* **2010**, *71* (1), 1-34.

124. Silver, J.; Withnall, R. In *Luminescent Materials*, Kitai, A., Ed.; John Wiley & Sons: Chichester, 2008.
125. Yang, S.; Niu, W.; Wang, A. L.; Fan, Z.; Chen, B.; Tan, C.; Lu, Q.; Zhang, H. *Angew. Chem. Int. Ed.* **2017**, *56* (15), 4252-4255.
126. Stoumpos, C. C.; Malliakas, C. D.; Kanatzidis, M. G. *Inorg. Chem.* **2013**, *52* (15), 9019-9038.

Chapter 3

Experimental Methodology

This chapter describes the experimental methodologies utilized to acquire the data necessary to achieve the objectives and test the hypothesis of the thesis. It starts with the general design of the organic cations that act as templating moieties for the formation of final material. It is then followed by the elaboration of organic metal-halide (perovskite) preparation and optoelectronic devices fabrication. Lastly, the characterization techniques used throughout the study along with the underlying principles behind them are discussed in detail.

3.1 Materials fabrication

3.1.1 General design and synthesis of organic cations

The unifying theme across the studies in this thesis is the use of alkylated cyclic structures such as *N,N'*-dialkyl-4,4'-bipyridinium, pyridiniums, imidazoliums, and piperidiniums that are connected to different functional groups by a linker (**Figure 3.1**). Such design is chosen because of the synthetic simplicity and flexibility that it carries. In particular, this strategy enables various combination of cationic moiety to be probed *via* variation of the cyclic cores and their substituents. As such, insight on formability of the final material bearing desirable optoelectronic properties can be systematically investigated and rationally targeted. The general organic compound synthetic procedures are described as follows. The purity of organic compounds thus obtained were characterized mainly by ^1H and $^{13}\text{C}\{^1\text{H}\}$ nuclear magnetic resonance (NMR) spectroscopy and the details can be found in each chapter of study where the compounds are utilized or discussed.

Figure 3.1 General schematic of organic cations used throughout all studies in this thesis. Examples of the cyclic ring cores and functional groups acting as their substituents are shown.

3.1.1.1 Alkylation of pyridines and 4,4'-bipyridines

As depicted in **Schemes 3.1** and **3.2**, alkylation of pyridine and 4,4'-bipyridine is a typical S_N2 reaction where the starting precursor is mixed with halide-containing electrophile to yield the desired *N*-alkyl-pyridinium or *N,N'*-dialkyl-4,4'-bipyridinium (or viologen) halide. Generally, a flame-dried two-neck round bottom flask was charged with pyridine or 4,4'-bipyridine and a slight excess of the requisite haloalkyl reagent (1.1 equivalent to pyridine and 2.2 equivalent to 4,4'-bipyridine) and put under an argon atmosphere. Dry acetonitrile was added and the resulting mixture was stirred under reflux for 1-2.5 days (synthesis involving iodide-based precursor would typically proceed faster than that of bromide counterpart due to iodide being a better leaving group). The course of the reaction was monitored using ^1H NMR spectroscopy and upon completion it was allowed to cool to room temperature. The precipitate obtained was isolated by filtration, washed thoroughly with diethyl ether, and dried *in vacuo* to give the desired products.

Scheme 3.1 General synthetic route to pyridinium halides used in this thesis.

Scheme 3.2 General synthetic route to viologen dihalides used in this thesis.

3.1.1.2 Hydrohalogenation of amines

Hydrohalogenation of amines is an acid base reaction (**Scheme 3.3**). To a round bottom flask containing ethanol and the requisite amine, cooled to 0 °C, was added a stoichiometric amount of concentrated hydrohalic acid. Due to the greater tendency of the iodide species to get oxidized to iodine (especially in the presence of light), a small amount of reducing

agent hypophosphorous acid (H_3PO_2 ~5 % v/v relative to hydroiodic acid) was also added in the reaction flask. 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 °C overnight before being transferred to argon-filled glovebox.

Scheme 3.3 General synthetic route to ammonium halides used in this thesis.

3.1.2 Preparation of organic metal-halide hybrids (perovskites)

3.1.2.1 Single crystals

In this thesis, two methods are applied in growing the single crystals of low dimensional perovskites, which was pursued after considering, mainly, the solubility of compounds of interest in organic and aqueous solvents.

The first method relies on the diffusion of ‘antisolvent’ or ‘bad solvent’ (i.e. solvent that the final materials are not soluble in) into a solution containing the stoichiometric amounts of starting precursors. As shown in **Figure 3.2**, this can be achieved either by slow diffusion of the bad solvent’s vapor (vapor diffusion) or the liquid solvent itself (solvent diffusion/layering). In general, concentrated solutions containing stoichiometric amounts of lead- and organic-halide salt in either DMSO or DMF were prepared in small vials before antisolvents, such as toluene, acetone, chloroform, or DCM, were introduced slowly through layering or the solvent vapour diffusion method. Single crystals, thus, formed were then collected by filtration and dried. High quality single crystals suitable for X-ray crystallography were typically obtained within 1-2 weeks.

Figure 3.2 Illustration of growing single crystals with a) vapor diffusion and b) layering techniques. The figure is adapted from ref. 1.

The second method is based on slow cooling of hot saturated perovskite precursor solution. This technique takes the advantage of the materials' low solubility in aqueous hydrohalic solution at room temperature, which can be improved at elevated temperatures (**Figure 3.3**). In general, mixtures of stoichiometric amounts of lead- and organic-halide salt in concentrated aqueous HBr or aqueous HI with 5 % v/v H_3PO_2 (concentrations of around 0.25-0.30 M of Pb^{2+}) were prepared in a two-necked round bottom flask and heated, with stirring, at $\sim 140^\circ\text{C}$ for around 30 mins to 1 h under the flow of inert argon gas. The clear solutions that resulted were then allowed to cool *very slowly* to room temperature, which afforded single crystals suitable for X-ray crystallography.

Figure 3.3 Illustration of growing single crystals with slow cooling method. The figure is adapted from ref. 1.

3.1.2.2 Thin films

In this thesis, spin-coating is the technique used to fabricate the thin film samples. Substrates used for the thin film spin-coating in this study are mainly glass and quartz

substrates, which is cut into 0.5-inch $\times$ 0.5-inch dimension. Before use, the substrates were cleaned by sequential 15-minute sonication in soap solution (Decon), deionized water, ethanol, and acetone, followed by ozone plasma treatment for 15 mins. The precursor materials in powder form were separately weighed, mixed and dissolved into DMF solvent according to the stoichiometry ratio with desired concentration (typically 0.5 M). The precursor solution was then dropped and spread on the substrate, before being spun with a standardized parameter of 3000 rpm for 30 s or otherwise stated. These spin-coated thin films were then annealed on a hot plate set at 100-140 $^{\circ}\text{C}$ for 5-15 mins to evaporate the residual solvent and to assist the crystallite's grain growth. All of the spin-coating and annealing processes throughout this study were conducted in an argon-filled glovebox.

3.2 Device fabrication

3.2.1 Solar cell devices based on mesoporous architectures

The solar cell configuration adapted in this thesis is based on the mesoscopic TiO_2 structure (**Figure 3.4**) and it inherits the architecture of a dye-sensitized solar cell consisting of multiple component layers fabricated on top of a transparent conductive oxide (TCO) glass substrate such as fluorinated tin oxide (FTO) bearing mesoporous TiO_2 scaffolds.²

Figure 3.4 Schematic of perovskite solar cell based on mesoscopic TiO_2 architecture. The figure is adapted from ref. 2.

As a start, the FTO substrates (Pilkington, TEC 15) were cut and cleaned by sequential 15 minute sonication in soap solution (Decon), deionized water, ethanol, and acetone.

Subsequently, the substrates were dried using a N₂ gun and treated with ozone plasma for 15 mins. A compact TiO₂ blocking layer with a thickness of approximately 50 nm was deposited on the cleaned substrates by spray pyrolysis of a precursor solution on a hot plate at 450 °C. The TiO₂ precursor used was a solution composed of 6 : 4 : 90 volume ratio of titanium diisopropoxide bis(acetylacetonate) (75 % in 2-propanol, Sigma-Aldrich), acetylacetone, and absolute ethanol. Upon cooling to room temperature, the substrates were treated by submersion in a 50 mM TiCl₄ solution (obtained by dilution of 5.0 M Aq. TiCl₄ solution, with deionized water) at 70 °C for 30 mins. After that, a 250 nm thick mesoporous TiO₂ scaffold was deposited by spin-coating a TiO₂ paste onto the dense TiO₂ coated substrates. The TiO₂ paste was prepared by stirring a 1 : 5 weight ratio of a commercial TiO₂ paste (Dyesol 30NRD) and absolute ethanol until it became homogenous. The diluted TiO₂ paste was spin-coated at 4500 rpm for 30 s, followed by a three-step annealing procedure at respective temperatures of 125 °C, 375 °C and 500 °C, each for 30 mins.

The perovskite layers were prepared by spin coating different concentrations of the stoichiometric precursor solutions in DMF (1.0, 0.75 , 0.50, 0.25, and 0.125 M, based on Pb²⁺) at 3000 rpm for 30 s. Subsequently, the substrate was placed on a hot plate to anneal at 130 °C for 10 mins. After cooling to room temperature, solutions of the hole transporting material *N*²,*N*²,*N*^{2'},*N*^{2'},*N*⁷,*N*⁷,*N*^{7'},*N*^{7'}-octakis(4-methoxyphenyl)-9,9'-spirobi[9H-fluorene]-2,2',7, 7'-tetramine (spiro-OMeTAD, Merck livlux SHT-263) were deposited onto the perovskite film by spin-coating at 4000 rpm for 30 s. The spiro-OMeTAD solutions were prepared by dissolving spiro-OMeTAD in chlorobenzene (70 mg/ml), and adding 28 µl of *tert*-butylpyridine (96 % from Sigma-Aldrich) and 17 µl of lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI stock solution, 520 mg/ml in acetonitrile) to it. Co-dopant tris(2-(1*H*-pyrazol-1-yl)-pyridine)cobalt(III) tris(trifluoromethylsulfonyl)imide (FK 102 Co(III) TFSI salt, Dyesol) was predissolved in acetonitrile (15 mol% concentration) and added to the hole-transport material solution (28 µl). Finally, a gold electrode of approximately 100 nm of thickness was deposited through a mask with a device area of 0.2 cm², using a thermal evaporator.

3.2.2 Photodetector devices with lateral electrodes configuration

Preparation of photodetector devices with lateral electrodes configuration (i.e. ‘horizontal devices’) involved spin coating 0.50 M DMF solutions of stoichiometric mixtures of the 2D perovskite precursors onto pre-cleaned glass substrates at 3000 rpm for 30 s, after which the resulting films were heated at 130 °C for 10 mins to remove residual solvent and promote better crystallization. Subsequently, a 100 nm thick gold electrode (distance = 125 μm , width = 4000 μm) was deposited through a mask of appropriate dimensions using a thermal evaporator (**Figure 3.5**).

Figure 3.5 Schematic of photodetector thin film devices with lateral electrodes configuration (i.e. ‘horizontal devices’).

For pellet samples, single crystals of the compounds were firstly ground into fine polycrystalline forms. They were then pressed into circular disk-shaped pellets by applying a uniaxial pressure of 100 MPa (diameter = 1.35 cm, thickness $\approx$ 0.1 cm) using a hydraulic press. Finally, similar to that of thin film samples, 100 nm thick gold electrode (distance = 125 μm , width = 4000 μm) was deposited through a mask of appropriate dimensions using a thermal evaporator (**Figure 3.6**).

Figure 3.6 Schematic of photodetector devices with lateral electrodes configuration (i.e. ‘horizontal devices’) prepared from polycrystalline samples.

3.2.3 Photodetector devices with lateral interdigitated electrodes

Interdigitated FTO electrodes (3 Fingers) with lateral spacing of $100\ \mu\text{m}$ and total effective length of $3.17\ \text{cm}$ was used in fabrication of lateral device as shown in **Figure 3.7**. The interdigitated electrode configuration was used to facilitate the application of voltage to the materials during the measurement (i.e. poling), which is suitable to study the effect of ionic migration within the material towards its photoconductivity profile. $0.50\ \text{M}$ solutions of stoichiometric amounts of the respective 2D perovskites, dissolved in DMF, was spin coated onto pre-cleaned glass or FTO-patterned ($100\ \mu\text{m}$ spaced) substrates (cleaned by sequential 15-minute sonication in soap solution (Decon), deionized water, ethanol, and acetone, followed by ozone plasma treatment for 15 mins) at 3000 rpm for 30 s. The resulting films were, subsequently, heated at $100\ ^\circ\text{C}$ for 5 mins to remove residual solvents.

Figure 3.7 Schematic of photodetector devices with lateral interdigitated electrodes.

3.3 Characterization techniques

Herein, quantitative description of each characterization technique, employed throughout the study to investigate structural and optoelectronic properties of low-dimensional metal halide hybrids, is given. More detailed information regarding the instrumentations and relevant parameters to acquire the data presented in this thesis can be found in the corresponding result chapters.

3.3.1 Nuclear magnetic resonance (NMR) spectroscopy

NMR spectroscopy is a spectroscopic technique to observe local magnetic fields around atomic nuclei. An NMR active nucleus must have a nuclear spin (I) and therefore, a nuclear magnetic moment. The size of the magnetic moment depends both on I , which can take values of 0, $1/2$, 1, $3/2$, 2, $5/2$, ... and on its magnetogyric ratio (γ). In the presence of a magnetic field, Zeeman splitting (splitting of a spectral line into several components in the presence of a static magnetic field) occurs and $2I + 1$ nondegenerate spin states are formed, between which $2I$ allowed transitions can take place between adjacent energy levels. **Figure 3.8** presents an exemplary schematic showing how the energy levels are arranged for $I = 1/2$ nucleus (^1H). A radio frequency signal at the NMR frequency then causes transitions between the spin states to give the NMR spectrum, which is detected with sensitive radio receivers.

Figure 3.8 The splitting of the degenerate nuclear energy levels (in this example, $I = 1/2$) under an applied magnetic field. The green spheres represent atomic nuclei which are either aligned with (low energy) or against (high energy) the magnetic field. E , m , γ , h , and B_0 represent energy level, magnetic quantum number, magnetogyric ratio, Planck constant, and external magnetic field, respectively. The figure is adapted from ref. 3.

The intramolecular magnetic field around an atom in a molecule changes the resonance frequency, thus giving access to details of the electronic structure of a molecule and its individual functional groups. As the signals are unique to or highly characteristic of

individual compounds, NMR spectroscopy is a very useful method to identify monomolecular organic compounds. Besides identification, NMR spectroscopy provides detailed information about the structure, dynamics, reaction state, and chemical environment of certain nuclei of particular compounds.

3.3.2 X-ray single crystallography

X-ray crystallography is a non-destructive analytical technique used for determining the atomic and molecular structure of a single crystal. The crystal is typically mounted on a goniometer where its position can be adjusted at selected orientations before it is illuminated with a finely focused monochromatic beam of X-rays, producing a diffraction pattern of regularly spaced spots, loosely termed as “reflections.” Such reflections occur only at specific orientations of the crystal with respect to the source and detector, where conditions for constructive interference are fulfilled (“Bragg reflection”; **Figure 3.9**).

Figure 3.9 Schematic illustration of Bragg reflection from a set of crystal planes with a spacing d_{hkl} . The figure is adapted from ref. 4.

By measuring the angles and intensities of these diffracted beams, a three-dimensional picture of the density of electrons within the crystal can be produced using the mathematical method of Fourier transforms, combined with chemical data known for the sample. From this electron density, the mean positions of the atoms in the crystal can after that be determined, as well as their internal lattice of crystalline substances, including unit

cell dimensions, bond-lengths, bond-angles, crystallographic disorder and details of site-ordering. The aforementioned data generated from the X-ray analysis is typically interpreted and refined to obtain the crystal structure during single-crystal refinement process.

3.3.3 Powder and glancing angle X-ray diffractometry

Similar to X-ray single crystallography, powder- and glancing angle-X-ray diffractometries (PXRD and GAXRD, respectively) are also non-destructive techniques useful to qualitatively characterize solid-state materials. However, unlike in the former, PXRD and GAXRD allow the structure of a polycrystalline sample to be analyzed directly from the associated X-ray diffraction peaks or “patterns”. The patterns are the result of diffraction of a monochromatic X-ray beam (λ) that occur due to interaction with planes in the sample crystallites that happen to be oriented at the correct angle, thus satisfying the Bragg condition (**Eqn. 3.1**):

$$n\lambda = 2d\sin\theta \quad (\text{Eqn. 3.1})$$

Information that can be obtained from the X-ray diffraction pattern are as following:

- 1) types of crystalline phases present in the solid-state samples,
- 2) unit cell structure, lattice parameters and Miller indices,
- 3) estimation of the crystalline/amorphous content in the sample,
- 4) evaluation of the mean crystalline domain size from the widths of the peaks with higher intensity in a particular phase pattern by using of the Scherrer equation (**Eqn. 3.2**).⁵ A large crystal size gives rise to sharp peaks, while the peak width increases with decreasing crystal size.

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad (\text{Eqn. 3.2})$$

where τ is the mean crystalline domain size, $K = 0.94$ is a dimensionless shape factor, $\lambda = 1.54178 \text{ \AA}$ is the Cu K α X-ray wavelength, β is the full width at half maximum (FWHM) in radians, and θ is the Bragg angle.

3.3.4 UV-vis spectroscopy

3.3.4.1 Linear absorption spectroscopy

This spectroscopy technique is used to acquire the linear absorption spectrum of a material (typically thin film samples in this study) that contains information regarding optically active energy states or excited species (e.g. excitons or free carriers). The basic principle behind linear absorption spectroscopy is straightforward. White light from a lamp source is collimated and split into two beams: one for the measurement and another for the reference. The sample is then placed in the optical path of the measurement beam. These two beams are then sent to detectors for simultaneous measurement. By simultaneously analyzing the spectrum of the transmitted beam in comparison to the reference, the linear absorption spectrum of the sample can be obtained.

One common assumption in this measurement is negligible scattering and back reflections from the sample. Apart from absorption, such processes might reduce the intensity of the transmitted light, and hence create artifacts of strong absorption. While the assumption is valid for smooth transparent thin film samples, it might not be applicable for rough and reflecting samples. Hence, an integrating sphere set-up is chosen for the study to eliminate the aforementioned issue.

3.3.4.2 Diffuse reflectance spectroscopy (DRS)

Diffuse reflectance is a UV-Vis spectroscopic technique applied to crystalline or amorphous materials. Diffuse reflectance depends on the focused projection of the spectrometer beam onto the sample where it is reflected, scattered, transmitted through, and absorbed partially by the sample material. The reflected, diffusely scattered light is then collected and directed to the detector optics. Generally, the sample is ground up appropriately before being applied on a non-light-absorbing matrix such as barium sulfate (BaSO_4). A Kubelka-Munk conversion can be applied to a diffuse reflectance spectrum to compensate for these differences. The Kubelka-Munk equation (**Eqn. 3.3**) is shown below:

$$F(R) = \frac{(1-R)^2}{2R} \quad (\text{Eqn. 3.3})$$

where $F(R)$ is equivalent to the absorption coefficient (α/S) and R is reflectance.

The Kubelka-Munk function gives a correlation between the reflectance and the concentrations of absorbing species in weak absorbing samples, something like the Lambert-Beer law for absorbance. However, as it was developed to analyze “coated” surfaces, it is desirable for the analyzed sample to feature surface that is totally plane and with infinitesimal thickness. As such, one limitation of the technique is that its accuracy will be compromised by the use of samples with different particles sizes featuring high light scattering.

3.3.5 Photoluminescence (PL) spectroscopy

PL spectroscopy technique is used to study the emission spectrum of the material due to photoexcitation by a light source. PL is a process by which the material absorbs photons (promoting electrons to a higher energy states), before radiating photons (when the electrons return to their equilibrium states). When variables such as temperature, excitation power, and time are incorporated, the technique is very useful to investigate the behavior

of photo-generated electron-hole pairs (e.g. their bleaching, binding energy and oscillator strength), trap state density, and mechanistic origin of the materials emissions.

3.3.6 Field- emission scanning electron microscopy (FE-SEM)

SEM is a technique to obtain the morphology on the surface of sample by collecting the signal from electron-sample interaction. In SEM, electron is produced by filament cathode which is heated by a current. The electron is then accelerated and focused by condenser and objective lenses. These are electromagnetic lenses which able to alter electron trajectory as it passes by. The working principle is similar to optical microscope, but instead of light and optical lenses, focused electron beam and electromagnetic lenses are used to “scan” the samples. As accelerated electron reaches the samples, electron-sample interaction decelerates the electron and yield various signals. The electron will sweep across rectangular shaped area (called ‘Raster’), the signals generated from electron-sample interaction forms image on the screen.

Figure 3.10 Electron-specimen interaction volume illustration. The figure is adapted from ref. 6.

Figure 3.10 shows the various signals produced from electron-specimen interaction. Secondary and backscattered electrons are most common signals in SEM. Secondary

electrons are used to do topology imaging in SEI (secondary electrons imaging) mode. It is the most common mode in SEM. Backscattered electrons is used to distinguish different components in a multicomponent material in BEI (backscattered electrons imaging) mode. In this study, SEI mode is the main focus. Secondary electrons are produced through inelastic scattering between k -shell in the atom and focused electron beam. Secondary electrons are low in energy and only obtainable near surface. These emitted secondary electrons are collected by a detector, called Everhart-Thornley detector. This detector has positively charged surface to attract secondary electrons and emit light as the secondary electrons are collected. Light is then guided by total internal reflection in a light pipe to a photomultiplier which converts the light and amplifies to an electronic signal and converted into digital image on screen. Beside surface images, SEM can also study the cross-section image of thin film by preparing and putting the samples on a specific sample holder.

3.3.7 Atomic force microscopy (AFM)

AFM is a microscopic technique that uses a cantilever with a very sharp tip to scan over a sample surface. As the tip approaches the surface, the close-range, attractive force between the surface and the tip cause the cantilever to deflect towards the surface. However, as the cantilever is brought even closer to the surface, such that the tip makes contact with it, increasingly repulsive force takes over and causes the cantilever to deflect away from the surface. A laser beam is used to detect cantilever deflections towards or away from the surface. By reflecting an incident beam off the flat top of the cantilever, any cantilever deflection will cause slight changes in the direction of the reflected beam. A position-sensitive photo diode (PSPD) can be used to track these changes. Thus, if an AFM tip passes over a raised surface feature, the resulting cantilever deflection (and the subsequent change in direction of reflected beam) is recorded by the PSPD.

An atomic force microscope images the topography of a sample surface by scanning the cantilever over a region of interest. The raised and lowered features on the sample surface influence the deflection of the cantilever, which is monitored by the PSPD. By using a

feedback loop to control the height of the tip above the surface, thus maintaining constant laser position, the AFM can generate an accurate topographic map of the surface features.

3.3.8 Raman spectroscopy

Raman spectroscopy is a technique employed to obtain chemical information of a material through identification of the inelastic scattering phenomenon. When light shines to a material, most of them are scattered, in addition to being absorbed or transmitted. Scattering phenomenon can be described as the electron in the material excited to virtual energy level before relaxing back to lower levels. Such scattering can be elastic (Rayleigh scattering) or inelastic. In the former, the electrons fall back to same energy level, but in latter, the electrons fall back to either energy level above the initial level (Stokes scattering) or energy level below initial level (anti-stokes scattering).

When the electrons return to lower levels, they are also emitting light/photons which equate to energy difference between the virtual and final levels. These are signals which Raman spectroscopy used and collected. As such, the signal is characterized by the difference between wavelength of incident photons/lights and scattered photons/lights (i.e. Raman shift (cm^{-1}));

$$\bar{\nu} = \frac{1}{\lambda_{incident}} - \frac{1}{\lambda_{scattered}} \quad (\text{Eqn. 3.4})$$

Raman spectroscopy can identify chemical phases and composition of a system, because each chemical phases and composition carry a fingerprint. The inelastic scatterings that occur are dependent on vibrational, electronic and rotational energy of the material. These variables are related to the atomic bonding and position in a phase, these atoms interaction with photons are unique. Thus, by analyzing the value of Raman shifts in the system and comparing it with literature, identification of material phases and structure can be investigated.

3.3.9 Solar cells current density-voltage (J - V) measurement

J - V measurement is the most common and essential measurement for solar cells, where photovoltaic parameters, such as short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), and power conversation efficiency (PCE or η) are investigated. During the measurement, the light source (xenon arc lamp; **Figure 3.11**) is simulated such that it mimics the spectrum and intensity of the light being emitted by the Sun (AM 1.5 G spectrum and 1000 Wcm^{-2} light intensity.)

The efficiency of a solar cell (η) is given by the ratio of the maximum output power (P_{max}) to the power of the input light (P_{in}):

$$\eta = \frac{P_{max}}{P_{in}} \quad (\text{Eqn. 3.5})$$

The measurement is performed by applying a voltage at a desirable range and recording the photocurrent response. Parameter V_{oc} is obtained at current density equals to zero (i.e. open circuit condition) while J_{sc} is determined at zero bias (i.e. short circuit condition). From these two points, J - V curve is then yielded. The shape of the curve indicates the quality of solar cells fabricated and it is represented by a factor called FF. FF is often used to describe how “square” the J - V curve is, relative to the extension of the J_{sc} and V_{oc} . Specifically it is defined as the ratio between Pmax and the product of Jsc and Voc:

$$FF = \frac{P_{max}}{P_T} = \frac{J_{max} \times V_{max}}{J_{sc} \times V_{oc}} \quad (\text{Eqn. 3.6})$$

Considering all aforementioned parameters, the efficiency of the solar cells can be determined, which is defined as the following:

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \quad (\text{Eqn. 3.7})$$

Figure 3.11 Spectral comparison of xenon arc lamp solar simulator utilized in this study and measured natural solar radiation. The figure is adapted from ref. 7.

3.3.10 Incident photon-to-current efficiencies (IPCE) or external quantum efficiencies (EQE) measurement

IPCE measurement is a wavelength dependent photocurrent generation measurement that describes how many incoming photons are converted carriers and collected as current in the photovoltaic devices. Specifically, the solar cell is illuminated by monochromatic light with various wavelength, and has the generated photocurrent recorded. This photocurrent is dependent on various processes in the solar cells; namely the amount of light absorbed (η_{abs}), the proportion of the generated electrons that are injected from the light absorbing layer to the electron transport layer (η_{inj}), and the efficiency of the device in charge collection (η_{coll}). As such, the IPCE value is defined as the product of those three efficiencies:

$$\eta = \eta_{abs} \times \eta_{inj} \times \eta_{coll} \quad (\text{Eqn. 3.8})$$

3.4 Bibliography

1. <https://web.mit.edu/x-ray/crystallize.html> (accessed 27 Jul 2019).
2. Im, J.-H.; Lee, C.-R.; Lee, J.-W.; Park, S.-W.; Park, N.-G. *Nanoscale* **2011**, 3 (10), 4088-4093.
3. [https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_\(Physical_and_Theoretical_Chemistry\)/Spectroscopy/Magnetic_Resonance_Spectroscopies/Nuclear_Magnetic_Resonance/Nuclear_Magnetic_Resonance_II](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Spectroscopy/Magnetic_Resonance_Spectroscopies/Nuclear_Magnetic_Resonance/Nuclear_Magnetic_Resonance_II) (accessed 27 Jul 2019).
4. Smart, L. E.; Moore, E. A. *Solid State Chemistry: An Introduction*; CRC Press: Danvers, 2012.
5. Patterson, A. L. *Phys. Rev.* **1939**, 56 (10), 978-982.
6. https://commons.wikimedia.org/wiki/File:Electron_Interaction_with_Matter.svg (accessed 27 Jul 2019).
7. Reber, G.; Steiner, R.; Oelhafen, P.; Romanyuk, A. CISBAT Proceedings EPFL **2005**, 173-178.

Chapter 4

Inducing panchromatic absorption and photoconductivity in polycrystalline molecular 1D lead-iodide perovskites through π -stacked viologens

As a consequence of their quantum- and electronically-confined inorganic lattices, molecular 1D lead-iodide perovskites are ill suited to photovoltaic (PV) applications. In order to circumvent these problems electron accepting viologen (N,N'-dialkyl-4,4'-bipyridinium) dications incorporating hydrogen bond donor functionalities are utilized, which served to induce π - π stacking interactions. The resulting 'viologen dimers' display enhanced charge-transfer (CT) interactions with the 1D lead-iodide nanowires. This manifests in extended light absorption (up to 800 nm), reduced band gaps (1.74 eV to 1.77 eV), and longer photoluminescence lifetimes. More importantly, significant photoconductivity behavior in polycrystalline molecular 1D lead-iodide perovskites is demonstrated for the first time. Thus, the work described in this chapter offers a strategy for inducing the properties required for PV applications in molecular 1D lead-iodide perovskites.

4.1 Background

Molecular one-dimensional (1D) lead-iodide hybrid perovskites are an interesting class of solution-processed materials.¹⁻² Relative to the corresponding 3D materials, they have the advantages of being thermally, mechanically, and chemically stable, especially against moisture,³ whilst also being able to incorporate a much wider range of organic cations.⁴⁻⁷ However, due to narrower light absorption ranges, high excitonic binding energies and band gaps, as well as greatly compromised electrical conductivity,⁸⁻¹⁰ molecular 1D perovskites based on inert organic cations are not suitable for photovoltaic (PV) applications. In particular, although good photoconductivity has been demonstrated in single crystals of molecular 1D perovskites,¹¹⁻¹³ it has never been observed in more defective settings, such as polycrystalline forms.

In an attempt to alleviate some of the aforementioned deficiencies, molecular 1D perovskites incorporating chromophoric protonated naphthalene diimide,¹⁴ and electronically active tetrathiafulvalene (TTF) radical,¹⁵ cyclic tropylium cation,¹⁶ and doubly charged viologens (*N,N'*-dialkyl-4,4'-bipyridinium)¹⁷ have been generated. However, these materials were found to exhibit either good light harvesting capabilities *or* to be semiconducting. Both properties are required for PV applications. In principle, it should be possible to meet these requirements by selection of appropriate organic cations and crystal engineering techniques.

The synthetic simplicity and versatility of viologens (V^{2+}), combined with the lead-iodide-to- V^{2+} charge transfer (CT) interactions they display, made them a particularly appealing platform for purposes of this study. More specifically, this study sought to enhance the aforementioned CTs by inducing ordering (π - π stacking) of V^{2+} *via* introduction of *N*-alkyl substituents containing hydrogen bonding functionality. To this end, the hydroxyethyl and carboxyethyl viologens HyEtV²⁺ and CaEtV²⁺ (**Figure 4.1**) were synthesized, and the respective iodoplumbates, (HyEtV)Pb₂I₆ (**1**) and (CaEtV)Pb₂I₆ (**2**), prepared. To clarify the influence of the hydrogen bonding functionality and viologen moiety upon any properties

observed for **1** and **2**, 1D perovskites templated by propyl viologen and bis(methylammonium)biphenyl, (PrV)Pb₂I₆ (**3**) and (BpbmA)Pb₂I₆ (**4**), were also studied.

Figure 4.1 Molecular structures and notation of dicationic viologens used in this chapter.

4.2 Results and discussions

4.2.1 π - π stacking and induced charge transfer interaction

Figure 4.2a shows the UV-Vis diffuse reflectance spectra (DRS) of **1-4**, and **Table 4.1** summarizes absorption profiles of each hybrid perovskite. All compounds display sharp, high energy bands at 372 – 377 nm that are characteristic of the inorganic intrachain electronic transitions of 1D lead-iodide lattices.¹⁸⁻¹⁹ In addition, the spectra of the V²⁺-containing compounds **1-3** possess relatively broad absorptions centered in the visible region. Notably, this feature is significantly red-shifted in hydrogen bond donor-containing **1** and **2** relative to **3**, which renders the former two materials black and the latter red. The panchromatic absorptions displayed by **1** and **2** are reminiscent of the light absorption capability of methyl ammonium-based 3D perovskite²⁰ (MAPbI₃; see **Figure 4.3** for comparison), and greatly surpasses that of molecular 1D perovskites derived from conventional ammonium cations, as exemplified by **4**.

In analogy with studies conducted by Fujisawa, *et. al.* on 1,1'-dimethyl-4,4'-bipyridinium (methyl viologen; MeV²⁺)-based 1D lead-iodide perovskite, which concluded that type-II band alignment is adopted, the low energy transitions in the UV-Vis spectra of **1-3** can be assigned as CT bands between the valence band localized on the lead-iodide chains (donor)

and the V^{2+} -centered conduction bands (acceptor).^{18, 21} Extrapolation of the linear parts of the CT transitions of **1-3**, yield band gaps of 1.74, 1.77 and 2.21 eV, respectively.^{18, 22}

Figure 4.2 (a) UV-Vis spectra of polycrystalline powders of (HyEtV)Pb₂I₆ (**1**; red solid line), (CaEtV)Pb₂I₆ (**2**; blue solid line), (PrV)Pb₂I₆ (**3**; orange solid line), and (BpbmA)Pb₂I₆ (**4**; green solid line). The dashed lines obtained by extrapolation of the linear part of each spectrum correspond to the band gaps of each material. (b) Schematic energy diagram of the molecular 1D perovskites **1-4**. Valence band energies were obtained from photoelectron spectroscopy in air (PESA) measurements and optical band gaps from the UV-vis spectra.

Estimation of the valence band energies for compounds **1-4** using photoelectron spectroscopy in air (PESA) yielded similar values of -5.79, -5.68, -5.70, and -5.73 eV, respectively (**Figure 4.4**). Coupling this data with that obtained from the UV-Vis measurements, allowed construction of band energy diagrams, shown in **Figure 4.5**. Given the similarity of the valence band energies in all materials, the reduced band gaps in **1** and **2** relative to **3** and **4** are clearly a consequence of the lower energy of the lowest unoccupied molecular orbitals (LUMOs) of their constituent V^{2+} organic cations. Furthermore, the hydrogen bond donor groups in HyEtV²⁺ and CaEtV²⁺ are electronically isolated from the viologen moiety, so the low energies of the LUMOs in **3** and **4** can be safely ascribed to supramolecular effects.

Table 4.1 UV-Vis DRS spectral parameters of iodide salts and perovskite hybrids.

Compounds	Valence-to-conduction band maxima	Excitonic transition peaks	Charge transfer (CT) transition maxima	Absorption onset	Inorganic band gap (E_g)	Intermolecular electronic transitions (VB→LUMO)
(HyEtV)Pb ₂ I ₆	372 nm	-	500 nm	800 nm	3.08 eV	1.74 eV
(HyEtV)I ₂	-	-	405 nm	500 nm	-	-
(CaEtV)Pb ₂ I ₆	377 nm	-	492 nm	800 nm	2.83 eV	1.77 eV
(CaEtV)I ₂	-	-	405 nm	492 nm	-	-
(PrV)Pb ₂ I ₆	376 nm	-	442 nm	650 nm	2.96 eV	2.21 eV
(PrV)I ₂	-	-	467 nm	585 nm	-	-
(BpbmA)Pb ₂ I ₆	386 nm	410 nm	-	500 nm	2.94 eV	-

Figure 4.3 UV-vis absorbance spectra of 1D perovskites (HyEtV)Pb₂I₆ (**1**) and (CaEtV)Pb₂I₆ (**2**), plus that of 3D methyl ammonium lead iodide (MA)PbI₃. Panchromatic visible light absorption of MAPbI₃ is due to expanded orbital overlap of lead-iodide octahedra in three dimensions. Although the inorganic components of **1** and **2** are 1D in nature, absorption features similar to the 3D material are realized due to enhanced CT interactions of the inorganic chains with the viologen dications.

Figure 4.4 Photoelectron spectroscopy in air (PESA) measurements for (HyEtV)Pb₂I₆ (**1**; red), (CaEtV)Pb₂I₆ (**2**; blue), (PrV)Pb₂I₆ (**3**; orange), and (BpbmA)Pb₂I₆ (**4**; green). Solid lines are linear fittings of the points where the intersections between the linear fits of the two domains provides estimates of the valence bands energies of each 1D perovskite (5.79 eV, -5.68 eV, -5.70 eV, and -5.73 eV for **1**, **2**, **3**, and **4**, respectively).

Figure 4.5 Schematic energy diagrams of (a) (BpbmA)Pb₂I₆, (b) (PrV)Pb₂I₆, (c) (CaEtV)Pb₂I₆, and (d) (HyEtV)Pb₂I₆. All valence bands are of similar energy and are localized on the iodoplumbate lattice. In the viologen containing materials, the cation-centred LUMOs act as the ‘conduction band’. As can be seen, the change in optical gap is dominated by lowering of the energy of the LUMOs of the organic component.

X-ray crystal structures of **1**, **2** and **3** (**Figure 4.6**; see **Section 4.5** for summary of crystallographic refinement data) all show long 1D lead-iodide chains surrounded by parallel-oriented organic cations. However, the relative packing arrangement of the

viologens is observed to vary, depending on the *N*-alkyl substituents incorporated. More specifically, the viologens possessing hydrogen bonding functionality, in **1** and **2**, are found to exist as π - π stacked dimers with interplane distances ranging from 3.642 to 3.662 Å and from 3.593 to 3.687 Å, respectively (**Figures 4.6a** and **4.6b**). The alcohol and carboxylic acid functionality in their respective dications, HyEtV²⁺ and CaEtV²⁺, hydrogen bond to DMSO (dimethyl sulfoxide) solvent molecules incorporated into the lattice. In compound **3**, where such interactions are unavailable, the PrV²⁺ dications adopt multiple orientations (**Figure 4.6c**).

Figure 4.6 Crystal structures of (a) (HyEtV)Pb₂I₆ (**1**), (b) (CaEtV)Pb₂I₆ (**2**), and (c) (PrV)Pb₂I₆ (**3**). Left insets indicate the relative orientation of organic viologens in the crystal lattice. Right insets show the visual appearances of the polycrystalline 1D perovskites. Gray, purple, brown, red, blue, and yellow spheres represent Pb, I, C, O, N, and S atoms, respectively. H atoms are omitted for clarity.

In contrast, amongst the iodide salts of the viologen dications, π - π stacking of V²⁺ is seen only in the X-ray structure of [PrV]I₂ (**Figure 4.7**; see **Section 4.5** for summary of crystallographic refinement data). Intriguingly, the iodide-to-V²⁺ CT band observed in the UV-Vis spectrum of this compound, $\lambda_{\text{max}} = 467$ nm, is red-shifted relative to those of [HyEtV]I₂ and [CaEtV]I₂ (**Figure 4.8**), for which $\lambda_{\text{max}} = 405$ nm. Thus, it appears that the observed shifts in anion-to-V²⁺ CTs to lower energy are associated with formation of π - π stacked dimers. This can be attributed to resultant delocalization and attendant stabilization of the V²⁺-based LUMOs.

Figure 4.7 Crystal structures of (a) (HyEtV)I₂ and (b) (CaEtV)I₂ showing random orientation and no significant π - π stacking of viologen cations, while (c) (PrV)I₂ shows the presence of π - π stacking to give PrV²⁺ dimers. Brown, red, blue, and yellow spheres represent C, O, N, and S atoms, respectively. H atoms are omitted for clarity. Crystallography and refinement data for each of the structures is summarized in **Section 4.5**.

Figure 4.8 (a) UV-Vis absorbance spectra of polycrystalline viologen iodides (HyEtV)I₂, (CaEtV)I₂, and (PrV)I₂ (solid lines), plus their hybrid perovskite counterparts (dash lines). (b) Visual appearances of (HyEtV)I₂, (CaEtV)I₂, and (PrV)I₂, alongside the corresponding 1D lead-iodide perovskites (HyEtV)Pb₂I₆ (**1**), (CaEtV)Pb₂I₆ (**2**), and (PrV)Pb₂I₆ (**3**). See **Table 4.1** for a summary of the observed optical features.

The assertion is reinforced by the UV-Vis absorption profiles of (HyEtV)Pb₂I₆ (**1a**) and (CaEtV)Pb₂I₆ (**2a**) recrystallized from DMF (dimethylformamide) solution. The X-ray structures of these compounds (**Figure 4.9**) exhibit face-sharing 1D inorganic backbone structures. In contrast to **1** and **2**, the incorporated solvent molecules do not hydrogen bond to the HyEtV²⁺ and CaEtV²⁺ cations and, as a consequence, π - π stacked V²⁺ dimers are not

formed. Commensurately, these materials exhibit attenuated absorption, with onsets at 550 and 650 nm, respectively (**Figure 4.10**).

Figure 4.9 Single crystal X-ray structures of alternative structures (HyEtV)Pb₂I₆ (**1a**; (a) & (c)) and (CaEtV)Pb₂I₆ (**2a**; (b) & (d)), for which there is no π - π stacking of the viologen dications. **1a** was obtained by slow diffusion of benzene into vials containing DMF precursor solutions, while **2a** was achieved using DMSO-benzene solvent combinations. Grey, purple, brown, red, blue, and yellow spheres represent Pb, I, C, O, N, and S atoms, respectively. H atoms are omitted for clarity. Crystallographic and refinement data for these structures is summarized in **Section 4.5**. Lack of π - π stacking leads to compromised light absorption capabilities (**Figure 4.10**) and an absence of photoconductivity (**Figure 4.11**).

Figure 4.10 UV-Vis absorbance spectra of alternative structures (HyEtV)Pb₂I₆ (**1a**) and (CaEtV)Pb₂I₆ (**2a**). The spectrum of (PrV)Pb₂I₆ (**3**) is included for comparison. Absorption onsets for **1a** and **2a** occur at ~550 nm and ~650 nm, respectively. Charge transfer maxima are observed at 435 nm (**1a**) and 442 nm (**2a**).

Figure 4.11 Current-voltage (I - V) curves of alternative structures (a) (HyEtV)Pb₂I₆ (**1a**) and (b) (CaEtV)Pb₂I₆ (**2a**), showing no significant current generated upon white light irradiation. Average dark conductivities are $2.243 \times 10^{-11} \text{ S cm}^{-1}$ for **1a** and $2.005 \times 10^{-11} \text{ S cm}^{-1}$ for **2a**, while their respective average conductivities in the presence of light (1 sun illumination) are $2.385 \times 10^{-11} \text{ S cm}^{-1}$ and $2.244 \times 10^{-11} \text{ S cm}^{-1}$.

4.2.2 Optoelectronic properties improvement due to π - π stacking

Photoluminescence (PL) spectra of the viologen-based 1D perovskites (**Figure 4.12a**) show features that are fully consistent with the UV-vis absorption profiles. In particular, the emission spectra of **1** and **2** display broad bands centered at 647 and 649 nm, respectively, values that are significantly lower in energy than that of the corresponding

feature in **3** at 544 nm. These features can be attributed to CT relaxation. The emissions related to the inorganic chain band transition appear for all compounds (**1-4**) at characteristically high energy.¹⁹

Figure 4.12 Photoluminescence (PL) spectra (a) and time-resolved PL decay curves (b) of (HyEtV)Pb₂I₆ (**1**) (red circle and triangle), (CaEtV)Pb₂I₆ (**2**) (blue circle and triangle), and (PrV)Pb₂I₆ (**3**) (orange circle and triangle), obtained using an excitation wavelength at 405 nm.

To obtain further insight into the luminescent properties of polycrystalline samples of perovskites **1-3**, time-resolved photoluminescence (TRPL) experiments were performed. TRPL spectra recorded at the highest intensity emissions show that **3** exhibits much faster average charge carrier recombination than both **1** and **2** (**Figure 4.12b**). More specifically, best fits (summarized in **Table 4.2**) reveal that while **3** exhibits a biexponential decay composed of 336 ps (89%) and 2.88 ns (11%) components, **1** and **2** display longer lifetime decay in both radiative (τ_1) and nonradiative (τ_2) processes. More specifically, 354 ps (79%) and 2.91 ns (21%) components in the former case, and 723 ps (70%) and 3.56 ns (30%) components in the latter. The longer average lifetime of charge carriers in **1** and **2** suggests a higher probability of generating free charge carriers compared to **3**.

Table 4.2 Semiconducting parameters of the 1D perovskites.

Parameters	Compounds			
	(HyEtV)Pb ₂ I ₆ (enhanced CT)	(CaEtV)Pb ₂ I ₆ (enhanced CT)	(PrV)Pb ₂ I ₆ (CT)	(BpbmA)Pb ₂ I ₆ (no CT)
PL peak (nm)	647	649	544	-
PL Stoke shift (nm)	147	157	102	-
PL decay τ_1 (ps)	350 (79%)	723 (70%)	340 (89%)	-
PL decay τ_2 (ns)	2.900 (21%)	3.565 (30%)	2.870 (11%)	-
PL decay τ_{ave} (ns)	0.891	1.576	0.616	-
Conductivity (S cm ⁻¹)	1.754×10^{-11}	5.793×10^{-11}	1.530×10^{-11}	9.598×10^{-12}
Photoconductivity (S cm ⁻¹)	1.245×10^{-10}	1.232×10^{-9}	1.871×10^{-11}	9.906×10^{-12}
On/off current generation ratio at 3.0V	6.40	20.60	1.08	1.02

Inspired by the aforementioned data, the photoconductivity of polycrystalline samples of **1-4**, plus **1a** and **2a**, were investigated *via* four-probe measurements (**Figure 4.13a**). Unsurprisingly, the polycrystalline 1D perovskites based on the ammonium cation **4** and V²⁺ that do not form π - π stacked dimers (i.e., **3**, **1a** and **2a**) do not show enhanced photocurrent (**Figure 4.13b**, **Figures 4.14** and **4.11**). However, **1** and **2** exhibit a significant increase in charge transport under white light illumination (**Figure 4.13b**, **Figure 4.15**). At a bias as low as 3.0 V, the photocurrent increased from 24.4 pA (dark) to 159 pA (light) in the case of **1** and from 71.5 pA (dark) to 1470 pA in the case of **2**. This corresponds to on/off ratios of 6.4 and 20.6, respectively. Interestingly, the on/off ratio measured for **2** is comparable to that observed for 2D lead-iodide perovskites templated by related isomeric organic dication, 4,4'-bis(ammonium-ethyl)-1,1'-biphenyl (~33.1, **Figures 4.16** and **4.17**). This is the first example of photoconductivity in a polycrystalline 1D lead-halide perovskite, and it demonstrates that such behavior can be induced by enhancement of CT between the inorganic anions and organic cations.

Figure 4.13 (a) Schematic diagram of the four-probe electrical conductivity measurements performed upon the polycrystalline samples. (b) Current-voltage (I - V) characteristics of (HyEtV)Pb₂I₆ (**1**; red line), (CaEtV)Pb₂I₆ (**2**; blue line), (PrV)Pb₂I₆ (**3**; orange line), and (BpbmA)Pb₂I₆ (**4**; green line) under white light irradiation (1 sun illumination). (c) Time-dependent photoresponses of the 1D perovskites at 2.0 V bias, upon repetitive on and off white light (1 sun AM1.5G) illumination (interval 10 s), measured for 300 s.

Figure 4.14 Current-voltage (I - V) curves of polycrystalline samples of (a) (PrV)Pb₂I₆ (**3**) and (b) (BpbmA)Pb₂I₆ (**4**) showing no significant current generated upon white light irradiation. Average dark conductivities are $1.530 \times 10^{-11} \text{ S cm}^{-1}$ for **3** and $9.598 \times 10^{-12} \text{ S cm}^{-1}$ for **4**, while average conductivities in the presence of light (1 sun illumination) are $1.871 \times 10^{-11} \text{ S cm}^{-1}$ for **3** and $9.906 \times 10^{-12} \text{ S cm}^{-1}$ for **4**. The on/off current generation ratio at 3.0V for **3** and **4** are 1.08 and 1.02, respectively.

Figure 4.15 Current-voltage (I - V) curves of polycrystalline samples of (a) (HyEtV)Pb₂I₆ (**1**) and (b) (CaEtV)Pb₂I₆ (**2**) showing significant current generated upon white light irradiation. Average dark conductivities are $1.754 \times 10^{-11} \text{ S cm}^{-1}$ for **1** and $5.793 \times 10^{-11} \text{ S cm}^{-1}$ for **2**, while average photoconductivities (1 sun illumination) are $1.245 \times 10^{-10} \text{ S cm}^{-1}$ for **1** and $1.232 \times 10^{-9} \text{ S cm}^{-1}$ for **2**.

Figure 4.16 Current-voltage (I - V) curve of 2D perovskite based on 4,4'-bis(ammonium-ethyl)-1,1'-biphenyl diiodide ((BpbeA)PbI₄) (see **Figure 4.17** for structure of BpbeA and UV-vis absorption feature of the corresponding 2D perovskite). Average dark conductivity is $7.735 \times 10^{-11} \text{ S cm}^{-1}$, while average conductivity in the presence of light (1 sun illumination) is $2.558 \times 10^{-9} \text{ S cm}^{-1}$. At 2.0 V, the on/off ratio of current generation is ~ 33.1 .

In order to probe the short-term stability of the materials to voltage and light, time-dependent photoconductivity studies were conducted. As shown in **Figure 4.13c**, over the course of 300 s, compound **2** consistently exhibits a much stronger photocurrent response than **1** upon repetitive on and off white light illumination (1 sun AM1.5G, interval 10 s). The increase in current obtained during the course of measurements is attributed to ion migration, which can be especially significant in defect-rich settings, such as polycrystalline samples. The greater photoconductivity response observed in **2**, relative to **1**, can be attributed not only to the former possessing a smaller inorganic band gap (2.83 vs. 3.08 eV) and significantly slower photodecay (1.576 ns vs. 0.891 ns), but also to it possessing better inherent conductivity. The latter is borne out by dark conductivity measurements for **2** yielding values approx. 3.3 times greater than for **1** (**Table 4.2**).

Figure 4.17 (a) BpbmA and BpbeA are typical ammonium-based organic cations used in low-dimension perovskite formation. They are both electronically inert organics, despite the presence of biphenyl rings, where no charge transfer interaction can be induced with the 1D inorganic lattices. While BpbmA templates the formation of 1D perovskite, BpbeA is able to form a 2D hybrid structure, resulting in distinct light harvesting capabilities. Reorganization of BpbeA on a molecular level leads to its structural isomer, PrV²⁺, which is a potent electron acceptor. (b) The UV-vis absorbance spectrum of 1D (PrV)Pb₂I₆ shows that it has an extended absorption profile compared with inert 1D perovskites. Indeed, its absorptivity is comparable to that of 2D counterparts. 2D (BpbeA)PbI₄ (PbI₄²⁻ denotes molecular formula of 2D inorganic layer) has an excitonic peak at 513 nm and an inorganic band-gap of 2.41 eV, both of which are significantly red-shifted relative to those of 1D (BpbmA)Pb₂I₆ (410 nm and 2.94 eV) due to relaxation of quantum confinement effects. As a consequence of CT interactions, the optical features of 1D (PrV)Pb₂I₆ (intermolecular electronic gap of 2.21 eV) are not limited by quantum confinement effects of the lead-iodide lattices.

4.2.3 Solvent-dependent formation and processability issues

Thin film fabrication was attempted as such films more closely mimic the PV device settings required for application. This was performed by spincoating the perovskite precursor solution in DMSO, with annealing as the post-treatment. However, it was discovered that the structures of **1** and **2** are different in single crystals than in thin films, evidenced from the disagreeing patterns between the simulated powder XRD and thin films' glancing angle XRD of the materials (**Figure 4.18**). Instead, **1** and **2** exhibit similar features as that of **3** in thin film forms (**Figure 4.19**). As **3** tends to not attract DMSO solvents during crystallization (evident from the X-ray crystal structure), it was postulated that the

difference between bulk and thin film forms of **1** and **2** derives from the absence of DMSO molecules in the perovskite thin films that could have liberated during annealing process. Therefore, it was deduced that the π - π stacking of viologens had diminished in thin films, resulting in materials with similar arrangement as **3** on top of substrates.

Figure 4.18 Experimental glancing-angle XRD (GAXRD) and simulated powder XRD (pXRD) of thin films (a) (HyEtV)Pb₂I₆ (**1**) and (b) (CaEtV)Pb₂I₆ (**2**).

Figure 4.19 Glancing angle-XRD patterns of thin films (HyEtV)Pb₂I₆ (**1**), (CaEtV)Pb₂I₆ (**2**), and (PrV)Pb₂I₆ (**3**).

As the consequence of the absence of π - π stacking, thin films **1** and **2** feature optical properties that are very different than those of the bulks (**Figure 4.20**, solid lines). Despite the excitonic transitions of 1D iodoplumbate chain being very apparent at ca. 390 nm, it is not the case with the inorganic-organic charge-transfer (CT) transition. In particular, while distinct intense and Gaussian-shaped absorption are observed in the bulk forms, the

transition appears as relatively weak absorption tails occurring at longer wavelength. This could be attributed to the weak CT interaction in the absence of π - π stacking and also the nature of the transition itself where the valence ($[\text{PbI}_6]^{-4}$ donor) and conduction (V^{2+} acceptor) bands are spatially separated from each other (i.e. type-II band alignment; **Figure 4.5**). The latter makes the overall electronic gap to be ‘indirect’ in character. Although more detailed investigation is needed to get a full understanding of this transition, its indirect nature typically leads to low absorption coefficient feature owing to a low possibility for electrons to get excited into the conduction bands. As a result, the optical features of the charge-transfer transition become very much dependent on the thickness of the films (**Figure 4.20**, dotted lines).

Figure 4.20 UV-vis absorbance spectra of thin films $(\text{HyEtV})\text{Pb}_2\text{I}_6$ (**1**) and $(\text{CaEtV})\text{Pb}_2\text{I}_6$ (**2**). The thicknesses of thin and thick samples are ca. 200 and 400 nm, respectively.

The absence of π - π stacking leading to compromised optoelectronic properties is supported by photoconductivity investigation conducted on the thin films **1** and **2**. Similar device configuration as that shown in **Figure 4.13a** was employed. The image of the typical device sample is presented in **Figure 4.21a** and as expected, negligible photocurrents were obtained from the materials under white-light irradiation (**Figure 4.22**), which mimics the photo-unresponsivity of **3** in the bulk. This is very different, for example, in comparison to conventional 2D perovskite that was fabricated from phenylethylammonium (PEA), serving as a control in this study. As shown in **Figure 4.23a**, discernable photoresponse can be observed using the same device configuration despite similar appearance and UV-

vis absorption feature (**Figures 4.21b and 4.23b**). The result highlights the disadvantage of photocurrents generation in lower inorganic dimensionality in the absence of π - π stacking. Thus, the inability to form stable thin films of **1** and **2** greatly inhibits preparation of photovoltaic devices *via* solution process and clearly, this limits the practical utility of these materials. As such, alternative pathway in improving optoelectronic properties of lead-iodide hybrids *via* improving the dimensionality of the inorganic lattice was sought.

Figure 4.21 Images of a) 1D (HyEtV)Pb₂I₆ and b) 2D perovskite (PEA)₂PbI₄ thin films (PEA is phenylethylammonium) where gold electrodes with distances of 200 μ m each are evaporated on top of them.

Figure 4.22 Current-voltage (I - V) curves of devices based on (a) (HyEtV)Pb₂I₆ (**1**) and (b) (CaEtV)Pb₂I₆ (**2**) in the dark and in the presence of light (1 sun illumination).

Figure 4.23 a) Current-voltage (I - V) curves of device based on 2D perovskite $(\text{PEA})_2\text{PbI}_4$ (PEA is phenylethylammonium) in the dark and in the presence of light (1 sun illumination). b) UV-vis absorbance of 2D perovskite $(\text{PEA})_2\text{PbI}_4$ thin film.

4.3 Summary

In this chapter, it has been demonstrated for the first time that molecular 1D perovskites can be endowed with photoconductivity in randomly oriented (i.e., polycrystalline) samples. The requisite improvement in optical and electronic properties was attained *via* amplification of CT interactions between the lead-iodide lattice and organic counteranions. This was achieved using a molecular engineering approach that involved incorporation of hydrogen bonding functionality into *N*-alkyl substituents of viologens. As such, the work demonstrates a strategy that can be used to improve the optoelectronic characteristics of lower dimensional perovskites, thereby offering a route by which they might become of practical use in photovoltaic applications. However, the inability to form stable thin films of **1** and **2** greatly inhibits preparation of photovoltaic devices. Thus, alternative pathway in improving optoelectronic properties of lead-iodide hybrids *via* improving the dimensionality of the inorganic lattice was sought and understanding of formability of 2D perovskites will be described in the next chapter.

4.4 Bibliography

1. Mercier, N.; Louvain, N.; Bi, W. *Cryst. Eng. Comm.* **2009**, *11* (5), 720-734.
2. Wu, L.-M.; Wu, X.-T.; Chen, L. *Coord. Chem. Rev.* **2009**, *253* (23-24), 2787-2804.
3. Koh, T. M.; Thirumal, K.; Soo, H. S.; Mathews, N. *ChemSusChem*. **2016**, *9* (18), 2541-2558.
4. Duan, H. B.; Zhao, H. R.; Ren, X. M.; Zhou, H.; Tian, Z. F.; Jin, W. Q. *Dalton Trans.* **2011**, *40* (8), 1672-1683.
5. Eppel, S.; Fridman, N.; Frey, G. *Cryst. Growth Des.* **2015**, *15* (9), 4363-4371.
6. Liu, G. N.; Shi, J. R.; Han, X. J.; Zhang, X.; Li, K.; Li, J.; Zhang, T.; Liu, Q. S.; Zhang, Z. W.; Li, C. *Dalton Trans.* **2015**, *44* (28), 12561-12575.
7. Weber, O. J.; Marshall, K. L.; Dyson, L. M.; Weller, M. T. *Acta Crystallogr. B Struct. Sci. Cryst. Eng. Mater.* **2015**, *71* (Pt 6), 668-678.
8. Kamminga, M. E.; Fang, H.-H.; Filip, M. R.; Giustino, F.; Baas, J.; Blake, G. R.; Loi, M. A.; Palstra, T. T. M. *Chem. Mater.* **2016**, *28* (13), 4554-4562.
9. Yuan, Z.; Zhou, C.; Tian, Y.; Shu, Y.; Messier, J.; Wang, J. C.; van de Burgt, L. J.; Kountouriotis, K.; Xin, Y.; Holt, E.; Schanze, K.; Clark, R.; Siegrist, T.; Ma, B. *Nat. Commun.* **2017**, *8*, 14051-14057.
10. Wu, Z.; Ji, C.; Wang, S.; Zhang, W.; Wang, Y.; Li, L.; Zhao, S.; Sun, Z.; Luo, J. *J. Mater. Chem. C* **2017**, *5*, 11466-11471.
11. Fujisawa, J.; Tajima, N. *Phys. Rev. B* **2005**, *72* (12), 125201(1)-125201(6).
12. Matsuishi, K.; Kubo, Y.; Ichikawa, T.; Onari, S. *AIP Conf. Proc.* **2005**, *772*, 1075-1076.
13. Koutselas, I. B.; Mitzi, D. B.; Papavassiliou, G. C.; Papaioannou, G. J.; Krautscheid, H. *Synth. Met.* **1997**, *86*, 2171-2172.
14. Liu, J. J.; Guan, Y. F.; Jiao, C.; Lin, M. J.; Huang, C. C.; Dai, W. X. *Dalton Trans.* **2015**, *44* (13), 5957-5960.
15. Devic, T.; Canadell, E.; Auban-Senzier, P.; Batail, P. *J. Mater. Chem.* **2004**, *14* (2), 135-137.
16. Maughan, A. E.; Kurzman, J. A.; Neilson, J. R. *Inorg. Chem.* **2015**, *54* (1), 370-378.

17. Monk, P. M. S., The viologens: physicochemical properties, synthesis, and applications of the salts of 4,4'-bipyridine. *Wiley*: 1998.
18. Fujisawa, J.; Ishihara, T. *Phys. Rev. B* **2004**, *70* (11), 113203(1)-113203(4).
19. Pradeesh, K.; Agarwal, M.; Rao, K. K.; Prakash, G. V. *Solid State Sci.* **2010**, *12* (1), 95-98.
20. 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.; Gratzel, M.; Park, N. G. *Sci. Rep.* **2012**, *2*, 591-597.
21. Fujisawa, J.; Giorgi, G. *Phys. Chem. Chem. Phys.* **2014**, *16* (33), 17955-17959.
22. Li, M.-Q.; Hu, Y.-Q.; Bi, L.-Y.; Zhang, H.-L.; Wang, Y.; Zheng, Y.-Z. *Chem. Mater.* **2017**, *29* (13), 5463-5467.
23. Perera, A. S.; Subbaiyan, N. K. Kalita, M. Wendel, S. O. Samarakoon, T. N.; D'Souza, F.; Bossmann, S. H. *J. Am. Chem. Soc.* **2013**, *135* (18), 6842-6845.
24. Sun, C.; Xu, G.; Jiang, X.-M.; Wang, G.-E.; Guo, P.-Y.; Wang, M.-S.; Guo, G.-C. *J. Am. Chem. Soc.* **2018**, *140* (8), 2805-2811.
25. Liu, W.; Liu, Y.; Zhang, H.; Xie, C.; Shi, L.; Zhou, Y.-G.; Li, X. *Chem. Commun.* **2019**, *55*, 4801-4804.
26. Han, Y.; Guo, J.; Chen, C. *Chin. J. Chem.* **2014**, *32*, 721—726.
27. Shia, H.; Zheng, L.-M.; Lina, R.-L.; Fanga, G.-S.; Suna, W.-Q.; Liu, J.-X. *Supramol. Chem.* **2018**, *30*(8), 713–721.
28. Vedernikov, A. I.; Ushakov, E. N.; Efremova, A. A; Kuz'mina, L. G.; Moiseeva, A. A.; Lobova, N. A. Churakov, A. V.; Strelenko, Y. A.; Alfimov, M. V.; Howard, J. A. K.; Gromov, S. P. *J. Org. Chem.* **2011**, *76*, 6768-6779.
29. Thomas, J. R.; Liu, X.; Hergenrother, P. J. *J. Am. Chem. Soc.* **2005**, *127* (36), 12434-12435.
30. Pascu, M.; Ruggi, A.; Scopelliti, R.; Severin, K. *Chem. Commun.* **2013**, *49*, 45-47.
31. von Krbek, L. K. S.; Achazi, A. J.; Schoder, S.; Gaedke, M.; Biberger, T.; Paulus, B.; Schalley, C. A. *Chem. Eur. J.* **2017**, *23*, 2877-2883.
32. Masciocchi, N.; Galli, S.; Colombo, V.; Maspero, A.; Palmisano, G.; Seyyedi, B.; Lamberti, C.; Bordiga, S. *J. Am. Chem. Soc.* **2010**, *132* (23), 7902-7904.

33. Makhloufi, G.; Francis, B.; Dechnik, J.; Strzelczyk, A.; Janiak, C. *Polyhedron* **2017**, *127*, 59-67.

4.5 Instrumentations and additional data

Nuclear Magnetic Resonance (NMR) spectroscopy. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of organic compounds were recorded in DMSO- d_6 solution using either Bruker AV300, AV400, or AV500 spectrometers. Chemical shift values (ppm) are referenced against residual protic solvent peaks.

UV-vis spectroscopy. UV-vis spectra of polycrystalline samples were collected using a Shimadzu UV-3600 UV-VIS-NIR Spectrophotometer with BaSO_4 as the 100% reflectance reference. The measurements were conducted in a 300 – 800 nm wavelength range, with a scanning resolution of 0.5 nm s^{-1} , in the diffuse reflectance mode, using an integrating sphere. Relative absorbance was obtained from Kubelka–Munk transformation of the reflectance spectra: $\alpha/S = (1 - R)^2(2R)^{-1}$, where R is the reflectance, and α and S are the absorption and scattering coefficients, respectively.

Steady-State Photoluminescence (PL) spectroscopy. The finely ground polycrystalline perovskites were pressed and encapsulated within two fused silica windows before they were mounted in the spectrometer. The photoluminescence (PL) spectra were measured using a Horiba Fluoromax-3 spectrometer, with a slit width of 0.4 nm and a 0.1 s integration time.

Time-Resolved Photoluminescence (PL) spectroscopy. The micro-PL setup used is based on a fibre-coupled microscope system. The excitation path and emission collection come from a VIS-NIR microscope objective (10x, NA = 0.65). Samples were excited with a 40 MHz repetition rate, picosecond-pulse light source at 405 nm (Picoquant P-C-405B) light-emitting diode, and the spot size was about 10 μm . The time-resolved emitted signal was collected through a fibre-coupled Acton monochromator (SpectraPro 2300), to filter the desired wavelength, and detected by a Micro Photon Devices single-photon avalanche

photodiode (LDH-P-670). The signal was then acquired by a time-correlated single photon counting card (Pico Harp TSCPC module and Picosecond Event Timer 300). Temporal resolution is ~ 50 ps. Decay curves were fitted with a double exponential function.

X-ray single crystallography. Diffraction data of each single crystal sample was collected using a graphite-monochromated Mo-K α source ($\lambda = 0.71073$ Å) on a CCD area detector (Bruker X8 CCD diffractometer), at cryogenic temperatures (100 K – 253 K). Data reduction and absorption corrections were performed with the SAINT and SADABS software packages, respectively. All structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 using the Bruker SHELXTL-2014 software package. Non-hydrogen atoms were anisotropically refined before hydrogen atoms were introduced at calculated positions for further refinement of data. The graphical illustrations of crystal structures used throughout the main paper and supporting information were produced using the programs Mercury and VESTA.

Four-probe conductivity measurements. Finely ground polycrystalline samples of the compounds were pressed into circular disk-shaped pellets by applying a uniaxial pressure of 100 MPa (diameter = 1.35 cm, thickness ≈ 0.1 cm) using a hydraulic press. They were connected to a Keithley 2400 source meter by evaporated gold electrodes (distance = 150 μm , width = 4000 μm). The current generated between two gold electrodes upon variation of electrical potential was then measured. The conductivity (σ) was calculated based on the following equations, where R is resistance, V is voltage, I is current, ρ is resistivity, and A and l are the cross section and length of the electrode, respectively:

$$R = \frac{V}{I} \quad (\text{Eqn. 4.1})$$

$$\rho = R \frac{A}{l} \quad (\text{Eqn. 4.2})$$

$$\sigma = \frac{1}{\rho} \quad (\text{Eqn. 4.3})$$

1,1'-bis(2-hydroxyethyl)-4,4'-bipyridilium diiodide (hydroxyethyl viologen iodide, HyEtVI₂). Isolated as a yellow solid (1.43g; 85% yield), ¹H NMR (300 MHz, DMSO-d₆): δ 9.31 (d, J = 6.9 Hz, 4 H, ArH), 8.79 (d, J = 6.9 Hz, 4 H, ArH), 5.31 (s, 2 H, OH), 4.77 (t, J = 4.8 Hz, 4 H, CH₂), 3.94 (not well resolved t, 4 H, CH₂). ¹³C{¹H} NMR (75 MHz, DMSO-d₆): δ 148.7, 146.1, 126.2, 63.2, 59.9. The NMR spectroscopic data match the reported values.^{23,24}

1,1'-bis(2-carboxyethyl)-4,4'-bipyridilium diiodide (carboxyethyl viologen iodide; CaEtVI₂). Isolated as an orange solid (1.25g; 74% yield), ¹H NMR (300 MHz, DMSO-d₆): δ ~12.71 (bs, 2 H, C(O)OH), 9.42 (d, J = 6.3 Hz, 4 H, ArH), 8.81 (d, J = 6.3 Hz, 4 H, ArH), 4.90 (t, J = 6 Hz, 4 H, CH₂), 3.18 (t, J = 6.3 Hz, 4 H, CH₂). ¹³C{¹H} NMR (75 MHz, DMSO-d₆): δ 171.4, 148.6, 146.3, 126.2, 56.6, 34.3. The NMR spectroscopic data match the reported values.²⁵

1,1'-bis(propyl)- 4,4'-bipyridilium diiodide (propyl viologen iodide; PrVI₂). Isolated as a red solid (1.37g; 87% yield), ¹H NMR (300 MHz, DMSO-d₆): δ 9.39 (d, J = 6.5 Hz, 4 H, ArH), 8.80 (d, J = 6.5 Hz, 4 H, ArH), 4.66 (t, J = 7.5 Hz, 4 H, CH₂), 2.01 (q, J = 7.5 Hz, 4 H, CH₂), 0.93 (t, J = 7.5 Hz, 6 H, CH₃). ¹³C{¹H} NMR (75 MHz, DMSO-d₆): δ 148.5, 145.6, 126.6, 62.0, 24.1, 10.2. The NMR spectroscopic data match the reported values.^{26,27}

1,1'-bis(ethyl)- 4,4'-bipyridilium diiodide (ethyl viologen iodide; EtVI₂). Isolated as an orange solid (1.51g; 91% yield), ¹H NMR (300 MHz, DMSO-d₆): δ 9.39 (d, J = 6.5 Hz, 4 H, ArH), 8.77 (d, J = 6.5 Hz, 4 H, ArH), 4.72 (q, 4 H, CH₂), 1.61 (t, 6 H, CH₃). ¹³C{¹H} NMR (75 MHz, DMSO-d₆): δ 148.4, 145.5, 126.5, 56.5, 16.3. The NMR spectroscopic data match the reported values.²⁸

Synthesis of biphenyl-based bis-amines. These organic amines were prepared *via* multiple step syntheses, as shown in the following schemes:

Scheme 4.1 Synthetic route to 4,4'-bis(aminomethyl)-1,1'-biphenyl

Scheme 4.2 Synthetic route to 4,4'-bis(2-aminoethyl)-1,1'-biphenyl

4,4'-bis(azidomethyl)-1,1'-biphenyl (2). To a DMSO solution of 4,4'-bis(chloromethyl)-1,1'-biphenyl (1.0 eq) was added excess NaN_3 (2.5 eq). The mixture obtained was stirred for at least 2 h at room temperature (RT). Subsequently, deionized H_2O was added and upon cooling to room temperature, 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 solvent was removed *in vacuo* to give **2** as a white powder (3.11 g; 93%). ^1H NMR (300 MHz, DMSO-d_6): δ 7.73 (d, $J = 8.2$ Hz, 4 H, ArH), 7.47 (d, $J = 8.2$ Hz, 4 H, ArH), 4.50 (s, 4 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, DMSO-d_6): δ 139.4, 135.0, 129.0, 127.0, 53.3. The NMR spectroscopic data match the reported values.^{29,30}

4,4'-bis(aminomethyl)-1,1'-biphenyl (3). To the solid **2** (1.0 eq), was added PPh_3 (3.0 eq), and a THF- H_2O 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 CH_2Cl_2 , and washed twice with 1 M aqueous HCl. The combined acidic aqueous layers were washed with ethyl acetate (four times) and carefully basified (pH $\sim$ 10) by the addition of 3 M aqueous NaOH. The resulting mixture was extracted with CH_2Cl_2 (3 times), and the combined

organic portions were dried (MgSO_4) and all volatiles removed under reduced pressure to give the product **3** as a light yellow solid (2.77 g; 71 %). ^1H NMR (500 MHz, DMSO-d_6): δ 7.57 (d, J = 8.0 Hz, 4 H, ArH), 7.39 (d, J = 8.0 Hz, 4 H, ArH), 3.74 (s, 4 H, CH_2), 3.27 (bs, 2 H, OH). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, DMSO-d_6): δ 143.2, 138.1, 127.6, 126.2, 45.3. The NMR spectroscopic data match the reported values.^{30,31}

4,4'-bis(cyanomethyl)-1,1'-biphenyl (4). Under a flow of N_2 gas, 4,4'-Bis(chloromethyl)-1,1'-biphenyl (1 eq) was added in small portions to a two-necked round-bottomed flask containing a stirring suspension of KCN (2.2 eq) in dimethyl sulfoxide. After being stirred at 40 °C for 8 h, plus overnight at room temperature, the reaction mixture was poured into cold H_2O . The beige solid obtained was filtered off, washed with cold H_2O and dried under reduced pressure to afford the desired product **4** (2.52 g; 74 %). ^1H NMR (500 MHz, DMSO-d_6): δ 7.71 (d, J = 8.5 Hz, 4 H, ArH), 7.44 (d, J = 8.5 Hz, 4 H, ArH), 4.08 (s, 4 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, DMSO-d_6): δ 138.8, 130.6, 128.7, 127.2, 119.2, 22.1. The NMR spectroscopic data match the reported values.^{32,33}

4,4'-bis(aminoethyl)-1,1'-biphenyl (5). Under an argon gas atmosphere, a solution of AlCl_3 (6.0 eq) in dry THF was added dropwise to a suspension of LiAlH_4 (6.0 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 room temperature, 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 (1.63 g; 81 %). ^1H NMR (400 MHz, DMSO-d_6): δ 7.54 (d, J = 8.0 Hz, 4 H, ArH), 7.26 (d, J = 8.0 Hz, 4 H, ArH), 3.32

(bs, 2 H, OH), 2.78 (t, $J = 7.2$ Hz, 4 H, CH₂), 2.66 (t, $J = 7.2$ Hz, 4 H, CH₂). ¹³C{¹H}
NMR (100 MHz, DMSO-d₆): δ 138.3, 136.3, 129.3, 126.7, 39.9, 32.6.

Table 4.3 Crystallographic and refinement data for (HyEtV)Pb₂I₆, (CaEtV)Pb₂I₆, (PrV)Pb₂I₆, and (BpbmA)Pb₂I₆.

	Compounds			
	(HyEtV)Pb ₂ I ₆	(CaEtV)Pb ₂ I ₆	(PrV)Pb ₂ I ₆	(BpbmA)Pb ₂ I ₆
Empirical formula	C ₁₆ H ₂₄ I ₅ N ₂ O ₃ Pb _{1.50} S	C ₁₆ H ₁₆ I ₆ N ₂ O ₄ Pb ₂ S	C ₂₄ H ₃₃ I ₉ N ₃ Pb ₃	C ₂₂ H ₄₂ I ₆ N ₂ O ₄ Pb ₂ S ₄
Formula weight	1269.72 g/mol	1508.15 g/mol	2127.20 g/mol	1702.59 g/mol
Temperature	143(2) K	143(2) K	103(2) K	153(2) K
Wavelength	0.71073 Å	1.54178 Å	0.71073 Å	0.71073 Å
Crystal size	0.100 x 0.140 x 0.200 mm ³	0.080 x 0.040 x 0.020 mm ³	0.080 x 0.100 x 0.280 mm ³	0.120 x 0.160 x 0.280 mm ³
Crystal habit	black block	black needle	red needle	light yellow block
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	C 1 2/c 1	C2/c	P 1 21/c 1	P 1 21/c 1
Unit cell dimensions	a = 22.399(5) Å α = 90° b = 17.182(4) Å β = 104.975(3)° c = 15.348(3) Å γ = 90°	a = 29.0026(9) Å α = 90° b = 18.0994(5) Å β = 121.163(2)° c = 15.3625(5) Å γ = 90°	a = 12.2902(3) Å α = 90° b = 14.2431(3) Å β = 90.4986(9)° c = 24.8406(6) Å γ = 90°	a = 11.9843(6) Å α = 90° b = 22.8736(13) Å β = 109.6566(14)° c = 8.3377(4) Å γ = 90°
Volume	5706.(2) Å ³	6900.5(4) Å ³	4348.20(18) Å ³	2152.37(19) Å ³
Z	8	8	4	2
Density	2.956 g/cm ³	2.903 g/cm ³	3.249 g/cm ³	2.627 g/cm ³
Absorption coefficient	14.351 mm ⁻¹	61.651 mm ⁻¹	17.996 mm ⁻¹	12.336 mm ⁻¹
F(000)	4496	5248	3684	1532
Theta range for data collection	1.51 to 25.44°	3.022 to 67.880°	1.64 to 31.07°	2.54 to 29.32°
Reflections collected	5242	36804	107308	38006
Coverage of independent reflections	99.30%	99.1 %	99.70%	99.50%
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan	Multi-Scan
Max. and min. transmission	0.3280 and 0.1610	0.014 and 0.104	0.3270 and 0.0810	0.3190 and 0.1300
Structure solution technique	direct methods	direct methods	direct methods	direct methods
Structure solution program	XT, VERSION 2014/4	XT, VERSION 2014/4	XS, VERSION 2013/1	XS, VERSION 2013/1
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	SHELXL-2014/7 (Sheldrick, 2014)	SHELXL-2014/7 (Sheldrick, 2014)	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	5242 / 925 / 466	6198 / 611 / 382	13913 / 210 / 413	5873 / 0 / 186
Goodness-of-fit on F2	0.973	1.014	1.084	1.063
Δ/σ_{max}	0.001	0.002	0.002	0.003
Final R indices	3220 data; I>2 σ (I) R1 = 0.0552, wR2 = 0.1175 all data R1 = 0.0966, wR2 = 0.1337 w=1/[$\sigma^2(F_o^2)$ + (0.0298P) ²]	R1 = 0.0785, wR2 = 0.2034 all data R1 = 0.1254, wR2 = 0.2539	10870 data; I>2 σ (I) R1 = 0.0388, wR2 = 0.0814 all data R1 = 0.0575, wR2 = 0.0886 w=1/[$\sigma^2(F_o^2)$ + (0.0312P) ² + 21.6920P]	4865 data; I>2 σ (I) R1 = 0.0358, wR2 = 0.0752 all data R1 = 0.0490, wR2 = 0.0801 w=1/[$\sigma^2(F_o^2)$ + (0.0225P) ² + 2.9050P]
Weighting scheme	where P=(F _o ² +2F _c ²)/3	where P=(F _o ² +2F _c ²)/3	where P=(F _o ² +2F _c ²)/3	where P=(F _o ² +2F _c ²)/3
Largest diff. peak and hole	1.341 and -1.457 eÅ ⁻³	6.279 and -1.414 eÅ ⁻³	2.227 and -2.083 eÅ ⁻³	1.233 and -1.982 eÅ ⁻³
R.M.S. deviation from mean	0.322 eÅ ⁻³		0.278 eÅ ⁻³	0.263 eÅ ⁻³

Table 4.4 Crystallographic and refinement data for (HyEtV)I₂, (CaEtV)I₂, and (PrV)I₂.

	Compounds		
	(HyEtV)I ₂	(CaEtV)I ₂	(PrV)I ₂
Empirical formula	C ₁₄ H ₁₈ I ₂ N ₂ O ₂	C ₂₀ H ₃₀ I ₂ N ₂ O ₆ S ₂	C ₁₆ H ₂₂ I ₂ N ₂
Formula weight	500.10 g/mol	712.38 g/mol	496.15 g/mol
Temperature	173(2) K	123(2) K	253(2) K
Wavelength	0.71073 Å	1.54178 Å	0.71073 Å
Crystal size	0.040 x 0.400 x 0.420 mm	0.020 x 0.160 x 0.420 mm	0.140 x 0.180 x 0.260 mm
Crystal habit	yellow plate	red plate	yellow block
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	P 1 21/c 1	C 1 2/c 1	P n n m
Unit cell dimensions	a = 11.3643(7) Å α = 90° b = 7.5190(5) Å β = 97.062(2)° c = 10.3051(6) Å γ = 90°	a = 33.8974(11) Å α = 90° b = 7.9210(3) Å β = 115.6427(14)° c = 32.8674(11) Å γ = 90°	a = 19.759(3) Å α = 90° b = 6.4897(10) Å β = 90° c = 7.6212(11) Å γ = 90°
Volume	873.87(9) Å ³	7955.8(5) Å ³	977.3(3) Å ³
Z	2	12	2
Density	1.901 g/cm ³	1.784 g/cm ³	1.686 g/cm ³
Absorption coefficient	3.602 mm ⁻¹	20.412 mm ⁻¹	3.212 mm ⁻¹
F(000)	476	4200	476
Theta range for data collection	1.81 to 33.87°	2.89 to 66.89°	2.87 to 31.21°
Reflections collected	25489	31282	9545
Coverage of independent reflections	99.90%	98.10%	99.70%
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan
Max. and min. transmission	0.8690 and 0.3130	0.6860 and 0.0430	0.6620 and 0.4890
Structure solution technique	direct methods	direct methods	direct methods
Structure solution program	XT, VERSION 2014/4	XS, VERSION 2013/1	XT, VERSION 2014/5
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	SHELXL-2014/7 (Sheldrick, 2014)	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	3528 / 0 / 92	6962 / 0 / 441	1697 / 0 / 56
Goodness-of-fit on F ²	1.041	1.017	1.335
$\Delta/\sigma_{\max}$	0.001	0.001	0.001
Final R indices	2779 data; $I > 2\sigma(I)$ R1 = 0.0412, wR2 = 0.1016 all data R1 = 0.0564, wR2 = 0.1104 $w = 1/[\sigma^2(F_o^2) + (0.0522P)^2]$	6353 data; $I > 2\sigma(I)$ R1 = 0.0759, wR2 = 0.2020 all data R1 = 0.0801, wR2 = 0.2098 $w = 1/[\sigma^2(F_o^2) + (0.1798P)^2]$	1460 data; $I > 2\sigma(I)$ R1 = 0.0514, wR2 = 0.1070 all data R1 = 0.0590, wR2 = 0.1094 $w = 1/[\sigma^2(F_o^2) + (0.0221P)^2 + 2.9808P]$
Weighting scheme	where $P = (F_o^2 + 2F_c^2)/3$	where $P = (F_o^2 + 2F_c^2)/3$	where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	1.641 and -1.007 eÅ ⁻³	3.825 and -2.003 eÅ ⁻³	0.702 and -1.882 eÅ ⁻³
R.M.S. deviation from mean	0.196 eÅ ⁻³	0.355 eÅ ⁻³	0.124 eÅ ⁻³

Table 4.5 Crystallographic and refinement data for alternative structures (HyEtV)Pb₂I₆ and (CaEtV)Pb₂I₆.

	Compounds	
	Alternative (HyEtV)Pb ₂ I ₆	Alternative (CaEtV)Pb ₂ I ₆
Empirical formula	C ₁₀ H ₁₆ I ₃ N ₂ O ₂ Pb	C ₁₅ H ₂₄ I ₃ NO ₄ PbS ₂
Formula weight	784.14 g/mol	934.36 g/mol
Temperature	253(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal size	0.010 x 0.040 x 0.080 mm	0.040 x 0.220 x 0.320 mm
Crystal habit	red plate	orange plate
Crystal system	triclinic	monoclinic
Space group	P -1	P 1 21/c 1
Unit cell dimensions	a = 7.8939(5) Å	a = 12.4683(4) Å
	α = 80.926(2)°	α = 90°
	b = 9.4600(6) Å	b = 26.6214(9) Å
	β = 79.957(2)°	β = 102.7380(13)°
	c = 12.4561(8) Å	c = 7.8875(3) Å
	γ = 85.806(2)°	γ = 90°
Volume	903.46(10) Å ³	2553.61(15) Å ³
Z	2	4
Density	2.882 g/cm ³	2.430 g/cm ³
Absorption coefficient	14.460 mm ⁻¹	10.415 mm ⁻¹
F(000)	694	1704
Theta range for data collection	2.18 to 31.19°	2.76 to 27.16°
Reflections collected	16313	34058
Coverage of independent reflections	99.30%	99.60%
Absorption correction	Multi-Scan	Multi-Scan
Max. and min. transmission	0.8690 and 0.3910	0.6810 and 0.1350
Structure solution technique	direct methods	direct methods
Structure solution program	XS, VERSION 2013/1	XT, VERSION 2014/5
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	5827 / 0 / 169	5629 / 0 / 240
Goodness-of-fit on F ²	0.978	1.08
$\Delta/\sigma_{\max}$	0.001	99.60%
Final R indices	3794 data; I>2 σ (I)	4468 data; I>2 σ (I)
	R1 = 0.0434,	R1 = 0.0338,
	wR2 = 0.0773	wR2 = 0.0516
	all data	all data
	R1 = 0.0863,	R1 = 0.0523,
	wR2 = 0.0913	wR2 = 0.0563
	$w=1/[\sigma^2(F_o^2) + (0.0259P)^2]$	$w=1/[\sigma^2(F_o^2) + 13.0805P]$
Weighting scheme	where $P=(F_o^2+2F_c^2)/3$	where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	1.129 and -2.151 eÅ ⁻³	0.887 and -2.075 eÅ ⁻³
R.M.S. deviation from mean	0.277 eÅ ⁻³	0.191 eÅ ⁻³

Chapter 5

Pyridinium-templated 2D lead-iodide perovskites: specific formability, reduced band gap, and relaxed dielectric confinement

In an attempt to investigate the formability of 2D lead-iodide perovskites, a series of hybrid low-dimensional lead-iodide materials based on N-substituted pyridinium cations were studied. X-ray crystallographic studies confirm that primary ammonium groups ($-\text{NH}_3^+$) are a prerequisite for formation of 2D perovskites, presumably due to the highly localized charge density and limited steric bulk of this functionality. The positioning of the intracyclic ammonium (i.e., pyridinium) cation (6 – 9) does not change this outcome. In the absence of $-\text{NH}_3^+$, 1D iodoplumbate inorganic architectures are obtained. This was the case for ethyl-, propyl-, hydroxyethyl-, carboxyethyl-, and propionamidyl-substituted pyridinium cations 1 – 5. The structures of the 2D perovskites 6[PbI₄]—9[PbI₄] exhibit reduced inter-octahedral distortions (their largest Pb-(μ -I)-Pb bond angles range from 170 – 179°) and very short separations of their inorganic layers (shortest I...I contacts $\leq 4.278 - 4.447 \text{ \AA}$). These features manifest in optoelectronic properties that are favourable for photovoltaic applications, including reduced band gaps (2.35 – 2.46 eV) and relaxed dielectric confinement (excitonic binding energies of 130 – 200 meV). Correspondingly, 6[PbI₄]—9[PbI₄] demonstrate improved electrical and photoconductivities (more than 10-fold) relative to conventional 2D lead-iodide perovskites, such as that templated by naphthyl methyl ammonium. On the whole, the properties of these $n = 1$ perovskites mimic those of their $n = 2$ analogues, where n refers to the number of contiguous 2D inorganic layers (i.e., not separated by organic cations). The origin of the more ‘3D-like’ behaviour of these materials was probed using computational studies and shown to derive from their structural features.

5.1 Background

Hybrid organic-inorganic APbI₃ perovskites with three-dimensional (3D) structures (where A is a small organic monocation, such as methyl ammonium or formamidinium) have attracted intense interest in recent years. This is largely due to the high power conversion efficiencies, of over 24%, and low-cost preparative methods available for solar cells based around these materials.¹⁻³ APbI₃ perovskites display a host of photophysical properties that make them ideal for use as solar-cell absorbers, including suitable band-gaps (1.50–1.55 eV), good visible light absorption, and low exciton binding energies.⁴⁻⁶ However, low intrinsic chemical instability towards external stimuli (e.g., moisture, oxygen, and UV) remains a major stumbling block towards practical application of this class of materials.⁷⁻⁹

Using cations that are larger and more hydrophobic in nature, such as butylammonium (BA) or phenylethylammonium (PEA), rather than the aforementioned small A cations, provides improved chemical and structural stability.¹⁰⁻¹² However, the interstitial sites of APbI₃ are of insufficient volume to accommodate them and, consequently, the cubic ionic lattice ruptures along specific crystallographic axes (i.e., the (100)-, (110)-, or (111)-planes). This yields 2D iodoplumbate perovskites, which are composed of inorganic sheets separated by layers of organic cations.¹³⁻¹⁵ Clearly, this allows for much greater diversity in cation structure, relative to 3D perovskites, which provides opportunities for tuning optoelectronic properties of the materials. However, despite the vast number of reports on 2D perovskites templated by organic cations of diverse architectures, such as those based around hydrocarbon-,¹⁶⁻¹⁷ heteroatom-endowed linear aliphatic,¹⁸⁻¹⁹ cyclic aliphatic and aromatic moieties,²⁰⁻²² systematic studies of the impact of cation structure upon the perovskite's structure and optoelectronic properties are still relatively scarce.²³⁻²⁵ In particular, the crucial role of the ammonium functional group (NH₃⁺) in the formability of the 2D inorganic lattice has never been systematically investigated.

In addition, although they are more resistant towards moisture and are synthetically more versatile, 2D lead-halide perovskites are, generally, considered ill-suited for photovoltaic applications. This is because their reduced dimensionality manifests in compromised

visible light absorption and poor charge transport.²⁶⁻²⁷ The latter results from strongly-bound electron-hole pairs, or excitons. In particular, 2D iodoplumbates with excitonic transitions ranging from 468 to 518 nm, which equates to bandgap energies (E_g) > 2.45 eV have been documented.²⁸⁻²⁹ The higher E_g and exciton binding energy (E_b) values seen for 2D relative to 3D materials is a consequence of the quantum confinement inherent to the layered structure of the former.³⁰⁻³³ A further contributing factor to the high E_b in these materials is the dielectric mismatch between the organic and inorganic layers.^{27, 34-35} More specifically, the low dielectric constant of the organic layers provides poor shielding of the electron-hole interactions in the inorganic layers, resulting in the exciton's dielectric confinement. E_b values for $n = 1$ 2D perovskites are typically above 300 meV,^{31, 34, 36} but a comparatively low E_b of 220 meV was reported for the material template by phenylethylammonium (PEA).³⁷⁻³⁸ This was attributed to the polarizability of its aromatic core. Post-synthetic intercalation of iodine (I_2) molecules into iodoethylammonium-based iodoplumbate was shown to be capable of temporarily reducing the E_b to 180 meV.³⁹ Loss of I_2 led to the value increasing to 230 meV within 3 days.

Figure 5.1 Molecular structures of the pyridinium-based organic cations used in this study.

This chapter focus on the systematic exploration of the impact of a series of organic cations within the context of low dimensional lead-iodide perovskites. In particular, examination on how primary ammonium moieties influence the propensity of 2D iodoplumbate lattices to form and how properties beneficial for photovoltaic application can be induced is carried

out. Among the plethora of organic frameworks available, substituted pyridines are highly appealing because they are readily available and straightforward to functionalize (**Figure 5.1**). Such versatility is exploited to develop a family of cations in which *N*-alkyl chains of various length and including a range of functional groups have been installed (**1 to 6**), some of whom have H-bond donor capabilities (**3 to 6**). To gain greater insight into the influence of the relative positioning of H-bond interactions, dications composed of pyridinium rings substituted with ethylammonium chains at various positions were also studied (**6 to 9**).

5.2 Results and discussions

5.2.1 Role of ammonium group in 2D iodoplumbate formation

Monocations **1** and **2** template formation of iodoplumbates **1**[PbI₃] and **2**[PbI₃], which both crystallize in the orthorhombic centrosymmetric space group *Pnma*. Although they are structural isomers of benzylammonium and phenylethylammonium, respectively,^{22, 37} **1** and **2** do not template the formation of a 2D inorganic lattice. Instead, they induce formation of 1D polymeric chains comprised of [PbI₃]⁻ monomers. The Pb²⁺ ions are six coordinate and the resulting [PbI₆]⁴⁻ octahedra connect to one another in a face-sharing fashion (**Figures 5.2a-b**). The deviation of the lead coordination sphere away from ideal octahedral symmetry is dependent upon the identity of the cation (**Table 5.1**). Overall, distortion of the [PbI₆]⁴⁻ octahedra in **1**[PbI₃] is greater than that in **2**[PbI₃]. In particular, in contrast with **1**[PbI₃], **2**[PbI₃] shows significant differences in the length of Pb–I bonds mutually *trans* to one another along two of the three coordination axes. Despite the potential existence of several C–H⋯I interactions between the inorganic chains and countercations, the dominant crystal packing force appears to be coulombic interactions with positively charged pyridinium rings. This interaction is directed perpendicular to the plane of the pyridinium rings and causes the cations to align parallel to the inorganic chains. Such an arrangement disfavours formation of a 2D iodoplumbate lattice and is, likely, the main reason a structure of lower dimensionality is obtained.

Figure 5.2 X-ray crystal structures of 1D lead-iodide hybrids (a) **1**[PbI₄], (b) **2**[PbI₄], (c) **3**[PbI₄], (d) **4**[PbI₄], and (e) **5**[PbI₄]. Ellipsoids are shown at 50% probability and H atoms are omitted for clarity. Gray, purple, brown, red, and blue spheroids represent Pb, I, C, O, and N atoms, respectively.

To examine whether neutral H-bond donor functional groups could perturb this situation, the ethyl and propyl chains of **1** and **2** were replaced by hydroxyethyl, carboxyethyl, and propionamidyl substituents. The resulting materials **3**[PbI₃], **4**[PbI₃], and **5**[PbI₃] crystallize in the triclinic centrosymmetric space group *P*-1, monoclinic centrosymmetric space group *P*12₁/*c*1, and triclinic centrosymmetric space group *P*-1, respectively. They display structures broadly analogous to those of **1**[PbI₃] and **2**[PbI₃] (**Figures 5.2c-e**). In other words, they contain infinite 1D, and not 2D, inorganic lattices. As such, it is apparent that any H-bonding interactions with the functionality in the alkyl substituents of monocations **3** – **4** is insufficient to disturb the parallel orientation of the pyridinium rings relative to the iodoplumbate lattice. From the structural parameters listed in **Table 5.1**, it is clear that the constituent [PbI₆]⁴⁻ octahedra of **4**[PbI₃] are more distorted than those of **3**[PbI₃] and **5**[PbI₃].

The observations and conclusions in this thesis are consistent with the precedent reports of same inorganic architectures constructed by different, but related pyridines derivatives.⁴⁰⁻⁴² In addition, it is empirically deduced that any hydrogen bonding interaction observed in **3**[PbI₃] - **5**[PbI₃] is most likely a byproduct of iodoplumbate lattice formation, which occurs in order to maximize the crystal packing. Were the cations able to template a 2D framework via their hydrogen bonding functionalities, one would be able to observe the remnant of it, as has been found in hybrids made using propyl ammonium and phenyl propyl ammonium cations. Therein, the inorganic frameworks that are built of mixtures of face-sharing and corner-sharing [PbI₆]⁴⁻ is templated.^{30, 43} In **3**[PbI₃] - **5**[PbI₃], on the other hand, definite formation of face-sharing lead-iodide chain is observed.

Table 5.1 Selected structural parameters for the 1D iodoplumbates templated by **1** – **5**.^a

Compound	Pb-I distance (Å)	<i>trans</i> I-Pb-I (°)
1 [PbI ₃]	3.187 – 3.256	171.42, 172.80, 176.07
2 [PbI ₃]	3.149 – 3.153	174.96, 176.24
3 [PbI ₃]	3.146 – 3.293	175.52, 176.76, 176.95, 177.03, 178.46, 178.54
4 [PbI ₃]	3.162 – 3.253	167.47, 174.85, 175.39
5 [PbI ₃]	3.191 – 3.262	180.00

^aEach Pb(II) atom is connected to six iodine atoms. As such, the Pb-I distances and *trans* I-Pb-I angles indicate the extent of octahedral geometry distortion exerted by different cations. Quantitatively, the degree of ‘intra-octahedral’ distortions can be assessed by comparing the following, previously reported, parameters:⁴⁴⁻⁴⁶ octahedral elongation (λ_{oct}), octahedral angle variance (σ^2_{oct}), and octahedral bond length distortion (Δ_{oct}) (see **Table 5.3** for details).

Having discovered that *N*-alkylated pyridinium cations with neutral pendant H-bond donors are insufficient to induce the formation of 2D perovskite, it was sought to incorporate *N*-ethylammonium functionality. Combination of the iodide salt of the target dication **6** with PbI₂ afforded the hybrid **6**[PbI₄], which crystallizes in the monoclinic centrosymmetric space group *P12₁/c12D*. Consistent with its [PbI₄]²⁻ formulation, it was found to contain single-Pb-thick 2D iodoplumbate layers, comprised of corner-sharing [PbI₆]⁴⁻ octahedra, which are separated from another by single layers of organic dication **6** (**Figure 5.3a**). Unlike other common 2D lead-iodide perovskites, the [PbI₆]⁴⁻ octahedra in adjacent inorganic sheets are staggered (when viewed down the *b* axis), rather than eclipsed, with respect to one another. The Pb–I bond distances to the axial halides, with an average value of 3.1845 Å, are comparable to the average length of the bridging Pb–I bonds, of 3.1838 Å.

Figure 5.3 X-ray crystal structures of 2D perovskites (a) $6[\text{PbI}_4]$, (b) $7[\text{PbI}_4]$, (c) $8[\text{PbI}_4]$, and (d) $9[\text{PbI}_4]$. The inorganic layer separations denoted in the figure (red text) are defined as the distances between mean equatorial planes, of adjacent inorganic sheets. Ellipsoids are shown at 50% probability. H atoms are omitted for clarity. Gray, purple, brown, red, and blue spheroids represent Pb, I, C, O, and N atoms, respectively.

Moving the 2-ethylammonium pendant group relative to other positions of the pyridinium ring (**7**, **8**, and **9**), which introduces an endocyclic NH^+ group, does not affect their propensity to template the formation of 2D inorganic frameworks. As such, the resulting hybrids $7[\text{PbI}_4]$, $8[\text{PbI}_4]$, and $9[\text{PbI}_4]$ (**Figures 5.3b, 5.3c, 5.3d, and 5.4**) share many structural similarities with $6[\text{PbI}_4]$. First, in all members of the series of 2D perovskites, each dication interacts with two inorganic layers, one with their pyridinium ‘head’ and the other the pendant primary ammonium ‘tail’. Within a monolayer, the dications orient in the same direction along one axis (‘heads’ pointing in the same direction), and alternate in orientation along the other (‘heads’ pointing in different directions). The compactness of the dications and the close proximity of their two positive charges results in very short separations between the lead-iodide sheets (mean interlayer Pb-Pb distances range from 9.899Å to 10.173Å). In particular, the interlayer iodide-iodide ($\text{I}\cdots\text{I}$) contacts of 4.278 , 4.322 , 4.445 , and 4.447Å in **1** $[\text{PbI}_4]$, **2** $[\text{PbI}_4]$, **3** $[\text{PbI}_4]$ and **4** $[\text{PbI}_4]$, respectively, are among the shortest distances between adjacent lead-iodide layers ever recorded (**Table 5.2**).

Figure 5.4 Depicted as red and green dashed lines are shortest distances between N atoms of primary ammonium group and aromatic ring's -NH⁺ functionalities of **6-9** and bridging or terminal Br atoms in cuboctahedral cavity of bromoplumbate lattice in a) **6**[PbI₄], b) **7**[PbI₄], c) **8**[PbI₄] and d) **9**[PbI₄]. Ellipsoids are shown at 50% probability. H atoms are omitted for clarity. Grey, purple, light brown and blue spheres represent Pb, I, C and N atoms, respectively.

Whereas the primary ammonium functionality of the 'tails' penetrate deeply into the cuboctahedral cavities of the iodoplumbate layers, which are built from the four nearest neighbour terminally-bound axial iodides, the pyridinium rings do not (**Figure 5.5**). More specifically, the distance between the N atoms of the primary ammonium functionality and the mean plane of the axial halogen atoms comprising the cuboctahedral cavities in **6**[PbI₄], **7**[PbI₄], **8**[PbI₄], and **9**[PbI₄] can be as big as 1.335, 1.442, 1.298, and 1.216 Å, respectively. In contrast, the bulky pyridinium rings in **6**[PbI₄], **7**[PbI₄], **8**[PbI₄], and **9**[PbI₄] display minimal penetration of ca. 0.184, 0.071, 0.152 and 0.137 Å. These figures are outside of the range of distances previously reported for conventional perovskites, (RNH₃)₂[PbI₄], for which distances of up to 0.7 Å have been observed.⁴⁷

Figure 5.5 Penetration of the pyridinium rings and primary 2-ethylammonium pendant groups into the cuboctahedral cavities, which are built from the axial Pb-I bonds of four nearest neighbor $[\text{PbI}_6]^{4-}$ octahedra, in (a) **6** $[\text{PbI}_4]$, (b) **7** $[\text{PbI}_4]$, (c) **8** $[\text{PbI}_4]$, and (d) **9** $[\text{PbI}_4]$. The N-atom to axial I⁻ mean plane distances are provided in the figure. Ellipsoids are shown at 50% probability. H atoms are omitted for clarity. Gray, purple, brown, red, and blue spheroids represent Pb, I, C, O, and N atoms, respectively.

Table 5.2 Iodoplumbate inter-layer separations (Å) and Pb-I-Pb angles (°) in **6** $[\text{PbI}_4]$, **7** $[\text{PbI}_4]$, **8** $[\text{PbI}_4]$, and **9** $[\text{PbI}_4]$, plus selected published 2D perovskites templated with aromatic ring-based dications.

Compound	Inorganic layer separation (Å)	Pb-I-Pb angle (°)
6 $[\text{PbI}_4]$	9.899	159 and 174
7 $[\text{PbI}_4]$	9.999	159 and 170
8 $[\text{PbI}_4]$	10.173	159 and 176
9 $[\text{PbI}_4]$	9.998	157 and 179
His $[\text{PbI}_4]^{\alpha}$	10.017	156 and 178
Bidzl $[\text{PbI}_4]^{\beta}$	9.540	174
DnpIn $[\text{PbI}_4]^{\gamma}$	11.163	151
Dpdmn $[\text{PbI}_4]^{\delta}$	11.282	167 and 177

^{α} Histammonium iodoplumbate²², ^{β} 2,2'-Biimidazolium iodoplumbate⁴⁸, ^{γ} 1,4-Diammonium naphthalene iodoplumbate¹⁶, ^{δ} *N,N*-Dimethyl-phenylene-*p*-diammonium iodoplumbate⁴⁹

Secondly, within their inorganic sheets, the 2D hybrids reported herein exhibit only minor out-of-plane inter-octahedral distortions. This is evident in the Pb-(μ-I)-Pb bond angles being as high as 174, 170, 176, and 179° in **6** $[\text{PbI}_4]$, **7** $[\text{PbI}_4]$, **8** $[\text{PbI}_4]$, and **9** $[\text{PbI}_4]$,

respectively (**Figure 5.6**). It is believed that these comparatively small inter-octahedral distortions (the ideal, non-distorted, value is 180°) are a consequence of the delocalized nature of the pyridinium-centred positive charge. The resulting low charge density, combined with the bulk nature of the pyridine ring, would be expected to minimize the strength of interaction with the iodoplumbate layer. Previously, it was proposed that the small steric profile and high charge density of primary ammonium ions would be expected to exert a strong attractive force upon the inorganic lattice and, in order to bring the oppositely charged species together, cause a contraction of the Pb-(μ -I)-Pb bond angles.^{29, 50-51} Since half of the positive charges in these materials are pyridinium-centre, this ‘crumpling’ is thus alleviated relative to hybrids that contain solely primary ammonium groups. Consistent with this notion, the highest Pb-(μ -I)-Pb bond angles in lead-iodide perovskites templated by histammonium, 2,2’-Biimidazolium, 1,4-Diammonium and *N,N*-Dimethyl-phenylene-*p*-diammonium are 178 , 174 , 151 and 177° , respectively (**Table 5.2**).

Figure 5.6 Plan views of limited portions of single iodoplumbate layers, intended to show inter-octahedral distortions, in the 2D perovskites (a) $6[\text{PbI}_4]$, (b) $7[\text{PbI}_4]$, (c) $8[\text{PbI}_4]$, and (d) $9[\text{PbI}_4]$. Pb-I-Pb bond angles along the two equatorial axes are included. Gray and purple spheriods represent Pb and I atoms, respectively. Ellipsoids are shown at 50% probability.

5.2.2 Reduced band-gap and relaxed dielectric confinement

Diffuse reflectance UV–vis–NIR spectra of powdered samples of **1**[PbI₃], **2**[PbI₃], **3**[PbI₃], **4**[PbI₃], and **5**[PbI₃] were measured and, the as-recorded reflectance data, transformed into absorption spectra using the Kubelka–Munk function. As is typical of 1D iodoplumbates with electronically ‘passive’ organic cations, absorption onsets only occur for wavelengths of 450 nm or less (**Figure 5.7**, solid lines). Shoulders at ca. 400 nm and high energy peaks at ca. 380 nm can be ascribed to the excitonic transition and 1D Pb-I chain band gap transition (approximate band gaps of around 3.0 eV) of the inorganic chain, respectively. The limited visible light absorption capabilities and high band-gap in these compounds arise directly from the lesser number of overlapping Pb⁺² and I⁻ orbitals in the 1D inorganic components that results in a less disperse band structure (i.e. narrower bandwidth).

Figure 5.7 Room temperature Ultra Violet-visible light (UV-vis) absorbance and photoluminescence (PL) spectra of 1D organic lead-iodide hybrids **1**[PbI₃] – **5**[PbI₃].

Room temperature excitation (λ_{ex}) at 335 nm induced weak and broad emissions centred at ca. 580 nm, and extending from 450 to 720 nm, in **1**[PbI₃] – **5**[PbI₃] (**Figure 5.7**, dotted lines). Such broad emissions have been reported for related pyridinium-templated 1D iodoplumbate systems and were attributed to band-edge emissions and energy transfer from the excited state of the inorganic chains to the excited triplet state of the organic

components.⁴⁰⁻⁴² Nonetheless, further investigations are needed to confirm the origin of the photoluminescence, as couplings between excitons and phonons are anticipated in the hybrids having distorted inorganic lattices (**Table 5.3**).²⁴ Images of the greenish-yellow emissions exhibited by powdered samples of the 1D compounds reported herein upon exposure to a UV lamp ($\lambda_{\text{ex}} = 365 \text{ nm}$), at ambient temperature, are displayed in **Figure 5.8**.

Figure 5.8 Images of 1D organic lead-iodide hybrids a) – b) **1**[PbI₃], c) – d) **2**[PbI₃], e) – f) **3**[PbI₃], g) – h) **4**[PbI₃] and i) – j) **5**[PbI₃] under ambient light and UV lamp irradiation (365 nm).

The 2D inorganic lattices of **6**[PbI₄], **7**[PbI₄], **8**[PbI₄], and **9**[PbI₄] experience significantly reduced quantum confinement relative to 1D iodoplumbates. It is, therefore, unsurprising

that the former have enhanced visible light harvesting capabilities, compared to the latter, with absorption commencing from ~ 600 nm and peaking at around ~ 525 nm (**Figure 5.9a**, solid lines). Interestingly, the excitonic peaks in **6**[PbI₄], **7**[PbI₄], **8**[PbI₄], and **9**[PbI₄] are significantly red-shifted relative to those of most previously reported 2D lead-iodide perovskites, which range from 464 to 518 nm.²⁸⁻²⁹ Indeed, **6**[PbI₄], **7**[PbI₄], **8**[PbI₄], and **9**[PbI₄] represent rare examples of a heavily bathochromically-shifted 2D perovskites, and there are only preceding eight compounds reported to exhibit similar absorption features.^{11, 19, 49, 52-53} Correspondingly, images of the ground powder appear redder than conventional 2D perovskites, represented here by NEA₂[PbI₄] (**Figure 5.9b**, NEA = 2-(1-naphthyl)ethylammonium). These red-shifted absorption properties are mirrored by excitonic emissions (553 to 563 nm) that occur at lower energy than those of other common 2D lead-iodide perovskites (**Figure 5.9a**, dashed lines), which range from 468 to 524 nm.

Figure 5.9 a) Room temperature UV-vis and photoluminescence (PL) spectra of 2D hybrid perovskites **6**[PbI₄]—**9**[PbI₄] represented using solid and dashed lines, respectively. The PL spectra were obtained using 457nm continuous-wave laser excitation. b) Photographs of polycrystalline samples of **6**[PbI₄]—**9**[PbI₄] and a representative conventional 2D perovskite, (NEA)₂[PbI₄], where NEA = 2-(1-naphthyl)ethylammonium.

Figure 5.10 Temperature-dependent UV-vis spectra of thin films a) **6**[PbI₄], b) **7**[PbI₄], c) **8**[PbI₄], and d) **9**[PbI₄].

The reduced band-gaps (E_{gs}) inferred from the red-shifted optical features of the 2D perovskites described herein were confirmed by UV-vis absorption measurements of very thin films at 80 K. (The absorption evolution spectra of the materials as a function of temperature are presented in **Figure 5.10**.) From the spectra of **6**[PbI₄], **7**[PbI₄], **8**[PbI₄], and **9**[PbI₄] (**Figure 5.11**) their respective bandgaps are estimated to be 2.35, 2.46, 2.34, and 2.38 eV, which are about 120 – 230 meV lower than those of common perovskites. These low band-gaps can be attributed to the high Pb-I-Pb bond angles observed in their inorganic lattices (vide infra), which derive from the delocalized charge in the pyridinium cores of templating cations **6** – **9**. This is because more ideal Pb–I–Pb angles (close to 180°) allow for increased overlap between the lead and iodide orbitals, thereby, yielding more dispersed bands (see calculations). More interestingly, the low band-gaps of **6**[PbI₄] – **9**[PbI₄] are of similar magnitude to those of bilayered ($n = 2$) perovskites (E_{gs} of ca. 2.43 eV), which are typically obtained by alloying monolayered ($n = 1$) perovskites with 3D

hybrid perovskite in an equimolar ratio. As such, this work demonstrates that relaxation of angle distortion achieved by judicious selection of templating organic cation can have a similar effect as alleviating quantum confinement of the layered materials.

Figure 5.11 UV-vis spectrum of a) 6[PbI₄], b) 7[PbI₄], c) 8[PbI₄], and d) 9[PbI₄] thin film at 80 K. E_g , E_x , and E_b denote optical band-gap, excitonic peak, and excitonic binding energy, respectively. E_g is obtained by extrapolation of the linear part of the bandgap onset in the spectrum.

Estimated excitonic binding energies (E_{bs}) of 130, 200, 150, and 110 meV can be also be extracted from the respective low-temperature UV-vis spectra of 6[PbI₄], 7[PbI₄], 8[PbI₄], and 9[PbI₄], respectively (**Figure 5.11**). The E_b values can also be assessed *via* temperature-dependent photoluminescence (PL) measurements. This was conducted using single crystals of the aforementioned compounds (**Figure 5.12**). Emission intensity was plotted against the inverse of temperature, and the data fitted to the following equation:

$$I(T) = \frac{I_0}{1 + Ae^{-E_a/k_B T}} \quad (\text{Eqn. 5.1})$$

where I_0 corresponds to the intensity at low temperature, E_a to the activation energy, k_B to the Boltzmann constant, and T to the temperature of measurement. This provided

approximate exciton activation energies (E_a) of 120(10), 190(30), 119(8), and 127(8) meV for **6**[PbI₄], **7**[PbI₄], **8**[PbI₄], and **9**[PbI₄], respectively (**Figure 5.13**). Although there are small differences, the E_a values display good agreement with those extracted from the UV-vis absorption data.

Figure 5.12 Temperature-dependent PL spectra of single crystals a) **6**[PbI₄], b) **7**[PbI₄], c) **8**[PbI₄], and d) **9**[PbI₄] under excitation of a 457 nm continuous-wave laser beam.

Importantly, the E_a values obtained by both methods are significantly lower than those of conventional lead-iodide perovskites, such as that of 1-butylammonium (300 meV). In fact, they are among the lowest values ever reported for $n = 1$ iodoplumbates. Furthermore, these E_a values are comparable to those obtained for 2D systems with higher number of contiguous inorganic layers. For example, the $n = 2$ perovskites built by mixing the cations phenylethylammonium and 1-hexylammonium with equimolar quantities of methylammonium were reported to possess E_b values of approx. 170 meV³⁴ and 260 meV,³¹ respectively.

Figure 5.13 Temperature-dependent integrated PL intensity of single crystals a) 6[PbI₄], b) 7[PbI₄], c) 8[PbI₄], and d) 9[PbI₄] under excitation of a 457 nm continuous-wave laser beam where the black solid line is the best fit based on the Arrhenius equation.

5.2.3 Improved (photo)conductivity properties and electronic structure calculations

The more ‘3D-like’ in character of 2D perovskites 6[PbI₄] – 9[PbI₄] indicates that separation of photogenerated charge carriers proceeds with comparative ease. As such, they would be expected to superior interlayer charge transport. To explore this possibility, electrical conductivities of polycrystallines 6[PbI₄], 7[PbI₄], 8[PbI₄], and 9[PbI₄] were measured, at 300 K, using a four-probe direct current (DC) set-up (**Figure 5.14a**). To avoid growth of crystallites with specific preferred orientations on top of substrates, which would provide different current profiles for different configurations of electrodes,¹⁴ pressed pellets of finely ground polycrystalline samples were used in this study. As a point of comparison, measurements were also performed for the more conventional 2D iodoplumbate (NEA)₂[PbI₄], whose inorganic layer separation is twice that of 6[PbI₄] – 9[PbI₄] (**Figure 5.15**) and has a band gap of around 2.58 eV (**Figure 5.16**). The conductivities of pellets of 6[PbI₄], 7[PbI₄], 8[PbI₄], 9[PbI₄], and (NEA)₂[PbI₄] were found

to be 5.04×10^{-12} , 6.50×10^{-12} , 1.82×10^{-12} , 1.29×10^{-12} and 1.29×10^{-13} S/cm, respectively (see **Figure 5.14b**). Thus, $6[\text{PbI}_4]$ – $9[\text{PbI}_4]$ 2D perovskites exhibit charge transport that is more than one order of magnitude superior to that of the $(\text{NEA})_2[\text{PbI}_4]$.

Figure 5.14 a) Schematic diagram of the four-probe electrical conductivity measurements performed upon the polycrystalline samples. b) Plots of current density versus electric field strength (J – E curves) for $6[\text{PbI}_4]$ – $9[\text{PbI}_4]$ at 297 K with $(\text{NEA})_2[\text{PbI}_4]$ serving as the control. c) Current versus voltage (I – V) characteristics of $6[\text{PbI}_4]$ – $9[\text{PbI}_4]$ and $(\text{NEA})_2[\text{PbI}_4]$ under white light irradiation (1 sun illumination). d) Time-dependent photoresponses of the 2D perovskites at 2.0 V bias, upon repetitive on and off white light (1 sun AM1.5G) illumination (interval 2.5 s), measured for around 20 s.

Photoconductivity of the pelleted samples was also measured. Upon exposure to a 450 W xenon lamp that imitates the 1 sun irradiation, at an applied potential of 1 V, photocurrents can be harvested for $6[\text{PbI}_4]$ – $9[\text{PbI}_4]$ (6.30, 9.52, 4.28, and 3.35 nA, respectively) that are 11–33 times greater than those obtained for $(\text{NEA})_2[\text{PbI}_4]$ (0.29 nA). The values obtained are proportional to and directly controlled by the conductivity of the inorganic frameworks (**Figure 5.14c**). Additionally, for $6[\text{PbI}_4]$ – $9[\text{PbI}_4]$ repeated switching between light on and

off had a minimal impact on photocurrent output (**Figure 5.14d**). This indicates that the light-response in these materials is reversible. The slight better photoresponsivity by **6**[PbI₄] and **8**[PbI₄] than **7**[PbI₄] and **9**[PbI₄] are attributed to lower band gaps and excitonic binding energies in the former relative to those in the latter.

Figure 5.15 Single crystal structures of 2D perovskites (NEA)₂[PbI₄] where NEA is 2-naphthyl ethyl ammonium. The crystal structure is obtained from ref. 47. The inorganic layer separations shown in the figure are defined as the distances between successive mean equatorial planes built by neighbouring four lead atoms of the lead-iodide octahedra within an inorganic sheet. Ellipsoids are shown at 50% probability. H atoms are omitted for clarity. Gray, purple, brown, red, and blue spheres represent Pb, I, C, O, and N atoms, respectively.

Figure 5.16 a) Room temperature UV-vis spectrum of conventional 2D perovskite (NEA)₂[PbI₄] where NEA is 2-naphthylethylammonium showing bandgap larger than **6**[PbI₄]-**9**[PbI₄] (ca. 2.58 eV). b) Pb-I-Pb bond angles shown on particular axes of (NEA)₂[PbI₄]. The higher bandgap can be attributed to the more ‘crumpled’ Pb-(μ-I)-Pb bond angles. The crystal structure is obtained from ref. 47. Ellipsoids are shown at 50% probability. Gray and purple spheres represent Pb and I atoms, respectively.

In order to gain more insights on the correlation between enhanced optoelectronic properties and their structural features, density functional theory (DFT) calculations were performed on **6**[PbI₄]-**9**[PbI₄]. Most discussions on the electronic structures of 2D lead-iodide perovskites revolve around the bonding and distortions of the iodoplumbate lattice.^{32, 54-57} This is because the organic cation states do not normally directly participate in the electronic states near the VB or CB edges. However, the density functional theory (DFT) calculated partial density of states (PDOS), shown in **Figure 5.17**, suggest that conjugated dications **6** – **9** could contribute to the optoelectronic properties of their 2D perovskites, **6**[PbI₄]-**9**[PbI₄]. More specifically, while the iodide 5p-orbitals are the major contributors to the valence band maximum (VBM) and the conduction band minimum (CBM) is comprised of lead (6p)/iodide (5p) orbitals mixing, dications **6** – **9** are found to contribute significantly to the near-edge conduction band region. As such, this would be expected to allow for charge transfer contributions. To verify the latter proposition, further experiments would be required, such as transient-absorbance or more complex multidimensional spectroscopies. However, the lowest unoccupied molecular orbitals (LUMOs) of the pyridinium cores of **6** – **9** are expected to be relatively low in energy and, therefore, the possibility of charge transfer interaction seems reasonable. This scenario has precedent in

lower dimensional perovskites based on electron withdrawing organics, such as tropyliums⁵⁸ and viologens,⁵⁹ which, in turn, leads to their contribution to the electronic structure of the overall material.

Figure 5.17 Calculated total and partial density of states (TDOS and PDOS, respectively) of 2D perovskites a) **6**[PbI₄], b) **7**[PbI₄], c) **8**[PbI₄] and d) **9**[PbI₄].

Band structures were also calculated for all of the 2D perovskites a function of K-space paths within the first Brillouin zone (**Figure 5.18**). For typical 2D perovskites, it was previously found that the charge carrier effective masses are much smaller for the in-plane directions (within the inorganic planes) than perpendicular to the inorganic plane (between two inorganic planes). This is consistent with the expectation that charge transport occurs predominantly within the inorganic sheets due to the low dielectric constants of the layers of organic cations. Interestingly, dispersions at the band edge for the direction perpendicular to the inorganic network are observed for **6**[PbI₄]**–9**[PbI₄]. Similar interactions were noted for (BdA)[PbI₄], but were absent in closely-related perovskites (HdA)[PbI₄] and (OdA)[PbI₄] (BdA, HdA, and OdA are 1,4-butyldiammonium, 1,6-

hexyldiammonium, and 1,8-octyldiammonium, respectively).⁵⁷ The dispersions in (BdA)[PbI₄] were interpreted as long-range Coulombic interactions between the inorganic layers, with the apparent distant-dependence suggesting that they are feasible only for short interlayer distances (< 6 Å). In other words, short interlayer separations lead to reduced dielectric confinement. By analogy, the dispersions in **6**[PbI₄]**–9**[PbI₄] can be assigned as interlayer interactions, which is a consequence of their very short inorganic layers separations (I···I contacts of below 4.5 Å). This explains the comparative low excitonic binding energies measured for these compounds and one can infer that electrons and holes travelling perpendicular to their constituent inorganic layers will likely have lower effective masses than in conventional 2D iodoplumbates.

Figure 5.18 Band structures of 2D perovskites a) **6**[PbI₄], b) **7**[PbI₄], c) **8**[PbI₄] and d) **9**[PbI₄] as functions of K-space paths calculated with density functional theory (DFT). Red arrows indicate the band gaps of the materials.

5.3 Summary

In summary, a series of new low dimensional lead-iodide perovskites based on pyridinium cations are reported. Through X-ray crystallographic analysis, it was demonstrated that incorporation of primary ammonium functionality (into templating organic cations) is a prerequisite for formation of 2D lead-iodide perovskites. In their absence, materials comprised of 1D iodoplumbate chains were obtained. The presence of *N*-alkyl substituents containing neutral hydrogen bond donors (alcohol, carboxylic acid, and primary amide functionality) did not change this outcome and the 1D structures were retained. Efforts to exploit the aforementioned templating tendencies of pyridinium monocations have been undertaken, to enforce formation of 1D lead-bromide hybrids, which have seen exploration as single-source broadband white-light emitters.

Employing 2-ethylammonium decorated pyridinium dications, 2D perovskites with reduced inter-octahedral distortions (i.e. low Pb-(μ -I)-Pb bond angles tiltings) and very short inorganic separations (I $\cdots$ I contacts of below 4.5 Å) are obtained. The formation of 2D perovskites is not affected by the position of -NH functionality within the aromatic ring. These structural features manifest in optoelectronic properties that are favourable for photovoltaic applications, such as reduced band gaps, relaxed dielectric confinement, which is evident from very low excitonic binding energies, and improved photo- and electrical conductivities. DFT calculations suggest that the superior conductivity of 6[PbI₄] – 9[PbI₄], relative to most 2D lead-iodide perovskites, is likely due to a combination of the charge transfer mediation by the pyridinium cations and interaction between the proximate neighbouring inorganic layers.

As such, this study not only provides information regarding the formability of 2D Pb-I perovskites, it also illustrates a means by which appealing photophysical properties can be induced. Both of these aspects may inform future molecular design in the field. Having understood the formability of 2D perovskites whose structures do not incorporate any solvent molecules, attempt to study their optoelectronic properties in thin films and

fabricate solar cells based on the materials were then conducted. The results are described in the next chapter.

5.4 Bibliography

1. Best Research-Cell Efficiencies Rev. 16-04-2019 (NREL, 2019);
<https://www.nrel.gov/pv/assets/pdfs/best-research-cell-efficiencies-190416.pdf>.
2. Mei, A.; Li, X.; Liu, L.; Ku, Z.; Liu, T.; Rong, Y.; Xu, M.; Hu, M.; Chen, J.; Yang, Y.; Grätzel, M.; Han, H. *Science* **2014**, *345*, 295-298.
3. Fu, F.; Feurer, T.; Jager, T.; Avancini, E.; Bissig, B.; Yoon, S.; Buecheler, S.; Tiwari, A. N. *Nat. Commun.* **2015**, *6*, 8932.
4. Pellet, N.; Gao, P.; Gregori, G.; Yang, T. Y.; Nazeeruddin, M. K.; Maier, J.; Gratzel, M. *Angew. Chem. Int. Ed.* **2014**, *53* (12), 3151-7.
5. McMeekin, D. P.; Sadoughi, G.; Rehman, W.; Eperon, G. E.; Saliba, M.; Hörantner, M. T.; Haghighirad, A.; Sakai, N.; Korte, L.; Rech, B.; Johnston, M. B.; Herz, L. M.; Snaith, H. J. *Science* **2016**, *351*, 152-155.
6. Sun, S.; Salim, T.; Mathews, N.; Duchamp, M.; Boothroyd, C.; Xing, G.; Sum, T. C.; Lam, Y. M. *Energy Environ. Sci.* **2014**, *7* (1), 399-407.
7. Leguy, A. M. A.; Hu, Y.; Campoy-Quiles, M.; Alonso, M. I.; Weber, O. J.; Azarhoosh, P.; van Schilfgaarde, M.; Weller, M. T.; Bein, T.; Nelson, J.; Docampo, P.; Barnes, P. R. F. *Chem. Mater.* **2015**, *27* (9), 3397-3407.
8. Aristidou, N.; Sanchez-Molina, I.; Chotchuangchutchaval, T.; Brown, M.; Martinez, L.; Rath, T.; Haque, S. A. *Angew. Chem. Int. Ed.* **2015**, *54* (28), 8208-12.
9. 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. *Adv. Energy Mater.* **2015**, *5* (15).
10. Koh, T. M.; Thirumal, K.; Soo, H. S.; Mathews, N. *ChemSusChem* **2016**, *9* (18), 2541-2558.
11. Passarelli, J. V.; Fairfield, D. J.; Sather, N. A.; Hendricks, M. P.; Sai, H.; Stern, C. L.; Stupp, S. I. *J. Am. Chem. Soc.* **2018**, *140* (23), 7313-7323.

12. Tremblay, M. H.; Thouin, F.; Leisen, J.; Bacsá, J.; Srimath Kandada, A. R.; Hoffman, J. M.; Kanatzidis, M. G.; Mohite, A. D.; Silva, C.; Barlow, S.; Marder, S. R. *J. Am. Chem. Soc.* **2019**, *141* (11), 4521-4525.
13. Saparov, B.; Mitzi, D. B. *Chem. Rev.* **2016**, *116* (7), 4558-96.
14. Febriansyah, B.; Koh, T. M.; Lekina, Y.; Jamaludin, N. F.; Bruno, A.; Ganguly, R.; Shen, Z. X.; Mhaisalkar, S. G.; England, J. *Chem. Mater.* **2019**, *31* (3), 890-898.
15. Wang, S.; Mitzi, D. B.; Feild, C. A.; Guloy, A. *J. Am. Chem. Soc.* **1995**, *117*, 5297-5302.
16. Lemmerer, A.; Billing, D. G. *CrystEngComm* **2012**, *14* (6).
17. Lemmerer, A.; Billing, D. G. *Dalton Trans.* **2012**, *41* (4), 1146-1157.
18. Lemmerer, A.; Billing, D. G. *CrystEngComm* **2010**, *12* (4), 1290-1301.
19. Sourisseau, S.; Louvain, N.; Bi, W.; Mercier, N.; Rondeau, D.; Boucher, F.; Buzaré, J.-Y.; Legein, C. *Chem. Mater.* **2007**, *19* (3), 600-607.
20. Billing, D. G.; Lemmerer, A. *CrystEngComm* **2007**, *9* (3), 236-244.
21. Billing, D. G.; Lemmerer, A. *CrystEngComm* **2006**, *8* (9), 686-695.
22. Mao, L.; Tsai, H.; Nie, W.; Ma, L.; Im, J.; Stoumpos, C. C.; Malliakas, C. D.; Hao, F.; Wasielewski, M. R.; Mohite, A. D.; Kanatzidis, M. G. *Chem. Mater.* **2016**, *28* (21), 7781-7792.
23. Gómez, V.; Fuhr, O.; Ruben, M. *CrystEngComm* **2016**, *18* (42), 8207-8219.
24. Mao, L.; Guo, P.; Kepenekian, M.; Hadar, I.; Katan, C.; Even, J.; Schaller, R. D.; Stoumpos, C. C.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2018**, *140* (40), 13078-13088.
25. Stoumpos, C. C.; Malliakas, C. D.; Kanatzidis, M. G. *Inorg. Chem.* **2013**, *52* (15), 9019-9038.
26. W. K. Chong, D. Giovanni, T. Sum, Excitonics in 2D Perovskites. In Halide Perovskites: Photovoltaics, Light Emitting Devices, and Beyond; Sum, T., Mathews, N.; Wiley-VCH Verlag GmbH & Co. KGaA, 2019; 55-79.
27. Muljarov, E. A.; Tikhodeev, S. G.; Gippius, N. A.; Ishihara, T. *Phys. Rev. B* **1995**, *51* (20), 14370-14378.
28. Zhang, S.; Lanty, G.; Lauret, J.-S.; Deleporte, E.; Audebert, P.; Galmiche, L. *Acta Materialia* **2009**, *57* (11), 3301-3309.
29. Pradeesh, K.; Nageswara Rao, K.; Vijaya Prakash, G. *J. Appl. Phys.* **2013**, *113* (8).

30. Kamminga, M. E.; Fang, H.-H.; Filip, M. R.; Giustino, F.; Baas, J.; Blake, G. R.; Loi, M. A.; Palstra, T. T. M. *Chem. Mater.* **2016**, *28* (13), 4554-4562.
31. Tanaka, K.; Kondo, T. *Sci. Tech. Adv. Mater.* **2004**, *4* (6), 599-604.
32. Umebayashi, T.; Asai, K.; Kondo, T.; Nakao, A. *Phys. Rev. B* **2003**, *67* (15).
33. Kitazawa, N.; Aono, M.; Watanabe, Y. *J. Phys. Chem. Solids* **2011**, *72* (12), 1467-1471.
34. Hong, X.; Ishihara, T.; Nurmikko, A. V. *Phys. Rev. B* **1992**, *45* (12), 6961-6964.
35. Ishihara, T.; Takahashi, J.; Goto, T. *Phys. Rev. B Condens. Matter.* **1990**, *42* (17), 11099-11107.
36. Kitazawa, N.; Aono, M.; Watanabe, Y. *Thin Solid Films* **2010**, *518* (12), 3199-3203.
37. Kitazawa, N.; Aono, M.; Watanabe, Y. *Mater. Chem. and Phys.* **2012**, *134* (2-3), 875-880.
38. Gauthron, K.; Lauret, J.-S.; Doyennette, L.; Lanty, G.; Al Choueiry, A.; Zhang, S. J.; Brehier, A.; Largeau, L.; Mauguin, O.; Bloch, J.; Deleporte, E **2010**, *18*(6), 5912-5919.
39. Smith, M. D.; Pedesseau, L.; Kepenekian, M.; Smith, I. C.; Katan, C.; Even, J.; Karunadasa, H. I. *Chem. Sci.* **2017**, *8* (3), 1960-1968.
40. Duan, H. B.; Yu, S. S.; Liu, S. X.; Zhang, H. *Dalton Trans.* **2017**, *46* (7), 2220-2227.
41. Duan, H.-B.; Yu, S.-S.; Liu, S.-X.; Zhang, H. *RSC Advances* **2017**, *7* (37), 23234-23237.
42. Duan, H. B.; Yu, S. S.; Tong, Y. B.; Zhou, H.; Ren, X. M. *Dalton Trans.* **2016**, *45* (11), 4810-8.
43. Billing, D. G.; Lemmerer, A. *Acta Crystallogr C* **2006**, *62* (Pt 6), m238-40.
44. Robinson, K.; Gibbs, G. V.; Ribbe, P. H. *Science* **1971**, *172*, 567-570.
45. Cortecchia, D.; Neutzner, S.; Srimath Kandada, A. R.; Mosconi, E.; Meggiolaro, D.; De Angelis, F.; Soci, C.; Petrozza, A. *J. Am. Chem. Soc.* **2016**, *139* (1), 39-42.
46. Mao, L.; Wu, Y.; Stoumpos, C. C.; Wasielewski, M. R.; Kanatzidis, M. G., *J. Am. Chem. Soc.* **2017**.
47. Du, K. Z.; Tu, Q.; Zhang, X.; Han, Q.; Liu, J.; Zauscher, S.; Mitzi, D. B. *Inorg. Chem.* **2017**, *56* (15), 9291-9302.
48. Tang, Z.; Guan, J.; Guloy, A. M. *J. Mater. Chem.* **2001**, *11* (2), 479-482.

49. Hautzinger, M. P.; Dai, J.; Ji, Y.; Fu, Y.; Chen, J.; Guzei, I. A.; Wright, J. C.; Li, Y.; Jin, S. *Inorg. Chem.* **2017**, *56* (24), 14991-14998.
50. Mitzi, D. B., Synthesis, Structure, and Properties of Organic-Inorganic Perovskites and Related Materials. *Prog. Inorg. Chem.* **1999**, *48*, 1-121.
51. Knutson, J. L.; Martin, J. D.; Mitzi, D. B. *Inorg. Chem.* **2005**, *44*, 4699-4705.
52. Mercier, N.; Poiroux, S.; Riou, A.; Batail, P. *Inorg. Chem.* **2004**, *43* (26), 8361-8366.
53. Mao, L.; Ke, W.; Pedesseau, L.; Wu, Y.; Katan, C.; Even, J.; Wasielewski, M. R.; Stoumpos, C. C.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2018**, *140* (10), 3775-3783.
54. Wang, D.; Wen, B.; Zhu, Y. N.; Tong, C. J.; Tang, Z. K.; Liu, L. M. *J. Phys. Chem. Lett.* **2017**, *8* (4), 876-883.
55. Pedesseau, L.; Jancu, J.-M.; Rolland, A.; Deleporte, E.; Katan, C.; Even, J. *Optical and Quantum Electronics* **2013**, *46* (10), 1225-1232.
56. Qian, J.; Guo, Q.; Liu, L.; Xu, B.; Tian, W. *J. Mater. Chem. A* **2017**, *5* (32), 16786-16795.
57. Phuyal, D.; Safdari, M.; Pazoki, M.; Liu, P.; Philippe, B.; Kvashnina, K. O.; Karis, O.; Butorin, S. M.; Rensmo, H.; Edvinsson, T.; Kloos, L.; Gardner, J. M. *Chem. Mater.* **2018**, *30* (15), 4959-4967.
58. Maughan, A. E.; Kurzman, J. A.; Neilson, J. R. *Inorg. Chem.* **2015**, *54* (1), 370-8.
59. Febriansyah, B.; Koh, T. M.; John, R. A.; Ganguly, R.; Li, Y.; Bruno, A.; Mhaisalkar, S. G.; England, J. *Chem. Mater.* **2018**, *30* (17), 5827-5830.
60. Thomas, N. W. *Acta Crystallographica Section B* **1989**, *45*, 337-344.
61. Ertl, A.; Hughes, J. M.; Pertlik, F.; Jr., F. F. F.; Wright, S. E.; Brandstatter, F.; Marler, B. *Can. Mineral.*, **2002**, *40*, 153-162.
62. Fleet, M. E. *Mineralogical Magazine* **1976**, *40*, 531-533.
63. Kanitskaya, L. V.; Elokhina, V. N.; Fedorov, S. V.; Shulunova, A. M.; Nakhmanovich, A. S.; Turchaninov, V. K.; Lopyrev, V. A. *Russ. J. Gen. Chem.* **2002**, *72*, 778-784.
64. Katritzky, A. R.; Dega-Szafran, Z. *Mag. Res. Chem.* **1989**, *27*, 1090-1105.
65. Lee, S.; Jeon, Y.; Lim, Y.; Cho, Y.; Lee, S.; Kim, W. *Bull. Korean Chem. Soc.* **2013**, *34* (9), 2583.

66. Benek, O.; Musilek, K.; Horova, A.; Dohnal, V.; Dolezal, R.; Kuca, K. *Med. Chem.* **2015**, *11* (1), 21-29.
67. Poterała, M.; Dranka, M.; Borowiecki, P. *Eur. J. Org. Chem.* **2017**, 2290-2304.
68. Królikowska, M.; Zawadzki, M.; Skonieczny, M. *J. Mol. Liq.* **2018**, *265*, 316-326.
69. Thorsteinsson, T.; Másson, M.; Kristinsson, K. G.; Hjálmarsson, M. A.; Hilmarsson, H.; Loftsson, T. *J. Med. Chem.* **2003**, *46* (19), 4173-4181.
70. Warneke, J.; Plaumann, M.; Wang, Z.; Böhrer, E.; Kemken, D.; Kelm, S.; Leibfritz, D.; Azov, V. A. *Tetrahedron Lett.* **2015**, *56*, 1124-1127.

5.5 Instrumentations and additional data

Nuclear Magnetic Resonance (NMR) spectroscopy. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of organic compounds were recorded in DMSO- d_6 solution, using a Bruker Avance 400 spectrometer. Chemical shift values (ppm) are referenced against residual protic solvent peaks.

X-ray crystallography. Single crystals were mounted on a Bruker Quest CPAD area detector diffractometer (Bruker X8 CCD diffractometer) and data collected using a I μ S 3.0 Microfocus Mo-K α source ($\lambda = 0.71073 \text{ \AA}$), at temperatures of 100 and 253 K. Data reduction and absorption corrections were performed with the SAINT and SADABS software packages, respectively. All structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 , using the Bruker SHELXTL-2014 software package. Non-hydrogen atoms were anisotropically refined, after which hydrogen atoms were introduced at calculated positions and the data was further refined. Graphical illustrations of crystal structures used throughout the main paper and supporting information were produced using the Mercury and VESTA software packages.

UV-vis spectroscopy. UV-vis spectra of polycrystalline samples were collected using a Shimadzu UV-3600 UV-VIS-NIR Spectrophotometer, with BaSO $_4$ as the 100% reflectance reference. The measurements were conducted over a 300 – 800 nm wavelength range, with a scanning resolution of 0.5 nm s^{-1} , in the diffuse reflectance mode, using an

integrating sphere. Relative absorbance was obtained from Kubelka–Munk transformation of the reflectance spectra: $\alpha/S = (1 - R)^2(2R)^{-1}$, where R is the reflectance, and α and S are the absorption and scattering coefficients, respectively.

Temperature-dependent photoluminescence spectroscopies. The photoluminescence (PL) and optical absorption spectra were recorded using a WITec alpha 300RAS confocal Raman microscope. The blue line of a linearly polarized CW solid laser (457 nm) was selected for PL measurements, during which the excitation power was kept below 0.8 μ W to avoid photodegradation of the sample and saturation of the detector. For the absorption measurements, a halogen lamp (15 V, 150 W, 3100 K) was used as a white light source. A long working distance of 20 $\times$ microscope objective (spot size of ~ 2 μ m) was used for the low temperature experiments. Temperature-dependent measurements were conducted in the range 78 – 293 K, using a nitrogen gas flow cryostat.

Density Functional Theory (DFT) calculations. Electronic structure calculations were performed using the projected augmented wave method (PAW) implemented in the Vienna Ab initio Simulation Package (VASP)⁵⁻¹⁰. An energy cutoff of 600 eV was used for plane-wave expansion, and the atomic coordinates were relaxed using a conjugate gradient algorithm until the force acting on the individual atoms was less than 0.05 eV/Å. The exchange-correlation functional was treated with the generalized gradient approximation (GGA) parameterized by Perdew-Burke-Ernzerhof (PBE). All the structural relaxations were performed with Gaussian smearing of 0.05 eV where a $3 \times 2 \times 1$ Gamma K-point grid are used during the process.

Four-probe conductivity measurements. Finely ground polycrystalline samples of the compounds were pressed into circular disc-shaped pellets (diameter = 1.35 cm, thickness ≈ 0.1 cm) by applying a uniaxial pressure of 100 MPa using a hydraulic press. They were connected to a Keithley 2400 source meter by evaporated gold electrodes (distance = 150 μ m, width = 4000 μ m). The current generated between two gold electrodes, upon variation of electrical potential, was then measured. The conductivity (σ) was calculated using the

following equations, where R = resistance, V = voltage, I = current, ρ = resistivity, and A and l are the cross section and length of the electrode, respectively:

$$R = \frac{V}{I} \quad (\text{Eqn. 5.2})$$

$$\rho = R \frac{A}{l} \quad (\text{Eqn. 5.3})$$

$$\sigma = \frac{1}{\rho} \quad (\text{Eqn. 5.4})$$

1-(ethyl)pyridinium (1) iodide. Isolated as yellow solid (2.11 g; 81% yield), ^1H NMR (400 MHz, DMSO-*d*6): δ 9.13 (d, 2 H, ArH), 8.61 (t, 1 H, ArH), 8.17 (t, 2 H, ArH), 4.66 (q, 2 H, CH₂), 1.54 (t, 3 H, CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO-*d*6): δ 145.3, 144.4, 128.0, 56.3, 16.3. The NMR spectroscopic data match the reported values.^{63,64}

1-(propyl)pyridinium (2) iodide. Isolated as yellow solid (2.32; 77% yield), ^1H NMR (400 MHz, DMSO-*d*6): δ 9.10 (d, 2 H, ArH), 8.62 (t, 1 H, ArH), 8.18 (m, 2 H, ArH), 4.58 (t, 2 H, CH₂), 2.49-2.50 (m, 2 H, CH₂), 1.95 (sext, 3 H, CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO-*d*6): δ 145.4, 145.0, 128.0, 61.9, 24.0, 10.1. The NMR spectroscopic data match the reported values.^{65,66}

1-(2-hydroxyethyl)pyridinium (3) iodide. Isolated as yellow solid (1.94; 82% yield), ^1H NMR (400 MHz, DMSO-*d*6): δ 9.02 (d, 2 H, ArH), 8.63 (s, 1 H, ArH), 8.18 (t, 2 H, ArH), 5.22 (t, 1 H, OH), 4.67 (t, 2 H, CH₂), 3.84-3.88 (m, 2 H, CH₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO-*d*6): δ 145.5, 145.0, 127.6, 63.0, 59.9. The NMR spectroscopic data match the reported values.^{67,68}

1-(2-carboxyethyl)pyridinium (4) iodide. Isolated as yellow solid (1.88; 82% yield), ^1H NMR (400 MHz, DMSO-*d*6): δ ~12.71 (bs, 1 H, C(O)OH), 9.05 (d, 2 H, ArH), 8.61 (s, 1 H, ArH), 8.20 (t, 2 H, ArH), 4.84 (t, 2 H, CH₂), 3.11 (t, 2 H, CH₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO-*d*6): δ 168.4, 145.6, 145.2, 127.8, 56.6, 34.3. The NMR spectroscopic data match the reported values.^{69,70}

1-(propionamidyl)pyridinium (5) iodide . Isolated as beige solid (1.51; 82% yield), ^1H NMR (400 MHz, DMSO-*d*6): δ ~8.97 (d, 2 H, ArH), 8.65 (s, 1 H, ArH), 8.18 (t, 2 H, ArH), 8.02 (s, 1 H, C(O)NH₂), 7.69 (s, 1 H, C(O)NH₂), 4.81 (t, 2 H, CH₂), 3.10 (t, 2 H, CH₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO-*d*6): δ 166.0, 146.2, 146.0, 127.4, 55.4, 35.2.

2-Iodoethan-1-ammonium iodide (precursor in Chapter 5, 6, and 7). Ethanolamine (15 g, 0.25 mole) was added dropwise to a round bottom flask containing concentrated aqueous HI (96 mL) at 0 °C. The volume of the solution was then reduced by half using a rotary

evaporator, before it was stored in a refrigerator at 4 °C overnight. The resulting precipitate was isolated by filtration and thoroughly washed with chloroform to remove trace iodine. After drying under vacuum, iodoethylammonium iodide was obtained as a white powder (42.7 g, 92 %) and transferred to an inert atmosphere glovebox. ^1H NMR (500 MHz, DMSO-*d*6): δ 7.86 (s, 3 H, NH_3^+), 3.26-3.29 (m, 2 H, CH_2), 3.19-3.22 (m, 2 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, DMSO-*d*6): δ 41.9, -0.1.

1-(2-Ammonioethyl)pyridin-1-ium (6) diiodide. Isolated as a beige solid (2.39g, 90% yield). ^1H NMR (400 MHz, DMSO-*d*6): δ 9.06 (d, J = 5.6 Hz, 2 H, ArH), 8.67 (t, J = 7.8 Hz, 1 H, ArH), 8.23 (t, J = 7.0 Hz, 2 H, ArH), 7.97 (bs, 3 H, NH_3^+), 4.86 (t, J = 5.8 Hz, 2 H, CH_2), 3.56 (t, J = 5.8 Hz, 2 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO-*d*6): δ 146.2, 145.3, 128.2, 57.9, 38.9.

2-(2-Ammonioethyl)pyridin-1-ium (7) diiodide. Isolated as a beige solid (1.61g; 85% yield). ^1H NMR (400 MHz, DMSO-*d*6): δ 8.88 (d, 1 H, ArH), 8.50 (t, 1 H, ArH), 8.13 (bs, 3 H, NH_3^+), 7.99 (d, 1 H, ArH), 7.92 (t, 1 H, ArH), 3.39-3.32 (m, 4 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO-*d*6): δ 152.7, 145.4, 142.7, 127.2, 125.2, 37.3, 31.0.

3-(2-Ammonioethyl)pyridin-1-ium (8) diiodide. Isolated as a beige solid (0.84g; 92% yield). ^1H NMR (400 MHz, DMSO-*d*6): δ 8.92 (s, 1 H, ArH), 8.86 (d, 1 H, ArH), 8.53 (d, 1 H, ArH), 8.04 (t, 2 H, ArH), 7.98 (bs, 1 H, NH_3^+), 3.23-3.20 (m, 2 H, CH_2), 3.16-3.12 (m, 2 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO-*d*6): δ 146.3, 142.5, 140.7, 137.1, 126.8, 38.8, 29.6.

4-(2-Ammonioethyl)pyridin-1-ium (9) diiodide. Isolated as a beige solid (1.20g; 83% yield). ^1H NMR (400 MHz, DMSO-*d*6): δ 8.92 (d, 2 H, ArH), 8.05 (bs, 3 H, NH_3^+), 8.04 (d, 2 H, ArH), 3.25-3.20 (m, 4 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO-*d*6): δ 157.9, 141.7, 127.6, 38.1, 32.6.

Table 5.3 Summary of distortion parameters of **1**[PbI₃] – **5**[PbI₃].

No.	Compound	λ_{oct}^a	σ_{oct}^{2b}	$\Delta d (x10^{-4})^c$
1.	1 [PbI ₃]	1.0073	25.31	0.65
2.	2 [PbI ₃]	1.0108	36.14	7.88
3.	3 [PbI ₃]	1.0076	27.05	1.76
4.	4 [PbI ₃]	1.0130	44.40	3.47
5.	5 [PbI ₃]	1.0036	12.90	0.54

^aOctahedral elongation (λ_{oct}), ^boctahedral angle variance (σ_{oct}^2), and ^coctahedral bond length distortion (Δ_{oct}). The equations for each parameter and an explanation of their meanings are as the followings:

$$\text{Octahedral elongation}^{44, 60}: \lambda_{oct} = \frac{1}{6} \sum_{i=1}^6 \left[\frac{d_i}{d_0} \right]^2 \quad (\text{Eqn. 5.5})$$

$$\text{Octahedral angle variance}^{44, 60-62}: \sigma_{oct}^2 = \frac{1}{11} \sum_{i=1}^{12} (\alpha_i - 90)^2 \quad (\text{Eqn. 5.6})$$

$$\text{Bond length distortion}^{61}: \Delta_{oct} = \frac{1}{6} \sum_{i=1}^6 \left[\frac{d_i - d_m}{d_m} \right]^2 \quad (\text{Eqn. 5.7})$$

where d_i represents Pb–Br bond length, d_m to average bond length, d_0 to center-to-vertex distance of a regular polyhedron of the same volume, and α_i to individual Br–Pb–Br angle. λ_{oct} , σ_{oct}^2 and Δ_{oct} provide a quantitative measure of polyhedral distortion independent of the polyhedron effective size. Crystallographic software, VESTA, was used to calculate the last two structural distortion parameters.

Table 5.4 Crystallographic and structure refinement data for **1**[PbI₃], **2**[PbI₃], and **3**[PbI₃].^a

	Compound		
	1 [PbI ₃]	2 [PbI ₃]	3 [PbI ₃]
Empirical formula	C ₇ H ₁₀ I ₃ NPb	C ₈ H ₁₂ I ₃ NPb	C ₇ H ₁₀ I ₃ NO ₂ Pb
Formula weight	696.05 g/mol	710.08 g/mol	712.05 g/mol
Temperature	273(2) K	253(2) K	280(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal size	0.200 x 0.280 x 0.380 mm	0.160 x 0.280 x 0.360 mm	0.040 x 0.060 x 0.220 mm
Crystal habit	yellow block	yellow block	colorless needle
Crystal system	orthorhombic	orthorhombic	triclinic
Space group	P n m a	P n m a	P -1
Unit cell dimensions	a = 18.2160(9) Å	a = 8.1205(4) Å	a = 8.0167(3) Å
	α = 90°	α = 90°	α = 89.0797(13)°
	b = 7.8521(4) Å	b = 9.2677(4) Å	b = 11.7951(4) Å
	β = 90°	β = 90°	β = 87.0994(12)°
	c = 19.5805(10) Å	c = 19.9344(8) Å	c = 15.5850(6) Å
	γ = 90°	γ = 90°	γ = 78.7533(12)°
Volume	2800.7(2) Å ³	1500.23(12) Å ³	1443.50(9) Å ³
Z	8	4	4
Density	3.302 g/cm ³	3.144 g/cm ³	3.276 g/cm ³
Absorption coefficient	18.623 mm ⁻¹	17.386 mm ⁻¹	18.075 mm ⁻¹
F(000)	2400	1232	1232
Theta range for data collection	1.53 to 24.99°	2.04 to 31.07°	2.59 to 30.64°
Reflections collected	26724	35801	53817
Coverage of independent reflections	97.60%	100.00%	99.50%
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan
Max. and min. transmission	0.1180 and 0.0530	0.1670 and 0.0620	0.5320 and 0.1090
Function minimized	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	2607 / 132 / 133	2530 / 0 / 72	8874 / 1 / 237
Goodness-of-fit on F ²	1.153	1.096	1.047
Δ/σ _{max}	0.017	0.001	0.001
Final R indices	2072 data	1971 data	4530 data
[I > 2σ(I)]	R1 = 0.0867, wR2 = 0.2027	R1 = 0.0505, wR2 = 0.1208	R1 = 0.0467, wR2 = 0.0636
R indices [all data]	R1 = 0.1051, wR2 = 0.2144	R1 = 0.0667, wR2 = 0.1347	R1 = 0.1368, wR2 = 0.0888
Largest diff. peak and hole	3.447 and -1.760 eÅ ⁻³	3.158 and -2.473 eÅ ⁻³	1.338 and -1.645 eÅ ⁻³
R.M.S. deviation from mean	0.390 eÅ ⁻³	0.322 eÅ ⁻³	0.288 eÅ ⁻³

^aR = Σ||F_o| - |F_c||/Σ|F_o|, wR = {Σ[w(|F_o|² - |F_c|²)²]/Σ[w(|F_o|⁴)]}^{1/2} and **1**[PbI₃], w = 1/[σ²(F_o²) + (0.0624P)² + 245.1967P]; **2**[PbI₃], w = 1/[σ²(F_o²) + (0.0506P)² + 8.5448P]; **3**[PbI₃], w = 1/[σ²(F_o²) + (0.0214P)² + 0.4700P]; where P = (F_o² + 2F_c²)/3.

Table 5.5 Crystallographic and structure refinement data for **4[PbI₃]** and **5[PbI₃]**.^a

	Compound	
	4[PbI ₃]	5[PbI ₃]
Empirical formula	C ₁₀ H ₁₆ I ₃ NO ₃ PbS	C ₁₀ H ₁₇ I ₃ N ₂ O ₂ PbS
Formula weight	818.19 g/mol	817.21 g/mol
Temperature	100(2) K	280(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal size	0.060 x 0.080 x 0.180 mm	0.040 x 0.220 x 0.320 mm
Crystal habit	light yellow needle	yellow plate
Crystal system	monoclinic	triclinic
Space group	P 1 21/c 1	P -1
Unit cell dimensions	a = 15.5746(4) Å	a = 7.8690(6) Å
	α = 90°	α = 97.691(3)°
	b = 15.3624(4) Å	b = 10.1454(9) Å
	β = 90.2397(10)°	β = 107.019(3)°
	c = 8.0371(2) Å	c = 13.1510(10) Å
	γ = 90°	γ = 93.718(3)°
Volume	1922.97(9) Å ³	988.88(14) Å ³
Z	4	2
Density	2.826 g/cm ³	2.745 g/cm ³
Absorption coefficient	13.701 mm ⁻¹	13.319 mm ⁻¹
F(000)	1456	728
Theta range for data collection	2.62 to 31.00°	2.72 to 26.44°
Reflections collected	51964	14028
Coverage of independent reflections	100.00%	99.40%
Absorption correction	Multi-Scan	Multi-Scan
Max. and min. transmission	0.4940 and 0.1920	0.6180 and 0.1000
Function minimized	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	6145 / 144 / 214	4056 / 138 / 216
Goodness-of-fit on F ²	1.101	1.039
Δ/σ _{max}	0.003	0.001
Final R indices [I > 2σ(I)]	5093 data	2991 data
	R1 = 0.0276,	R1 = 0.0404,
	wR2 = 0.0484	wR2 = 0.0977
R indices [all data]	R1 = 0.0429,	R1 = 0.0640,
	wR2 = 0.0547	wR2 = 0.1142
Largest diff. peak and hole	1.536 and -1.420 eÅ ⁻³	1.287 and -1.451 eÅ ⁻³
R.M.S. deviation from mean	0.241 eÅ ⁻³	0.222 eÅ ⁻³

^a $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR = \{\Sigma [w(|F_o|^2 - |F_c|^2)^2] / \Sigma [w(|F_o|^4)]\}^{1/2}$ and **4[PbI₃]**, $w = 1/[\sigma^2(F_o^2) + (0.0082P)^2 + 9.2781P]$; **5[PbI₃]**, $w = 1/[\sigma^2(F_o^2) + (0.0481P)^2 + 0.2231P]$; where $P = (F_o^2 + 2F_c^2)/3$.

Table 5.6 Crystallographic and structure refinement data for **6[PbI₄]** and **7[PbI₄]**.^a

	Compound	
	6[PbI₄]	7[PbI₄]
Empirical formula	C ₇ H ₁₂ I ₄ N ₂ Pb	C ₇ H ₁₂ I ₄ N ₂ Pb
Formula weight	838.98 g/mol	838.98 g/mol
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal size	0.044 x 0.150 x 0.291 mm	0.040 x 0.100 x 0.220 mm
Crystal habit	red plate	red block
Crystal system	monoclinic	monoclinic
Space group	P 1 21/c 1	P 1 21/n 1
Unit cell dimensions	a = 6.3354(3) Å	a = 6.3979(2) Å
	α = 90°	α = 90°
	b = 19.8007(9) Å	b = 12.5221(4) Å
	β = 90.757(2)°	β = 93.7937(14)°
	c = 12.5707(5) Å	c = 19.9591(7) Å
	γ = 90°	γ = 90°
Volume	1576.80(12) Å ³	1595.52(9) Å ³
Z	4	4
Density	3.534 g/cm ³	3.493 g/cm ³
Absorption coefficient	18.505 mm ⁻¹	18.288 mm ⁻¹
F(000)	1448	1448
Theta range for data collection	2.62 to 31.03°	2.61 to 31.57°
Reflections collected	45149	20025
Coverage of independent reflections	99.70%	99.60%
Absorption correction	Multi-Scan	Multi-Scan
Max. and min. transmission	0.4960 and 0.0750	0.5280 and 0.1080
Function minimized	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	5027 / 0 / 128	5334 / 0 / 128
Goodness-of-fit on F ²	1.294	1.078
Δ/σ _{max}	0.003	0.001
Final R indices [I > 2σ(I)]	4879 data	4667 data
	R1 = 0.0298,	R1 = 0.0335,
	wR2 = 0.0801	wR2 = 0.0692
R indices [all data]	R1 = 0.0309,	R1 = 0.0416,
	wR2 = 0.0806	wR2 = 0.0729
Largest diff. peak and hole	3.779 and -1.824 eÅ ⁻³	2.464 and -2.454 eÅ ⁻³
R.M.S. deviation from mean	0.282 eÅ ⁻³	0.379 eÅ ⁻³

^aR = Σ||F_o| - |F_c||/Σ|F_o|, wR = {Σ[w(|F_o|² - |F_c|²)²]/Σ[w(|F_o|⁴)]}^{1/2} and **6[PbI₄]**, w = 1/[σ²(F_o²) + (0.0213P)² + 19.5793P]; **7[PbI₄]**, w = 1/[σ²(F_o²) + (0.0193P)² + 3.7155P]; where P = (F_o² + 2F_c²)/3.

Table 5.7 Crystallographic and structure refinement data for **8**[PbI₄] and **9**[PbI₄].^a

	Compound	
	8 [PbI ₄]	9 [PbI ₄]
Empirical formula	C ₇ H ₇ I ₄ N ₂ Pb	C ₇ H ₁₂ I ₄ N ₂ Pb
Formula weight	833.94 g/mol	838.98 g/mol
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal size	0.020 x 0.140 x 0.200 mm	0.020 x 0.040 x 0.220 mm
Crystal habit	red plate	red needle
Crystal system	monoclinic	monoclinic
Space group	P 1 21/n 1	P 1 21/n 1
Unit cell dimensions	a = 6.3562(3) Å	a = 6.3507(3) Å
	α = 90°	α = 90°
	b = 12.4689(5) Å	b = 12.5001(6) Å
	β = 96.063(3)°	β = 95.354(3)°
	c = 20.3807(9) Å	c = 20.2005(13) Å
	γ = 90°	γ = 90°
Volume	1606.23(12) Å ³	1596.61(15) Å ³
Z	4	4
Density	3.449 g/cm ³	3.490 g/cm ³
Absorption coefficient	18.165 mm ⁻¹	18.276 mm ⁻¹
F(000)	1428	1448
Theta range for data collection	2.59 to 26.99°	2.60 to 33.72°
Reflections collected	3490	5924
Coverage of independent reflections	99.70%	97.90%
Absorption correction	Multi-Scan	Multi-Scan
Max. and min. transmission	0.7130 and 0.1220	0.7110 and 0.1080
Function minimized	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	3490 / 81 / 129	5924 / 184 / 129
Goodness-of-fit on F ²	1.132	1.258
Δ/σ _{max}	0.001	0.001
Final R indices [I > 2σ(I)]	3007 data	4260 data
	R1 = 0.0588,	R1 = 0.1140,
	wR2 = 0.1305	wR2 = 0.1916
R indices [all data]	R1 = 0.0695,	R1 = 0.1615,
	wR2 = 0.1353	wR2 = 0.2101
Largest diff. peak and hole	4.261 and -6.292 eÅ ⁻³	6.614 and -5.015 eÅ ⁻³
R.M.S. deviation from mean	0.499 eÅ ⁻³	1.010 eÅ ⁻³

^aR = Σ||F_o| - |F_c||/Σ|F_o|, wR = {Σ[w(|F_o|² - |F_c|²)²]/Σ[w(|F_o|⁴)]}^{1/2} and **8**[PbI₄], w = 1/[σ²(F_o²) + 149.1556P]; **9**[PbI₄], w = 1/[σ²(F_o²) + 159.2190P]; where P = (F_o² + 2F_c²)/3.

Chapter 6

Improved photovoltaic efficiency and amplified photocurrent generation in mesoporous $n = 1$ 2D lead-iodide perovskite solar cells

*This chapter describes the utilization of two organic dications containing, respectively, a pyridinium and an imidazolium core to construct $n = 1$ (where n refers to the number of contiguous 2D inorganic layers; i.e., not separated by organic cations) two-dimensional (2D) lead-iodide perovskites **1** and **2** with distinct inorganic architecture. The former material exhibits a (100)- and the latter a very rare 3×3 (110)-structural type. The compact nature of the dications produce super short lead-iodide sheet separations, with respective iodide-iodide ($I \cdots I$) distances as small as 4.149 Å and 4.278 Å. These are amongst the shortest separations of adjacent lead-iodide layers, in such materials, ever reported. When crystallized as thin films on top of substrates, the resulting 2D perovskite layers do not adopt a regular growth direction parallel to the surface. Instead, the crystallites grow with no fixed orientation. As a consequence of their proximate inorganic distances and unusual crystallization tendencies, the resulting 2D perovskites exhibit low excitonic activation energies (93.59 meV and 96.53 meV, respectively), enhanced photoconductivity in solar cells, and unprecedented incident photon-to-current conversion rates of up to 60%. More importantly, mesoporous 2D layered perovskite solar cells with power conversion efficiencies (PCEs) of 1.43% and 1.83% were achieved for **1** and **2**, respectively. These are the highest values obtained, thus far, for pure $n = 1$ lead-iodide perovskites and more than 20 times higher than those obtained for materials templated by more conventional cations, such as phenylethylammonium (0.08%).*

6.1 Background

Two-dimensional (2D) hybrid lead-iodide perovskites with chemical formulas $(\text{RNH}_3)_2\text{PbI}_4$ or $(\text{NH}_3\text{RNH}_3)\text{PbI}_4$, where R represents an organic functional group,¹⁻² are derived from their 3D congeners by slicing the inorganic lattice along certain crystallographic axes (e.g., the (100)- or (110)-planes). This can be induced through incorporation of moderately-sized organic cations, such as the commonly used phenylethylammonium (PEA)³⁻⁴ and 1-butylammonium (BA) ions.⁵⁻⁶ The resulting 2D materials possess greater synthetic versatility and moisture stability than pure 3D lead-iodide perovskites.⁷⁻⁸ Thus, attempts have been made to exploit these materials as solar absorbers in photovoltaic (PV) applications.⁷⁻⁸

However, the organic cations are known to possess much lower dielectric constants than the neighboring inorganic layers.⁹⁻¹⁰ This, combined with constraints imposed by growth of the inorganic lattice in one direction (e.g., parallel to the surface), causes the inorganic layers to experience quantum confinement.¹¹⁻¹² In addition, the separation of one inorganic layer from the next can be large. For example, in the BA-¹³ and PEA-based³ 2D perovskites the shortest iodide-iodide ($\text{I}\cdots\text{I}$) distances are ~ 8.40 and ~ 10.20 Å, respectively. As a consequence of these factors, 2D perovskites possess relatively poor semiconducting properties, such as limited interlayer charge transport, large bandgaps, and high excitonic binding energies (e.g. > 300 meV for aliphatic cation-based 2D perovskites).¹⁴⁻¹⁷ This manifests in typical solar cell and incident photon-to-current efficiencies significantly poorer than their 3D congeners. Thus far, the highest efficiencies reported for devices containing pure 2D lead-iodide perovskite photoactive layers are based upon 1,4-butyldiammonium,¹⁸ histammonium¹⁹ and, very recently, pyrene-O-propyl-ammonium⁸ cations. They exhibit respective PCEs of 1.08%, 1.13%, and 1.38%, with typical external quantum efficiencies ranging from 25 to 35%.

One might imagine that the aforementioned optoelectronic issues can be mitigated, and improved photovoltaic characteristics obtained, by judicious selection of ammonium cations. For instance, highly compact dications can engender small lead-iodide sheet

separations, which might allow for charge transport enhancement.¹⁸ Additionally, doubly-charged cations exhibit reduced solubility, which leads to rapid crystallization and might result in deviation from typical crystallization behaviour during spin coating.¹⁹ This could be advantageous. Similarly, incorporation of ‘diffuse’ positive charges would be expected to relax the inorganic inter-octahedral tilt angles, thereby resulting in a red shift of the UV-vis absorption profile and a reduced bandgap.²⁰⁻²¹ Lastly, it has been proposed that incorporating an aromatic core might allow for charge transport across the organic layers, thereby reducing electronic confinement.⁹

Figure 6.1 Molecular structures of the dications PyrEA, ImEA, and PEA.

Spurred by the aforementioned ‘design criteria’, two new organic dications (**Figure 6.1**) were prepared, designated as pyridinium ethyl ammonium (PyrEA) and imidazolium ethyl ammonium (ImEA), which successfully template formation of the 2D lead-iodide perovskites $\text{PyrEA}[\text{PbI}_4]$ (**1**) and $\text{ImEA}[\text{PbI}_4]$ (**2**). In order to disentangle the influence of these cations upon the structural and optoelectronic properties of the resulting materials, the 2D perovskite of the conventional cation phenylethylammonium ($(\text{PEA})_2[\text{PbI}_4]$; **3**) is included as a point of comparison. It was selected because PEA-based 2D perovskites have been widely explored for applications, including light emitting diodes (LEDs)²²⁻²³ and field-effect transistors (FETs),²⁴⁻²⁵ and in fundamental studies.²⁶⁻²⁹

6.2 Results and discussions

6.2.1 Structural features of (100)- and (110)-type 2D perovskites

The crystal structures of **1** and **2** shown in **Figures 6.2a** and **6.2b**, respectively, confirm successful formation of 2D lead-iodide perovskites. Despite the structural similarity of PyrEA and ImEA to PEA, the inorganic layer separations in **1** and **2** (9.899 Å and 9.537 Å, respectively) are almost half those in **3** (16.073 Å). This is due to the highly compact nature of the dications PyrEA and ImEA. Significantly, the shortest I⋯I contacts of 4.278 Å and 4.149 Å in **1** and **2**, respectively, are among the shortest interlayer distances ever recorded for 2D lead-iodide perovskites. For comparison, with histammonium,¹⁹ diimidazolium,³⁰ 1,4-diammonium naphthalene,³¹ and *N,N*-dimethylphenylene-*p*-diammonium²¹ cations respective I⋯I closest contacts of 4.386, 4.423, 4.902, and 4.978 Å are observed.

Figure 6.2 Single crystal X-ray structures of 2D perovskites (a) (PyrEA)[PbI₄] (**1**), (b) (ImEA)[PbI₄] (**2**), and (c) (PEA)₂[PbI₄] (**3**). Inorganic layer separations, defined as the distances between successive mean equatorial planes within an inorganic sheet, are 9.899, 9.537, and 16.073 Å for **1**, **2**, and **3**, respectively. Gray, purple, brown, and blue spheres represent Pb, I, C, and N atoms, respectively. H atoms are omitted for clarity.

Interestingly, whereas **1** adopts the more common (100) configuration, the inorganic layer in **2** is corrugated. More specifically, it displays a 3 × 3 (110) structural type. While the first 3 × 3 (110)-oriented lead bromide perovskite was published recently,³² **2** is the first example in the lead-iodide family templated by a single organic cation. This unusual structure is, obtained not only due to the presence and relative position of the N-H functionality within the imidazole core, which controls the hydrogen bonding interactions with neighboring bridging iodide ions of the inorganic layers (2.646 – 3.258 Å, **Figure 6.3**), but also the coulombic interactions between the alkylated endocyclic N-atoms of the ImEA²⁺ dications and terminally-bound iodide (3.698 – 3.877 Å). Notably, a similar

inorganic architecture was not obtained when the imidazolium-core was replaced with the isomeric pyrazolium-core. Instead, the latter templates formation of a 1D organic-inorganic lead-iodide hybrid, both in bulk materials and thin films (**Figure 6.4**). Meanwhile, the related histammonium cation only leads to formation of the conventional (100) structure (**Figure 6.5**). The associated crystallographic and refinement data of all hybrid perovskites crystal structures described herein summarized in **Section 6.5**.

Figure 6.3 Hydrogen bonding interactions between -NH functionality of the imidazolium cores and proximal bridging iodide ligands of the inorganic lattice (depicted as dashed lines) are believed to be the main driving force for corrugation of the lead-iodide sheets.

Analysis of the crystal structures of **1** and **2** reveals that they have, on the whole, more distorted inorganic lead-iodide octahedra than **3**. The degree of intra-octahedral distortion each perovskite exhibits can be quantified by comparing the following, previously reported, parameters:³³⁻³⁶ octahedral elongation (λ_{oct}), octahedral angle variance (σ^2_{oct}), and octahedral bond length distortion (Δ_{oct}). The equations for each parameter and an explanation of their meanings are as follows:

$$\text{Bond length distortion: } \Delta_{oct} = \frac{1}{6} \sum_{i=1}^6 \left[\frac{d_i - d_m}{d_m} \right]^2 \quad (\text{Eqn. 6.1})$$

$$\text{Octahedral elongation: } \lambda_{oct} = \frac{1}{6} \sum_{i=1}^6 \left[\frac{d_i}{d_0} \right]^2 \quad (\text{Eqn. 6.2})$$

$$\text{Octahedral angle variance: } \sigma^2_{oct} = \frac{1}{11} \sum_{i=1}^{12} (\alpha_i - 90)^2 \quad (\text{Eqn. 6.3})$$

where d_i corresponds to Pb–I bond length, d_m to average bond length, d_0 to center-to-vertex distance of a regular polyhedron of the same volume, and α_i to individual I–Pb–I angle. Δ_{oct} , λ_{oct} and σ^2_{oct} provide a quantitative measure of polyhedral distortion independent of the polyhedron effective size.

The resulting values (**Table 6.1**) represent the lead-iodide bond length and angle deformations in their constituent $[\text{PbI}_6]^{4-}$ octahedra, with larger values indicating a greater degree of distortion.^{33–36} The greater distortions in **1** and **2**, relative to **3**, are believed to stem from the comparatively large bulk of their ring-centred positive charges and the associated non-ideal (or absent) hydrogen bonding interactions with iodides of the inorganic layers.

Figure 6.4 (a) Molecular structure of pyrazolium ethyl ammonium (PyrzEA) dication. (b) Single crystal X-ray structure of 1D inorganic-organic hybrid $(\text{PyrzEA})\text{Pb}_2\text{I}_6$, where $\text{Pb}_2\text{I}_6^{2-}$ corresponds to the molecular formula of 1D lead-iodide chains. Gray, purple, brown, red, and blue spheres represent Pb, I, C, O, and N atoms, respectively. H atoms are omitted for clarity. (c) UV-Vis absorption spectra of $(\text{PyrzEA})\text{Pb}_2\text{I}_6$, spin coated onto a glass substrate. As is typical of a 1D lead-iodide hybrid material, it exhibits an excitonic peak at around 430nm. Inset is a photograph (i.e., visual appearance) of the corresponding thin film.

Table 6.1 Distortion parameters derived from the single crystal X-ray structures of 2D perovskites **1-3**^a

Compound	$\lambda_{\text{oct (avg)}}^b$	$\sigma^2_{\text{oct (avg)}}^c$	$\Delta_{\text{oct (avg)}}^d$ ($\times 10^{-4}$)
1	1.0070	24.18	1.24
2	1.0076	23.26	7.97
3	1.0009	2.80	0.61

^aAveraged distortion parameters are given because X-ray structures of ImEA[PbI₄] and (PEA)₂[PbI₄] contain three and two geometrically distinct octahedra, respectively. ^bOctahedral elongation. ^cOctahedral angle variance. ^dOctahedral bond length distortion.

The effect of structural distortions and ordering of octahedra manifest in single crystal Raman spectroscopy measurements. In order to resolve individual vibrational modes, Raman spectra of **1-3** were collected at room temperature (**Figure 6.6**) and also at 80 K (**Figure 6.7**), where more accurate data fitting can be achieved. It has previously been shown for lead-iodide perovskites that low wavenumber modes are mainly due to vibrations of the inorganic sublattice, while the modes above $\sim 150 \text{ cm}^{-1}$ originate from molecular vibrations of the organic cations.³⁷⁻³⁹

Figure 6.5 (a) Molecular structure of histammonium dication (HA). (b) Single crystal X-ray structure of 2D perovskite (HA)PbI₄, where PbI₄²⁻ corresponds to the molecular formula of 2D lead-iodide sheets. Gray, purple, brown, and blue spheres represent Pb, I, C, and N atoms, respectively. H atoms are omitted for clarity.

According to previous assignments, the modes below $\sim 70 \text{ cm}^{-1}$ are associated with I-Pb-I bending. In particular, the two bands around 40 cm^{-1} are likely vibrations distorting the

octahedra.⁴⁰⁻⁴² The presence of two distinct bands is due to inequivalence of the axial and equatorial iodine atoms, as well as distortion of the octahedra.

Figure 6.6 Low wavenumber Raman spectra of (PyrEA)PbI₄ (1), (ImEA)PbI₄ (2), and (PEA)₂PbI₄ (3), recorded at room temperature. Circles represent experimental data; red, blue, and green lines are the respective fitting components; and pink lines correspond to the resulting cumulative fits. Spectra are normalised and labels b_1 and b_2 correspond to the most intense vibrational modes.

Figure 6.7 Low wavenumber Raman spectra of the 2D perovskites (PyrEA)PbI₄ (1), (ImEA)PbI₄ (2), and (PEA)₂PbI₄ (3), recorded at 80 K.

Similarly, the vibrations in the range of 70-150 cm^{-1} , assigned to Pb-I stretching,⁴³ exhibit different frequencies for the in-plane and out-of-plane modes. Most notably, the frequency difference of the two most intense modes in **3** (b_1 and b_2) is equal to 6 cm^{-1} , while in **1** and **2** it reaches 8 and 9 cm^{-1} , respectively. Those two modes can be attributed to distortions of octahedra⁴² in different directions, with greater distortion resulting in larger splitting. The bands observed between 90 and 130 cm^{-1} are broader and more poorly resolved in **1** than they are in **3**. This is due to a higher number of distinct vibrational modes in the former relative to the latter, which results from a greater variety of Pb-I bond lengths. Such a scenario is consistent with the more distorted crystal structure of **1** compared to that of **3**.

Meanwhile, the case of **2** is more complicated than those of **1** and **3**. This is most likely due to the distinct 3×3 (110) structural type seen for **2**, wherein the frequency shifts and band broadening might be due to the different connectivity of the octahedra, in addition to the afore discussed structural distortions. It should be emphasized that a better understanding of how the vibrational properties of **1-3** depend upon their structural distortions would require precise assignment of their Raman spectra *via* computational studies.

6.2.2 Optical characteristics of 2D perovskite thin films

Investigation of the photophysical properties of **1-3** were then undertaken using thin film samples as they more closely mimic the PV device settings required for application. To ensure surface consistency, scanning electron microscope (SEM) images were recorded and confirm that all films are smooth and compact (**Figure 6.8**). Absorption spectra of all hybrid perovskites under study are presented in **Figure 6.9a** and their absorption profiles are summarized in **Table 6.2**.

In analogy to other 2D perovskites, the intense bands in the spectra of **1** and **2** at 544 and 522 nm, respectively, can be attributed to excitonic absorptions of the 2D lead-iodide lattices. Both are red shifted with respect to the analogous transition in **3** (514 nm). However, a fair comparison can only reasonably be made between **1** and **3**, since they are

both (100)-oriented (and **2** is not). As such, **1** represents a rare example of a heavily bathochromically shifted 2D perovskite, and there are only six other compounds reported to exhibit similarly shifted absorption features.^{21, 44-46} It is also noteworthy that **2** has a lower energy excitonic transition than **3**. This is because other works report that (110)-oriented structures characteristically display blue-shifted bandgaps relative to their (100) congeners.^{32, 43}

Figure 6.8 Field emission scanning electron micrographs of the surface morphologies of thin films of (a) (PyrEA)[PbI₄] (**1**), (b) (ImEA)[PbI₄] (**2**), and (c) (PEA)₂[PbI₄] (**3**) with insets showing the visual appearances of spin-coated thin films of the materials. Thin films of the 2D perovskites were created by spin coating onto glass substrates.

The aforementioned bathochromic shifts are attributed to higher overall Pb-I-Pb bond angles between the adjoining [PbI₆]⁴⁻ octahedra in **1** (159° to 174°) and **2** (146° to 166°) relative to **3** (151° to 153°) (see **Figure 6.10**). This is consistent with previous reports, in which it was revealed through Hückel tight-binding band structure calculations, that combinations of in-plane and out-of-plane distortion angles (**Figures 6.10d and 6.10e**) have the greatest impact on the tuning of the bandgap. More specifically, more ideal Pb-I-Pb angles were shown to allow for increased orbital overlap, which results in greater band dispersion and, thus, smaller bandgaps.^{20, 47-49} It is postulated that the observed Pb-I-Pb bond angle relaxation is due to the lower charge density of pyridinium and imidazolium cations relative to primary ammonium groups. As a consequence, there is a significantly reduced coulombic driving force for bringing the lead-iodide octahedra into close proximity with the organic counteranions, which would otherwise necessitate compression of the Pb-I-Pb bond angles between neighboring octahedra (thus, creating distortion).²⁰ As such, this work demonstrates that reduction of bond angle distortions can be achieved by judicious choice of organic counteranions.

Figure 6.9 (a) UV-vis absorption spectra of (PyrEA)PbI₄ (**1**), (ImEA)PbI₄ (**2**), and (PEA)₂PbI₄ (**3**). (b) Photoluminescence (PL) spectra of **1-3**, plus Gaussian fittings, recorded at RT, using excitation at 405 nm. (c) Time-resolved photoluminescence (TRPL) decays and fits for **1-3**. (d) Temperature-dependent integrated PL intensity for **1-3**. Excitonic binding energies (values given) were extracted by fitting to the Arrhenius equation.

In order to eliminate the possibility that the red shifted absorption features of **1** and **2** derives from charge transfer between the inorganic and organic components, the (100)-oriented 2D piperidinium ethylammonium perovskite (PipEA)[PbI₄] were synthesized (**Figure 6.11**). Consistent with observations for **1** and **2**, the resulting perovskite is still red in color (**Figure 6.11c**, inset), despite the cation used being aliphatic in nature and, thus, having no low-lying unoccupied molecular orbitals. Therefore, its bathochromically shifted excitonic band at 541 nm (**Figure 6.11c**) can be attributed to the mildly distorted Pb-I-Pb angles in its inorganic lattice (value of 164° to 174°), rather than charge transfer.

Figure 6.10 Top and side views of 2D inorganic lattices of (a) (PyrEA)[PbI₄] (**1**), (b) (ImEA)[PbI₄] (**2**) and (c) (PEA)₂[PbI₄] (**3**). Crystallographic axes are provided and the red lines denote particular Pb-I-Pb bond angles. The Pb-I-Pb bond angles between conjoined [PbI₆]⁴⁺ octahedra in **1** (159° to 174°), **2** (146° to 166°), and **3** (151° to 153°) are obtained from Mercury, where the smallest angles are measured without considering the exact planes in which in-plane and out-of-plane distortions occur. Thus, the values obtained are contributed to by both types of distortion and, in this report, there is no attempt to deconvolute the individual components. Schematic diagrams depict the (d) in-plane and (e) (complementary) out-of-plane distortion angles within the inorganic lattices. The blue line in (e) represents the mean plane of lead atoms within the 2D sheets.

At room temperature, upon excitation at 480 nm, both **1** and **2** show broad photoluminescences (PLs) consisting of respective narrow bandgap emissions peaks centred at 557 nm (P1a) and 529 nm (P2a) that overlap with broader, longer wavelength Gaussian-fitted peaks at 582 nm (P1b) and 540 nm (P2b), respectively (**Figure 6.9b**; **Table 6.2**). In contrast, **3** exhibits a typical narrow band emission (full width at half maximum, FWHM = 21 nm) at 525 nm (P3), with a Stokes shift of just 9 nm, that can be fit by a *single* Gaussian. As with that observed in the lead-iodide perovskite templated by 2,2-

(ethylenedioxy)bis(ethylammonium),⁴³ the existence of two types of emissions in **1** and **2** is attributed to the presence of a larger variety of distinct radiative centers in their highly distorted octahedra.

Table 6.2 Summary of selected optical parameters for **1-3**^a

Compound	Excitonic absorption (nm)	Bandgap (eV)	Excitonic emission (nm)	RT PL FWHM
1	544	2.48	558	44 nm
2	522	2.54	527	31 nm
3	514	2.58	525	21 nm

^aBandgaps are obtained through linear fitting of the thin-film UV-vis absorption spectra. Excitonic emission position and photoluminescence full width at half-maximum (PL FWHM) are taken from the actual room temperature PL spectra of the 2D perovskites, and not the constituent peaks of Gaussian fits of the data.

To evaluate the charge carriers dynamics of the materials, time-resolved (TR) PL spectroscopic measurements were performed for **1-3**. For all three compounds, two decay time constants were needed to accurately fit the fluorescence decay profiles (**Figure 6.9c** and **Table 6.3**), which were recorded at their respective PL wavelength maxima. (The residuals for the fit and the instrument response function can be found in **Figure 6.12**). It was found that **1** and **2** ($\tau_{ave} = \sim 620(60)$ and $\sim 730(70)$ ps, respectively) feature longer average decay lifetimes than **3** ($\tau_{ave} = \sim 400(40)$ ps). More specifically, **1** and **2** exhibit biexponential decay composed of $\sim 410(40)$ ps (90%) and $\sim 2.50(0.20)$ ns (10%) components and $\sim 350(30)$ ps (81%) and $\sim 2.35(0.20)$ ns (19%) components, respectively. On the other hand, fitting fluorescence decay of **3** requires $\sim 360(40)$ ps (99%) and $\sim 4.51(0.40)$ ns (1%) components. Although it is tempting to attribute these differences to structural factors, further investigations are required before assignment of the decay mechanisms can be made. Regardless, the slower PL decay of **1** and **2**, relative to **3**, which result from greater contributions of the slower decay component, infers that more useful free-charge carriers can be generated in the former two cases during use as solar absorbers.

Figure 6.11 (a) Molecular structure of piperidinium ethyl ammonium (PipEA) dication. (b) Single crystal X-ray structure of 2D perovskite (PipEA)PbI₄, where PbI₄²⁻ corresponds to the molecular formula of 2D lead-iodide sheets. Gray, purple, brown, and blue spheres represent Pb, I, C, and N atoms, respectively. H atoms are omitted for clarity. (c) UV-Vis absorption and photoluminescence (PL) spectra of (PipEA)PbI₄ spin coated onto a glass substrate. As is typical of a 2D lead-iodide perovskite, it exhibits excitonic absorption and PL peaks at about 540 and 575 nm, respectively. Inset is a photograph (i.e., visual appearance) of the corresponding thin film.

Table 6.3 Summary of the time-resolved photoluminescence (TRPL) parameters of the 2D perovskites **1** – **3**.

Parameters	Compounds		
	(PyrEA)PbI ₄ (1)	(ImEA)PbI ₄ (2)	(PEA)PbI ₄ (3)
PL decay τ_1 (ps)	~410 (90%)	~350 (81%)	~360 (99%)
PL decay τ_2 (ns)	~2.50 (10%)	~2.35 (19%)	~4.51 (1%)
PL decay τ_{ave} (ps)	~620	~730	~400

To further assess the photogenerated charge carriers behavior in **1**, **2** and **3**, their emission quenching behavior is also investigated by carrying out temperature-dependent PL measurements between 77 and 300 K. The resulting spectra are presented in **Figure 6.13**.

For clarity, intensities of the peak emissions have been normalized. (Figure 6.14 shows evolution of the PL spectra with retention of relative intensity information.) Satisfactory fitting of the low-temperature PL features of **3** and **1** requires one and two Gaussians, respectively, while three are required for **2**. Details of PL peak deconvolutions are presented in Figure 6.15. Using P1a, P2a, and P3 extracted from the temperature-dependent measurements, excitonic activation energies of **1**, **2**, and **3** can be estimated by plotting emission intensity against the inverse of temperature (Figure 6.9d) and fitting them to the following equation:

$$I(T) = \frac{I_0}{1 + Ae^{-E_a/k_B T}} \quad (\text{Eqn. 6.4})$$

where, I_0 corresponds to emission intensity at low temperature, E_a to the activation energy, and k_B to the Boltzmann constant.

Figure 6.12 (a) Time-resolved photoluminescence (TRPL) decays and fits for **1-3** along with the instrument response function (IRF). Residuals for the lifetime decay fittings of 2D perovskites **1** (b), **2** (c), and **3** (d).

From the fit of total PL intensity as a function of temperature to Equation 1,^{27-28, 53} approximate activation energies of 96.5 and 93.6 meV were extracted for **1** and **2**, respectively. Remarkably, these values are less than half of that obtained for **3**, which in agreement with previous work is estimated to be 229.9 meV.⁹ Moreover, the E_a values of **1** and **2** are among the lowest reported for an $n = 1$ lead-iodide perovskite. It is proposed that such low values derive from short separation between the inorganic layers, effectively, making them more ‘3D-like’ in character. The activation energy obtained for **3** may well represent the excitonic binding energy and, if that is the case, the decrease of integrated PL intensity upon lowering the temperature can be attributed to partial ionization of the excitons, as was the case in the study conducted in ref [8]. However, this may not be the case for **1** and **2**, as the higher density of defect states arising from their relatively more distorted lead-iodide octahedra could lead to other possibilities. To explore this possibility, investigations that include single crystal photophysical studies of the materials have been initiated.

Figure 6.13 Temperature-dependent PL spectra, recorded in the range 77 to 298 K, using an excitation wavelength (λ_{ex}) of 405 nm, of (a) (PyrEA)PbI₄ (**1**), (b) (ImEA)PbI₄ (**2**), and (c) (PEA)₂PbI₄ (**3**). For clarity, the PL intensities have been *normalized*.

Figure 6.14 Temperature-dependent photoluminescence (PL) spectra of thin films of (a) $(\text{PyrEA})[\text{PbI}_4]$ (1), (b) $(\text{ImEA})[\text{PbI}_4]$ (2), and (c) $(\text{PEA})_2[\text{PbI}_4]$ (3) with the relative intensity of each spectrum is shown. The samples were measured in the range 77 – 298 K, using an excitation wavelength (λ_{ex}) of 405 nm.

Figure 6.15 Peak deconvolution, using Gaussian fitting, of temperature-dependent photoluminescence (PL) spectra of thin films of (a) (PyrEA)[PbI₄] (**1**), (b) (ImEA)[PbI₄] (**2**), and (c) (PEA)₂[PbI₄] (**3**). Gaussians 1 and 2 in (a) correspond to the P1a and P1b PL peaks of **1** at RT. Gaussians 1 and 2 in (b) could be P2a peak of **2** at RT, while Gaussian 3 is related to P2b. In agreement with the previous report,¹¹⁻¹² only 1 Gaussian is needed to deconvolute the PL peaks of **3** in the range of temperatures 77K – 298 K. (Please note, the assignments of each of the PL peaks are speculative and verification of their origins is beyond the scope of this study.) Integrated intensity of Gaussian 1 in both (a) and (b) were used to estimate the excitonic activation energy in **1** and **2**, respectively.

6.2.3 Application in solar cells, crystallization behavior, and electrical properties

To exploit the superior semiconducting properties of **1** and **2**, ($n = 1$ where n refers to number of contiguous inorganic 2D layers; i.e., not separated by organic cations) 2D perovskite solar cells adopting the mesoporous architecture were fabricated (**Figure 6.16a**). The band energy diagram specifying the energies of the valence and conduction bands of **1-3** relative to the other charge transporting layers comprising the devices is given in **Figure 6.17**. The optimized precursor concentration for spin-coating DMF solutions of all materials was found to be 0.50 M. (Details of concentration-dependent device performance

parameters, average device performances, and corresponding characterization data can be found in **Tables 6.4-6.8**) Current density-voltage (J - V) characteristics of the best devices fabricated from each of the 2D perovskites are presented in **Figure 6.16b**. The band energy diagram of the each of the device stack is presented in **Figure 6.17**. Unsurprisingly, for active layers of similar thickness, as evidenced by scanning electron micrographs (**Figure 6.18**), much higher short circuit current densities (J_{sc}) could be harvested for photovoltaic devices containing **1** and **2** (2.23 and 3.12 mA/cm², respectively) compared with those of **3** (0.32 mA/cm²).

Table 6.4 Photovoltaic performance of the best performing 2D perovskite solar cells fabricated with different concentration solutions of precursors. Thickness of the perovskite layers was measured by field-emission scanning electron microscopy (FE-SEM).

Samples (best device)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	Efficiency (%)	Capping layer thickness (nm)
1 (1.000 M)	0.76	0.841	51.78	0.340	775
1 (0.500 M)	0.82	2.489	70.34	1.426	191
1 (0.250 M)	0.79	1.573	69.28	0.859	-
1 (0.125 M)	0.54	1.178	48.27	0.306	-
2 (1.000 M)	0.82	1.123	26.70	0.240	725
2 (0.500 M)	0.83	3.936	56.15	1.834	171
2 (0.250 M)	0.85	3.110	48.88	1.291	-
2 (0.125 M)	0.65	1.156	58.16	0.439	-
3 (1.000 M)	0.76	0.077	29.15	0.020	788
3 (0.500 M)	0.70	0.361	30.22	0.076	183
3 (0.250 M)	0.23	0.576	32.87	0.044	-
3 (0.125 M)	0.12	0.521	33.07	0.021	-

Table 6.5 Photovoltaic performance of devices fabricated from 0.50 M (PyrEA)[PbI₄] precursor solutions.

Samples	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	Efficiency (%)
Device 1	0.80	2.490	65.54	1.304
Device 2	0.78	2.514	68.17	1.341
Device 3	0.81	2.489	70.34	1.426
Device 4	0.80	2.507	69.33	1.391
Device 5	0.82	2.483	69.28	1.417
Device 6	0.82	2.461	65.35	1.315

Table 6.6 Photovoltaic performance of devices fabricated from 0.50 M (ImEA)[PbI₄] precursor solutions.

Samples	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	Efficiency (%)
Device 1	0.83	3.936	56.15	1.834
Device 2	0.87	3.780	55.28	1.809
Device 3	0.82	3.928	55.76	1.796
Device 4	0.84	3.854	56.54	1.828
Device 5	0.83	4.158	50.52	1.726
Device 6	0.85	3.9276	54.49	1.823

Table 6.7 Photovoltaic performance of devices fabricated from 0.50 M (PEA)₂[PbI₄] precursor solutions.

Samples	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	Efficiency (%)
Device 1	0.70	0.361	30.22	0.076
Device 2	0.80	0.398	25.17	0.076
Device 3	0.81	0.260	25.25	0.053
Device 4	0.80	0.291	25.48	0.059
Device 5	0.71	0.356	28.24	0.071
Device 6	0.71	0.365	27.57	0.073

Table 6.8 Average photovoltaic performance of devices fabricated from 0.50 M (PyrEA)[PbI₄], (ImEA)[PbI₄], and (PEA)₂[PbI₄] precursor solutions.

Samples (6 cells)	Average V_{oc} (V)	Average J_{sc} (mA/cm ²)	Average FF (%)	Average efficiency (%)
1 (0.50 M)	0.81 ± 0.02	2.491 ± 0.019	68.00 ± 2.10	1.366 ± 0.053
2 (0.50 M)	0.84 ± 0.02	3.931 ± 0.127	54.79 ± 2.21	1.803 ± 0.040
3 (0.50 M)	0.76 ± 0.05	0.338 ± 0.052	26.99 ± 2.05	0.068 ± 0.010

Figure 6.16 (a) Typical cross-sectional scanning electron micrograph of 2D perovskite solar cells, with mesoporous architecture, employed in this study. (b) Photovoltaic current density-voltage ($J-V$) characteristics of best performing solar cells fabricated using (PyrEA)PbI₄ (**1**), (ImEA)PbI₄ (**2**), and (PEA)₂PbI₄ (**3**) as the solar absorbers. Dotted and solid lines represent measurements in the absence and presence of white light irradiation (1 sun; AM 1.5G), respectively. (c) External quantum efficiency (EQE) spectra of the best performing solar cells containing **1-3** (standard, vertical device configuration). Statistical representations of (d) Short-circuit current density (J_{sc}) and (e) power conversion efficiency (PCE) measured for 6 photovoltaic devices each for **1**, **2**, and **3**.

Figure 6.17 Band energy diagrams of (PyrEA)[PbI₄] (**1**), (ImEA)[PbI₄] (**2**), (PEA)₂[PbI₄] (**3**), with the energies of the charge transport materials and electrodes comprising the solar cells included for reference. Valence band energies were estimated using photoelectron spectroscopy in air (PESA) measurements (**Figure 6.25**) and the band gaps were extracted from UV-Vis absorbance spectra (**Figure 6.26**).

Figure 6.18 Cross-sectional view of field emission scanning electron microscope (FESEM) images of different solar cells containing the 2D perovskites (a) (PyrEA)[PbI₄] (**1**), (b) (ImEA)[PbI₄] (**2**), and (c) (PEA)₂[PbI₄] (**3**). Insets show prototypes of the solar cells fabricated.

Closer examination revealed that, in addition to reduced inorganic sheet separations, orientation of the 2D perovskite crystallite grains also plays a role in the generation of higher photocurrent in **1** and **2**. Glancing angle X-ray diffraction (GAXRD) patterns for thin films of **1** and **2**, both on top of glass and on top of TiO₂-coated fluorine-doped tin oxide (FTO), show very different behavior to **3** (**Figure 6.19**). While **3** prefers to grow with the 2D lead-iodide layers parallel to the substrate, even in device settings (**Figure 6.19c**), the crystallites in **1** and **2** tend to display no fixed orientation (**Figures 6.19a** and **6.19b**), regardless of the nature of the substrates used. Such a tendency is more pronounced

in **1**, where peaks ascribed to (020), (002), (112), (140) and (034) reflections are found to coexist in comparable intensity. This unique crystallization property is distinct to that of histammonium-based lead-iodide perovskite, where a preferential perpendicular growth orientation was suggested.¹⁹

Figure 6.19 Glancing angle X-ray diffraction (GAXRD) patterns of thin layers of (a) (PyrEA)PbI₄ (**1**), (b) (ImEA)PbI₄ (**2**), and (c) (PEA)₂PbI₄ (**3**) deposited on glass (blue lines) and mesoporous titania-coated fluorinated tin oxide (TiO₂/FTO; red lines). For comparison, powder XRD patterns simulated using single crystal X-ray structures of **1**, **2**, and **3** are also included. Star symbols (*) denote peaks associated with the TiO₂/FTO substrate.

The effect of crystallite orientation on photocurrent collection was probed by performing conductivity measurements using a different configuration of electrodes. While the electrodes were placed perpendicular to the perovskite layers in the aforementioned solar cells devices (a ‘vertical’ configuration), in four-probe measurements they were evaporated

parallel to one another (**Figure 6.20a**). In the latter setting, upon white light irradiation, **3** displays higher photocurrent. At a bias as low as 2.0 V, the current generated by **3** increases from 14.79 pA (dark) to 63.39 nA (light), corresponding to an on/off ratio of ~ 4286 (**Figure 6.20d**). Meanwhile, induced current only increases from 12.67 pA (dark) to 1.13 nA (light) in the case of **1** and from 10.25 pA (dark) to 0.70 nA (light) for **2**, leading to respective on/off ratios of only 89 and 68 (**Figures 6.20b and 6.20c**). This represents an approximate fifty-fold greater current enhancement in **3** relative to **1** and **2**.

Figure 6.20 (a) Schematic diagrams of ‘vertical’ and ‘horizontal’ device configurations used to assess the charge transport properties of the 2D perovskites. I-V curves of ‘horizontal devices’ based on (b) (PyrEA)[PbI₄] (**1**), (c) (ImEA)[PbI₄] (**2**), and (d) (PEA)₂[PbI₄] (**3**). Straight and dotted lines correspond to conductivity in absence and presence of white light (1 sun), respectively. At 2.0 V, the on/off ratio of current generation is ~ 89 , 68, and 4286 for **1**, **2**, and **3**, respectively. (e) Time-dependent photoresponses of **1**, **2**, and **3** in devices fabricated with a horizontal configuration at 2.0 V bias, upon repeated on and off white light irradiation (1 sun, interval 20 s, measured for 250 s).

Figure 6.21 UV-Vis absorption coefficients of thin films of (PyrEA)PbI₄ (**1**), (ImEA)PbI₄ (**2**), (PEA)₂PbI₄ (**3**). The values at each wavelength were extracted using the following equation, which takes into account the reflectance and transmittance of the films: $\alpha_{film}(\lambda) = \frac{1}{d_{film}} \ln \left(\frac{1 - R_{film}(\lambda)}{T_{film}(\lambda)} \right)$.¹³ The films of **1**, **2**, and **3** used for measurement were 293, 278, and 338 nm thick, respectively.

The contrast in conductivity behaviour seen for **1-3** between the two device configurations derives from the relative orientations of the electrodes and inorganic lattices. More specifically, when studies are performed for **3** using the four-probe configuration conductivity *within* the lead-iodide layers is measured, while in the perpendicular arrangement of electrodes it is *between* layers. In contrast, regardless of electrode orientation, conductivity in **1** and **2** is always between less-oriented layers. Nonetheless, it is interesting to note that although charge carrier hopping from one less-oriented grain to another in **1** and **2** cannot proceed as efficiently as it does within the lead-iodide layers of **3**, it proves to be more efficient than inter-layer transport, where propagation through space is required for charge collection.

Finally, incident photon-to-current efficiency (IPCE) spectra presented in **Figure 6.16c** affirm the aforementioned device results. The integrated current densities were found to be 2.49 mA/cm² and 3.94 mA/cm² for **1** and **2**, while in the case of **3** it was only 0.73 mA/cm². In addition, they exhibit absorption onsets similar to their UV-vis absorption spectra, indicating that the bathochromic shifts in **1** and **2** contribute to generation of useful charge carriers. Moreover, the IPCE results also demonstrate better conversion of light to useful

charge carriers in **1** and **2**, despite them having similar absorption coefficients as **3** (Figure 6.21). The superior charge collection properties observed in devices based on **2** relative to those of **1** can be attributed to a number of factors. Not only does the former possess a longer charge carrier lifetime and lower exciton activation energy, it also features better crystallization properties and lower surface roughness. The latter two factors are evident from excitation power-dependent PL experiments (Figure 6.22), where trap densities of $(6.03 \pm 1.2) \times 10^{17}$ and $(5.68 \pm 1.82) \times 10^{17} \text{ cm}^{-3}$ were measured for **1** and **2**, respectively, and atomic force microscopy (AFM) measurements (Figure 6.23), from which respective surface roughness values of 43 and 17 nm were obtained.

Figure 6.22 (a) Photoexcited carrier density (n_c) vs. integrated PL density (I_{PL}) for **1-3**. Dashed lines are numerical fits that take into account film thickness and relative absorbance at the excitation wavelength.¹⁴ Laser fluence-dependent photoluminescence (PL) spectra of thin films (b) (PyrEA)[PbI₄] (**1**) and (c) (ImEA)[PbI₄] (**2**). The samples were measured in the range of fluence set between 2.0 – 13.7 $\mu\text{J} \cdot \text{cm}^{-2}$ at respective emission wavelengths of 558 nm and 529 nm.

In particular, the IPCE of up to 60% measured for **2** is, as far it can be determined, the best ever demonstrated for a pure $n = 1$ lead-iodide material. For comparison, histammonium-

¹⁹ and butyl-1,4-diammonium-based¹⁸ 2D perovskites with comparable inorganic layer separation were previously reported to be capable of demonstrating IPCEs of only 30% and 35%, respectively. The high IPCE values of **1** and **2**, coupled with good open circuit voltages (V_{oc}) of 0.82 – 0.83 V and fill-factors (FF) of over 50 %, allowed photovoltaic cells with power conversion efficiencies (PCEs) of 1.43 – 1.83 % to be obtained for these materials. Statistical representations of J_{sc} and PCE (See **Figures 6.24a** and **6.24b** for parameters V_{oc} and FF, respectively) of 6 devices based on **1**, **2**, and **3**, depicted in **Figures 6.16d** and **6.16e**, confirm reproducibility of the device fabrication process.

Figure 6.23 Topological images of the surfaces of (a) (PyrEA)[PbI₄] (**1**) and (b) (ImEA)[PbI₄] (**2**) films. Average films roughness for **1** and **2** are 43 nm and 17 nm, respectively. The size of the atomic force microscopy (AFM) images is 20 x 20 μm².

Figure 6.24 Statistical representations of 6 devices based on (PyrEA)PbI₄ (**1**), (ImEA)PbI₄ (**2**), and (PEA)₂PbI₄ (**3**) for parameters a) open-circuit voltage (V_{oc}) and b) fill-factor (FF).

Figure 6.25 Photoelectron spectroscopy in air (PESA) measurements for (PyrEA)[PbI₄] (**1**), (ImEA)[PbI₄] (**2**), and (PEA)₂[PbI₄] (**3**). Solid lines represent linear fits of the two distinct domains in each data set, and the intersection between them provides an estimate of the valence band energy of the 2D perovskites (-5.54, -5.54 and -5.61 eV for **1**, **2** and **3**, respectively).

Figure 6.26 Absorption spectra of thin films of (PyrEA)[PbI₄] (**1**), (ImEA)[PbI₄] (**2**), and (PEA)₂[PbI₄] (**3**). Solid lines are from extrapolation of the rising edge of the absorbance plots (i.e. the linear parts of the curves) and correspond to the band gaps of the 2D perovskites.

The improvement in photovoltaic devices made out of **1** and **2** represents a greater than 20-fold improvement over those fabricated using the well-studied PEA cation (**Table 6.9**). More importantly, the best performing cells represent the highest values reported, so far, for $n = 1$ lead-iodide 2D perovskites. This includes the recent report by Stupp and co-workers detailing enhancement of out-of-plane conductivity of a $n = 1$ perovskite by use of highly conjugated pyrene organic cations. Their work culminated in a device with a PCE of 1.38%.⁸ This study's distinct approach attests to the advantages of employing compact

organic dications, which can engender bathochromatically shifted optical features, very short inorganic layer separation and unique crystallization properties. **Figure 6.27** summarizes the progress in efficiency of solar cells based upon pure 2D lead-iodide perovskites templated by different organic cations.

Table 6.9 Summary of photovoltaic parameters from the best performing solar cells fabricated from **1-3**^a

Compound	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	Thickness (nm)
1	0.82	2.49	70.34	1.43	191 nm
2	0.83	3.94	56.15	1.83	171 nm
3	0.80	0.37	25.17	0.08	183 nm

^aConcentration of precursor solution used in spin-coating of all compounds was 0.50 M. V_{oc} = open circuit voltage; J_{sc} = short circuit current density; FF = fill factor; and PCE = power conversion efficiency. Thickness of the active layer was determined from scanning electron micrographs of each sample.

Figure 6.27 Summary of progress in efficiency of solar cells based upon pure $n = 1$ 2D lead-iodide perovskites as a function of templating organic cations.

6.3 Summary

In conclusion, pyridinium ethyl ammonium (PyrEA) and imidazolium ethyl ammonium (ImEA) dications have been successfully employed to template formation of new 2D hybrid lead-iodide perovskites (PyrEA)PbI₄ (**1**) and (ImEA)PbI₄ (**2**). Their properties were compared with the well-studied 2D perovskite (PEA)₂PbI₄ (**3**), templated by the phenyl

ethyl ammonium cation (PEA). As a consequence of the compact nature of their dications, **1** and **2** are endowed with super short 2D inorganic layer separations. Furthermore, the relatively low charge density of the cationic aromatic cores of PyrEA and ImEA leads to relaxation of the Pb-I-Pb inter-octahedral distortions. This causes **1** and **2** to have bathochromically shifted optical features relative to **3**. However, as is apparent from X-ray crystallographic and Raman spectroscopic analyses, the presence of bulky pyridinium and imidazolium rings in **1** and **2**, combined with their inefficient hydrogen bonding interactions with terminal and/or bridging iodides of the inorganic layers, results in an overall increase in structural intra-octahedral distortion compared with **3**. As a consequence, **1** and **2** both exhibit broad photoluminescences at room temperature. Based upon preliminary temperature- and flux density-dependent PL investigations, this can be attributed to the presence of defect states.

Low solubility of the organic dications PyrEA and ImEA, even in polar organic solvents like dimethylformamide (DMF), causes **1** and **2** to manifest unique crystallization behavior. More specifically, upon spincoating, the inorganic layers do not adopt a regular growth direction parallel to the surface of the substrates. Instead, their crystallites have no fixed orientation. Such unusual growth properties facilitate better charge transport and collection within conventional perovskite solar cell (PSC) architectures, in which the electrodes are located on the top and bottom of the devices. This, combined with longer lifetimes of photoinduced charge carriers and lower excitonic activation energies than those of **3**, allows harvest of short-circuit current densities (J_{sc}) from PSCs containing **1** and **2** of more than 2.5 mA/cm². Superior charge collection in these materials is affirmed by incident photons-to-current efficiency (IPCE) measurements for the corresponding devices, which show unprecedented 2D perovskite IPCE conversions of up to 60%. Coupled with good open circuit voltages (V_{oc}) of 0.82 – 0.83 V and fill-factors (FF) of over 50 %, photovoltaic cells with power conversion efficiencies of 1.43 – 1.83 % can be obtained for **1** and **2**. These values are the highest reported, so far, for pure 2D lead-iodide perovskite solar cells.

6.4 Bibliography

1. Saparov, B.; Mitzi, D. B. *Chem. Rev.* **2016**, *116*, 4558-4596.
2. Cheng, Z.; Lin, J. *Cryst. Eng. Comm.* **2010**, *12*, 2646-2662.
3. Smith, I. C.; Hoke, E. T.; Solis-Ibarra, D.; McGehee, M. D.; Karunadasa, H. I. *Angew. Chem. Int. Ed.* **2014**, *53*, 11232-11235.
4. 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. *J. Am. Chem. Soc.* **2016**, *138*, 2649-2655.
5. Cao, D. H.; Stoumpos, C. C.; Farha, O. K.; Hupp, J. T.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2015**, *137*, 7843-7850.
6. Tsai, H.; Nie, W.; Blancon, J. C.; Stoumpos, C. C.; Asadpour, R.; Harutyunyan, B.; Neukirch, A. J.; Verduzco, R.; Crochet, J. J.; Tretiak, S.; Pedesseau, L.; Even, J.; Alam, M. A.; Gupta, G.; Lou, J.; Ajayan, P. M.; Bedzyk, M. J.; Kanatzidis, M. G. *Nature*. **2016**, *536*, 312-316.
7. Koh, T. M.; Thirumal, K.; Soo, H. S.; Mathews, N. *ChemSusChem* **2016**, *9*, 2541-2558.
8. Passarelli, J. V.; Fairfield, D. J.; Sather, N. A.; Hendricks, M. P.; Sai, H.; Stern, C. L.; Stupp, S. I. *J. Am. Chem. Soc.* **2018**, *140* (23), 7313-7323.
9. Hong, X.; Ishihara, T.; Nurmikko, A. V. *Phys. Rev. B.* **1992**, *45*, 6961-6964.
10. Ishihara, T.; Takahashi, J.; Goto, T. *Phys. Rev. B* **1990**, *42*, 11099-11107.
11. Ishihara, T. *J. Lumin.* **1994**, *60&61*, 269-274.
12. Tanaka, K.; Kondo, T. *Sci. Technol. Adv. Mater.* **2016**, *4* (6), 599-604.
13. Stoumpos, C. C.; Cao, D. H.; Clark, D. J.; Young, J.; Rondinelli, J. M.; Jang, J. I.; Hupp, J. T.; Kanatzidis, M. G. *Chem. Mater.* **2016**, *28* (8), 2852-2867.
14. Wu, X.; Trinh, M. T.; Zhu, X. Y. *J. Phys. Chem. C* **2015**, *119* (26), 14714-14721.
15. Tabuchi, Y.; Asai, R.; Rikukawa, M.; Sanui, K.; Ishigure, K. *J. Phys. Chem. Solids* **2000**, *61*, 837-845.
16. Kamminga, M. E.; Fang, H.-H.; Filip, M. R.; Giustino, F.; Baas, J.; Blake, G. R.; Loi, M. A.; Palstra, T. T. M. *Chem. Mater.* **2016**, *28* (13), 4554-4562.
17. Muljarov, E. A.; Tikhodeev, S. G.; Gippius, N. A.; Ishihara, T. *Phys. Rev. B* **1995**, *51* (20), 14370-14378.

18. Safdari, M.; Svensson, P. H.; Hoang, M. T.; Oh, I.; Kloo, L.; Gardner, J. M. *J. Mater. Chem. A* **2016**, *4* (40), 15638-15646.
19. Mao, L.; Tsai, H.; Nie, W.; Ma, L.; Im, J.; Stoumpos, C. C.; Malliakas, C. D.; Hao, F.; Wasielewski, M. R.; Mohite, A. D.; Kanatzidis, M. G. *Chem. Mater.* **2016**, *28* (21), 7781-7792.
20. Knutson, J. L.; Martin, J. D.; Mitzi, D. B. *Inorg. Chem.* **2015**, *44*(13), 4699-4705.
21. Hautzinger, M. P.; Dai, J.; Ji, Y.; Fu, Y.; Chen, J.; Guzei, I. A.; Wright, J. C.; Li, Y.; Jin, S. *Inorg. Chem.* **2017**, *56* (24), 14991-14998.
22. Era, M.; Morimoto, S.; Tsutsui, T.; Saito, S. *Appl. Phys. Lett.* **1994**, *65* (6), 676-678.
23. Hattori, T.; Taira, T.; Era, M.; Tsutsui, T.; Saito, S. *Chem. Phys. Lett.* **1996**, *254*, 103-108.
24. Kagan, C. R.; Mitzi, D. B.; Dimitrakopoulos, C. D. *Science* **1999**, *286* (5541), 945-947.
25. Mitzi, D. B.; Dimitrakopoulos, C. D.; Rosner, J.; Medeiros, D. R.; Xu, Z.; Noyan, C. *Adv. Mater.* **2002**, *14* (23), 1772-1776.
26. Hong, X.; Ishihara, T.; Nurmikko, A. V. *Solid State Commun.* **1992**, *84* (6), 657-661.
27. Kitazawa, N.; Aono, M.; Watanabe, Y. *Mater. Chem. Phys.* **2012**, *134* (2-3), 875-880.
28. Gauthron, K.; Lauret, J-S.; Doyennette, L.; Lanty, G.; Al Choueiry, A.; Zhang, S. J.; Brehier, A.; Largeau, L.; Mauguin, O.; Bloch, J.; Deleporte, E. *Opt. Express* **2010**, *18* (6), 5912-5919.
29. Shimizu, M.; Fujisawa, J.-I.; Ishi-Hayase, J. *Phys. Rev. B* **2005**, *71* (20), 205306(1)-205306(9).
30. Tang, Z.; Guan, J.; Guloy, A. M. *J. Mater. Chem.* **2001**, *11* (2), 479-482.
31. Lemmerer, A.; Billing, D. G. *Cryst. Eng. Comm.* **2012**, *14* (6), 1954-1966.
32. Mao, L.; Wu, Y.; Stoumpos, C. C.; Wasielewski, M. R.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2017**, *139*(14), 5210-5215.
33. Robinson, K.; Gibbs, G. V.; Ribbe, P. H. *Science* **1971**, *172* (3983), 567-570.
34. Thomas, N. W. *Acta Cryst.* **1989**, *B45*, 337-344.
35. Lufaso, M. W.; Woodward, P. M. *Acta Crystallogr. B* **2004**, *60* (Pt 1), 10-20.
36. Alonso, J. A.; Martinez-Lope, M. J.; Casais, M. T.; Fernandez-Diaz, M. T. *Inorg. Chem.* **2000**, *39* (5), 917-923.

37. Niemann, R. G.; Kontos, A. G.; Palles, D.; Kamitsos, E. I.; Kaltzoglou, A.; Brivio, F.; Falaras, P.; Cameron, P. J. *J. Phys. Chem. C* **2016**, *120* (5), 2509-2519.
38. Yin, T.; Fang, Y.; Fan, X.; Zhang, B.; Kuo, J.-L.; White, T. J.; Chow, G. M.; Yan, J.; Shen, Z. X. *Chem. Mater.* **2017**, *29* (14), 5974-5981.
39. Brivio, F.; Frost, J. M.; Skelton, J. M.; Jackson, A. J.; Weber, O. J.; Weller, M. T.; Goñi, A. R.; Leguy, A. M. A.; Barnes, P. R. F.; Walsh, A. *Phys. Rev. B* **2015**, *92* (14), 144308(1)-144308(8).
40. Gottesman, R.; Gouda, L.; Kalanoor, B. S.; Haltzi, E.; Tirosh, S.; Rosh-Hodesh, E.; Tischler, Y.; Zaban, A.; Quarti, C.; Mosconi, E.; De Angelis, F. *J. Phys. Chem. Lett.* **2015**, *6* (12), 2332-2338.
41. Ledinsky, M.; Loper, P.; Niesen, B.; Holovsky, J.; Moon, S. J.; Yum, J. H.; De Wolf, S.; Fejfar, A.; Ballif, C. *J. Phys. Chem. Lett.* **2015**, *6* (3), 401-406.
42. Leguy, A. M.; Goni, A. R.; Frost, J. M.; Skelton, J.; Brivio, F.; Rodriguez-Martinez, X.; Weber, O. J.; Pallipurath, A.; Alonso, M. I.; Campoy-Quiles, M.; Weller, M. T.; Nelson, J.; Walsh, A.; Barnes, P. R. *Phys. Chem. Chem. Phys.* **2016**, *18* (39), 27051-27066.
43. Cortecchia, D.; Neutzner, S.; Srimath Kandada, A. R.; Mosconi, E.; Meggiolaro, D.; De Angelis, F.; Soci, C.; Petrozza, A. *J. Am. Chem. Soc.* **2017**, *139* (1), 39-42.
44. Sourisseau, S.; Louvain, N.; Bi, W.; Mercier, N.; Rondeau, D.; Boucher, F.; Buzaré, J.-Y.; Legein, C. *Chem. Mater.* **2007**, *19* (3), 600-607.
45. Mercier, N.; Poiroux, S.; Riou, A.; Batail, P. *Inorg. Chem.* **2004**, *43* (26), 8361-8366.
46. Mao, L.; Ke, W.; Pedesseau, L.; Wu, Y.; Katan, C.; Even, J.; Wasielewski, M. R.; Stoumpos, C. C.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2018**, *140* (10), 3775-3783.
47. Pradeesh, K.; Nageswara Rao, K.; Vijaya Prakash, G. *J. Appl. Phys.* **2013**, *113* (8), 083523(1)-083523(9).
48. Takahashi, Y.; Obara, R.; Nakagawa, K.; Nakano, M.; Tokita, J.-Y.; Inabe, T., *Chem. Mater.* **2007**, *19* (25), 6312-6316.
49. Amat, A.; Mosconi, E.; Ronca, E.; Quarti, C.; Umari, P.; Nazeeruddin, M. K.; Gratzel, M.; De Angelis, F. *Nano Lett.* **2014**, *14* (6), 3608-3616.
50. Wu, X.; Trinh, M. T.; Niesner, D.; Zhu, H.; Norman, Z.; Owen, J. S.; Yaffe, O.; Kudisch, B. J.; Zhu, X. Y. *J. Am. Chem. Soc.* **2015**, *137* (5), 2089-2096.

51. Mao, L.; Wu, Y.; Stoumpos, C. C.; Traore, B.; Katan, C.; Even, J.; Wasielewski, M. R.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2017**, *139* (34), 11956-11963.
52. Neogi, I.; Bruno, A.; Bahulayan, D.; Goh, T. W.; Ghosh, B.; Ganguly, R.; Cortecchia, D.; Sum, T. C.; Soci, C.; Mathews, N.; Mhaisalkar, S. G. *ChemSusChem* **2017**, *10* (19), 3765-3772.
53. Wu, K.; Bera, A.; Ma, C.; Du, Y.; Yang, Y.; Li, L.; Wu, T. *Phys. Chem. Chem. Phys.* **2014**, *16* (41), 22476-22481.

6.5 Instrumentations and additional data

Nuclear Magnetic Resonance (NMR) spectroscopy. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of organic compounds were recorded in DMSO- d_6 solution using a Bruker Avance 400 spectrometer. Chemical shift values (ppm) are referenced against residual protic solvent peaks.

UV-Vis spectroscopy, steady-state photoluminescence (SSPL) spectroscopy, field-emission scanning electron microscopy (FE-SEM), and atomic force microscopy (AFM). UV-vis absorption and SSPL spectra were recorded using a SHIMADZU UV-3600 spectrophotometer, with an integrating sphere (ISR-3100) in the wavelength range 300-800 nm, and Horiba Fluoromax-3 spectrometer, with 0.5 nm wavelength resolution, respectively. Surface morphology and cross-section images of the 2D perovskite thin films and solar cell devices were recorded using a JEOL JSM-7600F field emission scanning electron microscope (FESEM), with an accelerating voltage of 5 kV. AFM measurements were conducted using a Bruker Icon microscope. All measurements were performed in the standard tapping mode with OTESPA-R3 tips from Bruker.

Time-resolved photoluminescence (TRPL) spectroscopy. A micro-PL setup incorporating a fibre-coupled microscope system was used. Excitation path and emission collection come from a VIS-NIR microscope objective (10 $\times$ magnification, NA = 0.65). Samples were excited with a 40 MHz-repetition-rate, picosecond pulse light emitting diode (Picoquant P-C-405B; λ = 405 nm), and the spot size was approximately 10 μm . The time-

resolved emitted signal was collected through a fibre-coupled Acton monochromator (SpectraPro 2300), to filter the desired wavelength, and detected by a Micro Photon Devices single-photon avalanche photodiode (LDH-P-670). The signal was then acquired by a time-correlated single photon counting card (Pico Harp TSCPC module and Picosecond Event Timer 300). Temporal resolution is ~ 50 ps. Decay curves were all fitted with a double exponential function.

Temperature- and power-dependent photoluminescence spectroscopies. Time-resolved and steady state photoluminescence measurements were conducted using a micro-PL setup utilizing a Nikon objective microscope (20 $\times$ magnification, NA = 0.3) with a picosecond-pulsed laser diode (Picoquant P-C-405B; $\lambda = 405$ nm, $f = 40$ MHz) as the excitation source. For the time-resolved measurements the Picoquant PicoHarp 300 time-correlated single photon counting (TCSPC) set-up was used, with the output signal coupled to an Acton SP-2300i monochromator (300 mm focal length) for spectral selection of the emission wavelength. Another optical fiber connected to the output of the monochromator was used to couple spectral separated output light to an avalanche diode synchronized with the excitation laser via the TCSPC electronics. For the steady state measurements, the optical fiber was connected to the output of the monochromator, whereas the spectrally separated light was collected by a photomultiplier (PMT, Hamamatsu). The power dependent measurements were obtained in this configuration by changing the excitation power in the range of 25 – 220 μ W using a set of neutral density filters. For the temperature dependent steady-state photoluminescence spectra measurements, the samples were mounted onto a liquid nitrogen-cooled Linkam Stage (FTIR 600) adjusted to the optical plane of the inverted microscope and measured within the temperature range of 77 – 300 K.

X-ray single crystallography. Crystals were mounted on a Bruker X8 CCD area detector diffractometer and data was collected using graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at cryogenic temperatures (100K). Data reduction and absorption corrections were performed using the SAINT and SADABS software packages, respectively. All structures were solved by direct methods and refined by full-matrix least squares

procedures on F^2 , using the Bruker SHELXTL-2014 software package. Non-hydrogen atoms were anisotropically refined before hydrogen atoms were introduced at calculated positions for further refinement of data. The graphical illustrations of crystal structures used throughout the main paper and supporting information were created using the program VESTA.

Powder and glancing angle X-ray diffraction. Powder and glancing-angle X-ray diffraction measurements were conducted using a Bruker AXS D8 ADVANCE system with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The XRD spectra were recorded with an incident angle of 5° , a step size of 0.05° , and a delay time of 1 s for each step.

Solar cell devices and incident photon-to-current efficiencies. Photovoltaic characteristics of the solar cell devices were measured in the reverse scanning direction (from V_{oc} to J_{sc}), with a sweep rate of 100 mV s^{-1} , under AM1.5G (100 mW.cm^{-2}) spectral irradiation from a solar simulator (Newport 91190A) incorporating a 450W xenon lamp (model 81172, Oriel) calibrated with a Si reference cell (Oriel PN91150). Devices were characterized through a 0.09 cm^2 black mask. Incident photon-to-current efficiency (IPCE) was measured using a photovoltaic quantum efficiency (QE) instrument, PVE300 (Bentham), with a dual xenon/quartz halogen light source, measured in DC mode, and no bias light was used in the wavelength range 300 – 800 nm. A Coherent OPerA Solo optical parametric amplifier pumped with a Coherent LibraTM regenerative amplifier (50 fs, 1 kHz, 800nm) was used to generate a 600 nm excitation beam.

Raman spectroscopy. Raman scattering measurements were performed using a WITec alpha 300RAS confocal Raman microscope. An Acton spectrometer with a diffraction grating of $1800 \text{ grooves mm}^{-1}$ (1.3 cm^{-1} resolution) and a thermoelectrically cooled Andor CCD detector were used to collect Raman spectra. To avoid absorption by the samples that could lead to photoluminescence and degradation, the 633 nm (red) line from a He-Ne gas laser with a power of 5 mW was chosen, while the laser spot area was $\sim 1 \text{ }\mu\text{m}^2$. The backscattered Raman signal passed through two 633 nm BragGrate Notch Filters (BNF). Measurements at 80 K were conducted under a nitrogen gas flow cryostat.

Four-probe conductivity measurements. Preparation of “horizontal devices” involved spin coating 0.50 M DMF solutions of stoichiometric mixtures of the 2D perovskite precursors onto pre-cleaned glass substrates at 3000 rpm for 30 s, after which the resulting films were heated at 130 °C for 10 mins. Subsequently, 100 nm thick gold electrode (distance = 125 μm , width = 4000 μm) was deposited through a mask of appropriate dimensions using a thermal evaporator (see **Figure 3.6**). Finally, the samples were connected to a Keithley 2400 source meter through the evaporated gold electrodes and the current generated between the two electrodes upon variation of electrical potential measured.

1-(2-Ammonioethyl)pyridin-1-ium diiodide (referred to as pyridinium ethyl ammonium diiodide, PyrEAI). Isolated as a beige solid (2.39g, 90% yield). ^1H NMR (400 MHz, DMSO- d_6): δ 9.06 (d, $J = 5.6$ Hz, 2 H, ArH), 8.67 (t, $J = 7.8$ Hz, 1 H, ArH), 8.23 (t, $J = 7.0$ Hz, 2 H, ArH), 7.97 (bs, 3 H, NH_3^+), 4.86 (t, $J = 5.8$ Hz, 2 H, CH_2), 3.56 (t, $J = 5.8$ Hz, 2 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 146.2, 145.3, 128.2, 57.9, 38.9.

2-Phenethylammonium iodide (PEAI). Isolated as a white solid (2.38g; 88% yield). ^1H NMR (400 MHz, DMSO- d_6): δ 7.78 (bs, 3 H, NH_3), 7.32-7.20 (m, 5 H, ArH), 3.06-3.03 (m, 2 H, CH_2), 2.88-2.84 (m, 2 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 137.1, 128.6, 128.6, 126.7, 40.0, 32.8.

1-(2-Ammonioethyl)-1H-imidazol-3-ium diiodide (referred to as imidazolium ethyl ammonium diiodide, ImEAI). Isolated as a white solid (1.52g; 84% yield). ^1H NMR (400 MHz, DMSO- d_6): δ 9.13 (s, 1 H, ArH), 7.89 (bs, 3 H, NH_3), 7.79 (t, $J = 1.4$ Hz, 1 H, ArH), 7.72 (t, $J = 1.4$ Hz, 1 H, ArH), 4.44 (t, $J = 5.8$ Hz, 2 H, CH_2), 3.38 (t, $J = 5.9$ Hz, 2 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 136.0, 122.1, 120.2, 46.2, 38.6.

1-(2-Ammonioethyl)piperidin-1-ium diiodide (piperidinium ethyl ammonium diiodide, PipEAI). Isolated as a yellowish solid (1.37g; 87% yield). ^1H NMR (400 MHz, DMSO- d_6): δ 9.51 (bs, 1 H, NH), 8.08 (bs, 1 H, NH_3), 3.49 (d, $J = 9.5$ Hz, 2 H, CH_2), 3.30 (s, 4 H, CH_2), 3.02 (q, $J = 7.6$ Hz, 2 H, CH_2), 1.83-1.67 (m, 5 H, CH_2), 1.42-1.39 (m, 1 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 52.8, 52.7, 33.4, 22.5, 20.9.

1-(2-Ammonioethyl)-1H-pyrazol-2-ium diiodide (pyrazolium ethyl ammonium diiodide, PyrEAI). Isolated as a beige solid (1.31g; 81% yield). ^1H NMR (400 MHz, DMSO- d_6): δ 9.13 (bs, 1 H, NH), 7.83 (bs, 3 H, NH_3), 7.81 (d, $J = 2.1$ Hz, 1 H, ArH), 7.54 (d, $J = 1.6$ Hz, 1 H, ArH), 6.26 (t, $J = 2.1$ Hz, 1 H, ArH), 4.34 (t, $J = 6.1$ Hz, 2 H, CH_2), 3.21 (q, $J = 5.9$ Hz, 2 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 139.3, 131.4, 106.0, 48.3, 39.1.

Table 6.10 Crystallographic and structure refinement data for (PyrEA)[PbI₄] (1), (ImEA)[PbI₄] (2), and (PEA)[PbI₄] (3).^a

	Compounds		
	(PyrEA)[PbI ₄] (1)	(ImEA)[PbI ₄] (2)	(PEA)[PbI ₄] (3)
Empirical formula	C ₇ H ₁₂ I ₄ N ₂ Pb	C ₅ H ₁₁ I ₄ N ₃ Pb	C ₃₂ H ₄₅ I ₈ N ₄ Pb ₂
Formula weight	838.98 g mol ⁻¹	827.96 g mol ⁻¹	1915.30 g mol ⁻¹
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal size	0.044 x 0.150 x 0.291 mm	0.061 x 0.147 x 0.216 mm	0.020 x 0.040 x 0.060 mm
Crystal habit	red plate	orange plate	orange plate
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P 1 21/c 1	P 1 21/c 1	C 1 c 1
Unit cell dimensions	a = 6.3354(3) Å	a = 12.4948(3) Å	a = 12.3353(2) Å
	α = 90°	α = 90°	α = 90°
	b = 19.8007(9) Å	b = 19.7152(4) Å	b = 12.2206(3) Å
	β = 90.757(2)°	β = 96.4396(8)°	β = 94.2960(10)°
	c = 12.5707(5) Å	c = 12.5841(3) Å	c = 32.2371(8) Å
Volume	γ = 90°	γ = 90°	γ = 90°
	1576.80(12) Å ³	3080.38(12) Å ³	4845.92(19) Å ³
	Z = 4	Z = 8	Z = 4
Density	3.534 g/cm ³	3.571 g/cm ³	2.625 g/cm ³
Absorption coefficient	18.505 mm ⁻¹	18.944 mm ⁻¹	12.061 mm ⁻¹
F(000)	1448	2848	3412
Theta range for data collection	2.62 to 31.03°	2.41 to 33.17°	2.35 to 29.64°
Reflections collected	45149	84490	30212
Coverage of independent reflections	99.70%	99.70 %	97.80%
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan
Max. and min. transmission	0.4960 and 0.0750	0.3910 and 0.1050	0.7940 and 0.5310
Function minimized	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	5027 / 0 / 128	11733 / 0 / 240	12542 / 2 / 420
Goodness-of-fit on F ²	1.294	1.097	1.125
Δ/σ _{max}	0.003	0.002	0.002
Final R indices [I > 2σ(I)]	4879 data	9944 data	12154 data
	R ₁ = 0.0298	R ₁ = 0.0267	R ₁ = 0.0388
	wR ₂ = 0.0801	wR ₂ = 0.0451	wR ₂ = 0.1038
R indices [all data]	R ₁ = 0.0309	R ₁ = 0.0395	R ₁ = 0.0395
	wR ₂ = 0.0806	wR ₂ = 0.0494	wR ₂ = 0.1045
Largest diff. peak and hole	3.779 and -1.824 eÅ ⁻³	1.715 and -2.547 e.Å ⁻³	1.839 and -3.544 eÅ ⁻³
R.M.S. deviation from mean	0.282 eÅ ⁻³	0.306 eÅ ⁻³	0.246 eÅ ⁻³

^aR = Σ||F_o| - |F_c||/Σ|F_o|, wR = {Σ[w(|F_o|² - |F_c|²)²]/Σ[w(|F_o|⁴)]}^{1/2} and (PyrEA)[PbI₄], w = 1/[σ²(F_o²) + (0.0213P)² + 19.5793P]; (ImEA)[PbI₄], w = 1/[σ²(F_o²) + (0.0097P)² + 9.4095P]; (PEA)₂[PbI₄], w = 1/[σ²(F_o²) + (0.0710P)² + 6.9304P]; where P = (F_o² + 2F_c²)/3.

Table 6.11 Crystallographic and structure refinement data for (PyrzEA)[Pb₂I₆], (HA)[PbI₄], and (PipEA)[PbI₄].^a

	Compounds		
	(PyrzEA)[Pb ₂ I ₆]	(HA)[PbI ₄]	(PipEA)[PbI ₄]
Empirical formula	C ₁₀ H ₂₄ I ₁₀ N ₆ O ₂ Pb ₃	C ₅ H ₉ I ₄ N ₃ Pb	C ₁₄ H ₃₄ I ₈ N ₄ Pb ₂
Formula weight	2150.92 g mol ⁻¹	825.94 g/mol	1688.03 g mol ⁻¹
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal size	0.020 x 0.040 x 0.120 mm	0.100 x 0.140 x 0.160 mm	0.020 x 0.120 x 0.280 mm
Crystal habit	yellow prism	red block	red plate
Crystal system	monoclinic	monoclinic	monoclinic
Space group	C 1 2/c 1	P 1 21/n 1	P 1 21/n 1
Unit cell dimensions	a = 20.6609(6) Å	a = 8.8952(2) Å	a = 12.6656(3) Å
	α = 90°	α = 90°	α = 90°
	b = 8.9123(3) Å	b = 19.7237(5) Å	b = 20.5236(5) Å
	β = 115.7582(10)°	β = 92.2131(7)°	β = 94.6417(7)°
	c = 22.7613(6) Å	c = 8.9250(2) Å	c = 12.8846(3) Å
	γ = 90°	γ = 90°	γ = 90°
Volume	3774.7(2) Å ³	1564.69(6) Å ³	3338.29(14) Å ³
Z	4	4	4
Density	3.785 g/cm ³	3.506 g/cm ³	3.359 g/cm ³
Absorption coefficient	21.545 mm ⁻¹	18.647 mm ⁻¹	17.482 mm ⁻¹
F(000)	3672	1416	2936
Theta range for data collection	2.19 to 32.00°	2.51 to 33.16°	2.17 to 30.00°
Reflections collected	58051	23604	57068
Coverage of independent reflections	99.90%	99.00%	99.90%
Absorption correction	Multi-Scan	Numerical Mu Calculated	Multi-Scan
Max. and min. transmission	0.6730 and 0.1820	0.2570 and 0.1540	0.7210 and 0.0840
Function minimized	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	6551 / 0 / 143	5915 / 0 / 120	9736 / 0 / 255
Goodness-of-fit on F ²	1.111	1.224	1.034
Δ/σ _{max}	0.003	0.003	0.004
Final R indices [I > 2σ(I)]	6012 data	5754 data	8486 data
	R ₁ = 0.0221	R ₁ = 0.0300	R ₁ = 0.0244
	wR ₂ = 0.0422	wR ₂ = 0.0717	wR ₂ = 0.0530
R indices [all data]	R ₁ = 0.0263	R ₁ = 0.0310	R ₁ = 0.0317
	wR ₂ = 0.0437	wR ₂ = 0.0721	wR ₂ = 0.0571
Largest diff. peak and hole	2.007 and -1.157 eÅ ⁻³	2.700 and -1.875 eÅ ⁻³	2.262 and -1.319 eÅ ⁻³
R.M.S. deviation from mean	0.227 eÅ ⁻³	0.257 eÅ ⁻³	0.222 eÅ ⁻³

^aR = Σ||F_o| - |F_c||/Σ|F_o|, wR = {Σ[w(|F_o|² - |F_c|²)²]/Σ[w(|F_o|⁴)]}^{1/2} and (PyrzEA)[Pb₂I₆], w = 1/[σ²(F_o²) + (0.0050P)² + 13.2962P]; (HA)[PbI₄], w = 1/[σ²(F_o²) + (0.0159P)² + 4.6832P]; (PipEA)[PbI₄], w = 1/[σ²(F_o²) + (0.0198P)² + 8.6613P] where P = (F_o² + 2F_c²)/3.

Chapter 7

Structural and optoelectronic properties of a 3×3 corrugated 2D tin-iodide perovskite

In an attempt to boost visible light absorption capability of the 2D perovskite discussed in the previous chapter, Pb metal center is replaced with Sn. Specifically, this chapter describes synthesis of the first ' 3×3 ' (110)-oriented 2D tin-iodide perovskite, using dicationic 1-(2-ammonioethyl)-1H-imidazol-3-ium (ImEA) as a template. The formability, structural characteristics, and optoelectronic features of this hybrid material, ImEA[SnI₄], are described.

7.1 Background

Two-dimensional (2D) hybrid organic tin-halide perovskites were first demonstrated as semiconducting channels in thin-film field-effect transistors (FETs),¹⁻² but have recently attracted revitalized interest. This is because they show similar optical and electrical properties to their lead-based analogues,³⁻⁵ which have significant potential in applications such as photovoltaics, light-emitting diodes, and lasing, whilst being of lower toxicity. Unlike their three-dimensional (3D) counterparts, which can only be formed using the very small organic cations methylammonium (MA)⁶ or formamidinium (FA)⁷, 2D structures can be induced through incorporation of moderately-sized, relatively more hydrophobic organic cations, such as butyl ammonium (BA)⁸ or phenyl ethyl ammonium (PEA).^{2,9} This not only affords significant room for materials exploration and engineering,¹⁰⁻¹² but the more hydrophobic cations also provides improved stability against degradation by moisture and oxygen.¹³⁻¹⁶ Indeed, tuning of the organic cations has, for instance, provided access to 2D halostannates with properties required for application in transistors,¹⁷⁻¹⁸ photovoltaics,^{15,19} light emitting devices,^{16,20} chemisorption,²¹⁻²² and photocatalysis.²³

Conceptually, various 2D structures can be obtained by cutting/slicing the parent, cubic 3D perovskite along different crystallographic directions (e.g., the (100)- or (110)-plane).²⁴⁻²⁵ However, most layered halostannates are of the (100)-type, with more than 50 having been documented in the Cambridge Structural Database. Therein, the $[\text{SnX}_6]^{4-}$ octahedra corner-share their equatorial vertices and the remaining two halides (*trans* to one another) are terminally bound, which results in ‘flat’ inorganic layers (**Figure 7.1a**). On the other hand, corrugated (110)-oriented structures, which also contain octahedra possessing two *cis* oriented terminally-bound halides, are much rarer (**Figures 7.1b-d**). In fact, a literature search found only 2 examples having been published thus far. The first, reported in 1999 by Guloy and co-workers,²⁶ incorporated the dication $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3]^{+2}$ as a template; and the second, disclosed 17 years later by Kanatzidis and co-workers¹⁹, used diprotonated form of organic histamine (HA^{+2}). Both of these compounds, $\alpha\text{-(NH}_3(\text{CH}_2)_5\text{NH}_3)[\text{SnI}_4]$ and $\alpha\text{-(HA)}[\text{SnI}_4]$, feature a ‘4 × 4’ corrugated structure (**Figure 7.1d**), where ‘n × n’ refers to the number (n) of contiguous Pb octahedra comprising each ridge. The prefix ‘ α ’ is used

because these organic cations were also found to yield (100)-oriented structures as thermodynamically stable phases. Thus, although there are comprehensive studies dedicated to the synthesis, characterization, and use of their 3D and (100)-oriented 2D congeners in various applications, exploration of (110)-oriented 2D tin-halide perovskites is very limited.

Figure 7.1 Schematic representations of the structures of 2D metal-halide perovskites featuring a) (100)-orientation, b) ‘2 × 2’ (110)-orientation, c) ‘3 × 3’ (110)-orientation, and d) ‘4 × 4’ (110)-orientation.

Previously, with dication 1-(2-ammonioethyl)-1H-imidazol-3-ium (ImEA^{2+}), the first corner-sharing ‘3 × 3’ (110) Pb-I 2D perovskite was reported. In this chapter, the first ‘3 × 3’ (110)-type tin-iodide (SnI_4)⁻² perovskite (**Figure 7.1c**) that is selectively templated by 1-(2-ammonioethyl)-1H-imidazol-3-ium (ImEA^{+2}) is studied. In particular, the material’s structural characteristics are described and correlated with its spectroscopic features. At last, upon assessing charge carriers photogeneration in $\text{ImEA}[\text{SnI}_4]$, its photoconductivity behavior with and without application of electric fields is also investigated.

7.2 Results and discussions

7.2.1 Formability and structure of (110)-lattice

X-ray crystallographic analysis of ImEA[SnI₄], which crystallizes in the monoclinic space group $P 1 2_1/c 1$ (see **Section 7.5** for the associated crystallographic and refinement data), yielded the structure displayed in **Figure 7.2**. Similar to the corresponding Pb-halide compounds, a '3 × 3' (110)-type structure composed of alternating inorganic and organic monolayers was observed. Specifically, the material features very short distances between the inorganic layers, presumably, due to the compact nature of the dication and flexibility of the ammonioethyl pendant. Indeed, the shortest I⋯I contacts in this structure, of 4.174 Å, are amongst the shortest that have been ever recorded for 2D tin-iodide perovskite. For comparison, the organic cations 2-trimethylammonioethylammonium,¹² 1,5-pentanediammonium,⁴ and butyl ammonium⁴ impart closest I⋯I contacts of 4.186, 4.587, and 8.668 Å, respectively. Meanwhile, the more rigid cations biimidazolium,²⁷ benzodiimidazolium,¹⁵ and benzimidazolium²⁸ yield respective I⋯I closest contacts of 4.444, 4.855, and 8.077 Å.

Each asymmetric unit of ImEA[SnI₄] contains two inequivalent ImEA cations (**Figure 7.3**), which differ in terms of conformation and interactions with the iodostannate lattices. Despite the presence of hydrogen bonding between the primary ammonium (NH₃) and imidazolium's N-H moieties of both conformations with neighboring iodide ions (N⋯I contacts ranging from 3.586 to 4.257 Å), the major driving force to the unusual structure is believed to be the coulombic interaction between the alkylated endocyclic N-atom of ImEA and terminally-bound iodide ion that is perpendicular to the plane of the imidazolium ring (N⋯I contacts of 3.680 and 3.924 Å; **Figure 7.4**). Subtle alterations to the organic structure, such as variation in the position of the N-H functionality in the imidazolium-core (**Figure 7.5**) and replacement with pyridinium group (**Figure 7.6**), result in hydrogen bondings between endocyclic NH⁺ functionalities and iodide ions that occur exclusively in the plane of the heterocyclic ring. These, coupled with the absence of the coulombic interaction perpendicular to plane of the aromatic core, lead to the formation of conventional (100)-oriented 2D structures (see **Figure 7.7**).

Figure 7.2 X-ray crystal structure of ‘3 × 3’ (110)-oriented 2D perovskite ImEA[SnI₄]. Gray, purple, brown, and blue spheres represent Pb, I, C, and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.

Figure 7.3 Crystal structure of different organic conformations ImEA⁺² in corrugated 2D perovskite ImEA[SnI₄]. Grey and blue spheres represent C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.

Detailed analysis of the crystal structure of ImEA[SnI₄] reveals that its constituent tin-iodide octahedra are significantly more distorted than those in the reported (100)- and ‘4 × 4’ (110)-oriented systems (**Table 7.1**).

Table 7.1 Summary of distortion parameters of ImEA[SnI₄] in comparison to other (100)- and (110)-Sn-I perovskites.

No.	Organic cation	Δd (x10 ⁻⁴)	λ_{oct}	σ_{oct}^2	Ref.
1.		0.43	1.0015	4.96	5
2.		0.27	1.0006	2.13	6
3.		2.82	1.0010	2.46	5
4.		1.19	1.0043	14.78	7
5.		0.003	1.0034	12.05	8
6.		21.68	1.0044	7.62	9 ^a
7.		11.41	1.0064	17.88	This work

^a '4 × 4' (110)-type 2D iodostannate.

The degree of intra-octahedral distortion can be quantified by comparing the following, previously reported, parameters:²⁹⁻³¹

$$\text{Bond length distortion: } \Delta_{oct} = \frac{1}{6} \sum_{i=1}^6 \left[\frac{d_i - d_m}{d_m} \right]^2 \quad (\text{Eqn. 7.1})$$

$$\text{Octahedral elongation: } \lambda_{oct} = \frac{1}{6} \sum_{i=1}^6 \left[\frac{d_i}{d_0} \right]^2 \quad (\text{Eqn. 7.2})$$

$$\text{Octahedral angle variance: } \sigma_{oct}^2 = \frac{1}{11} \sum_{i=1}^{12} (\alpha_i - 90)^2 \quad (\text{Eqn. 7.3})$$

where d_i represents Pb–Br bond length, d_m to average bond length, d_0 to center-to-vertex distance of a regular polyhedron of the same volume, and α_i to individual Br–Pb–Br angle. Δ_{oct} , λ_{oct} and σ_{oct}^2 provide a quantitative measure of polyhedral distortion independent of the polyhedron effective size. The observed greater distortion is believed to stem from the inherently asymmetric cation possessing centres of positive charge (ammonium and imidazolium core) with greatly differing steric profiles. This, consequently, leads to an inherently asymmetric environment around the tin-iodide octahedra.

Figure 7.4 Depicted as red dashed lines are shortest distances between N atoms of primary ammonium group and imidazolium ring of ImEA⁺² and bridging or terminal I atoms in cuboctahedral cavity of bromoplumbate lattice in ImEA[SnI₄]. Green dashed line, on another hand, depict the shortest distances between alkylated endocyclic N atom of imidazolium ring with terminally bound iodide ion. Light purple, purple, light brown and blue spheres represent Sn, I, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.

Figure 7.5 Single crystal structures of histamonium-based 2D (100) tin-iodide perovskite $2[\text{SnI}_4]$. Light purple, purple, light brown and blue spheres represent Sn, I, C and N atoms, respectively. H atoms are omitted for clarity. In the insets are the molecular structures of **2**. The structure is obtained from ref. 19.

Figure 7.6 Single crystal structures of pyridinium-based 2D (100) tin-iodide perovskites a) **3** $[\text{SnI}_4]$, b) **4** $[\text{SnI}_4]$, c) **5** $[\text{SnI}_4]$, and d) **6** $[\text{SnI}_4]$. Light purple, purple, light brown and blue spheres represent Sn, I, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability. In the insets are the molecular structures of **3-6**.

Figure 7.7 Depicted as red dashed lines are shortest distances between N atoms of primary ammonium group and aromatic ring's -NH^+ functionalities of **4-6** and bridging or terminal Br atoms in cuboctahedral cavity of bromoplumbate lattice in **4[SnI₄]- 6[SnI₄]**. Light purple, purple, light brown and blue spheres represent Sn, I, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability. As shown in the figures, unlike in ImEA[SnI₄], the intermolecular interaction between the organic hydrogen functionalities of **4-6** and [SnI₆]⁴⁻ cuboctahedral cavity are not capable of yielding '*cis* two vacant vertexes', thus preventing the (110) inorganic lattices to form.

7.2.2 Effects of corrugated structure to spectroscopic features

The differing coordination environments of Sn in ImEA[SnI₄] and (100)-oriented 2D iodostannate 3-PyrEA[SnI₄], where 3-PyrEA²⁺ = 3-(2-ammonioethyl)pyridin-1-ium, can be discerned using static solid-state (SS) NMR measurements. In particular, the ¹¹⁹Sn static NMR spectrum of 3-PyrEA[SnI₄] contains single resonance at -135 ppm, whereas that of ImEA[SnI₄] contains two overlapping peaks (**Figure 7.8**). Gaussian fitting of the latter allows deconvolution into two resonances of equal intensity, centred at -107 and -306 ppm. These observations are in accordance with the X-ray structures of these compounds. As with all (100)-oriented structures, 3-PyrEA[SnI₄] contains only a single type of Sn coordination environment. In other words, all the Sn ions are magnetically identical. However, the Sn ions in ImEA[SnI₄] alternate (across a sheet) between having two terminally-bound iodide ions *cis* to another *trans* to one another. This corresponds to Sn ions that comprise the vertices and those on flat slopes between them, respectively.

Figure 7.8 Room temperature, static ^{119}Sn solid-state NMR spectra of (a) ImEA[SnI₄] and (b) 3-PyrEA[SnI₄]. Experimental data, total simulated line-shapes, and deconvoluted simulated resonances are depicted using black, red and blue lines, respectively.

Variations in the environments of the organic counteranions in ImEA[SnI₄] and 3-PyrEA[SnI₄] are also apparent in their ^{13}C magic angle spinning (MAS) SS NMR spectra (**Figure 7.9**). Each chemically distinct carbon atom in 3-PyrEA²⁺ yields a single resonance, but two magnetically distinct ImEA²⁺ are observed (i.e., the number of peaks is doubled). This is consistent with the number of distinct Sn ions and, by extension, magnetic environments available in the respective iodostannates (**Figure 7.10**).

Figure 7.9 Room temperature magic angle spinning (MAS) ^{13}C solid state (SS)-NMR spectra of 3-PyrEA[SnI₄] (top) and ImEA[SnI₄] (bottom).

Figure 7.10 Single crystal structures of a) (110)-type ImEA[SnI₄] and b) (100)-type 3-PyrEA[SnI₄] showing different number conformations of organic dications within the two-dimensional inorganic lattices. Light purple, purple, light brown and blue spheres represent Sn, I, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.

The UV-vis absorption spectrum of ImEA[SnI₄] is presented in **Figure 7.11a** and, in analogy to other 2D perovskites, the band centred at ~580 nm can be attributed to excitonic absorptions of the tin-iodide lattice. This is bathochromically-shifted with respect to excitonic transitions in the corresponding lead-iodide compounds.³² The lower band gaps in the Sn compounds, that this equates to, are a consequence of the greater electronegativity

of Sn^{2+} relative to Pb^{2+} .³³ However, the excitonic transition of $\text{ImEA}[\text{SnI}_4]$ is blue-shifted compared with those of previously reported (100)-oriented 2D tin iodide perovskites, which range from 600 nm to 700 nm.^{3, 15} This can be attributed to the less effective orbital overlap (Sn-5s and I-5p orbitals) due to greater deviation from the linearity in the corrugated sheets.^{31-32, 34}

Figure 7.11 a) Room temperature UV-visible absorbance and photoluminescence (PL) spectra of $\text{ImEA}[\text{SnI}_4]$. b) Temperature-dependent PL spectra of single crystal $\text{ImEA}[\text{SnI}_4]$ (normalized intensity), recorded using a 573 nm excitation wavelength continuous-wave laser beam. c) Temperature-dependent integrated PL intensity of single crystal $\text{ImEA}[\text{SnI}_4]$. The solid line is a best fit of the experimental data (red circles) to the Arrhenius equation, where I_0 corresponds to the intensity at 0 K, E_a to the activation energy, and k_B to the Boltzmann constant.

Upon excitation at 573 nm, the photoluminescence (PL) emission spectrum of $\text{ImEA}[\text{SnI}_4]$ shows a moderately intense peak at 611 nm, with a full width at half-maximum (fwhm) of ca. 300 meV and a Stokes shift of ca. 109 meV (**Figure 7.11a**). The observed PL signature, while being significantly broader than seen for conventional (100)-oriented compounds, is typical of (110)-oriented hybrid halometallate in general. Such behaviour has been hypothesized to arise from both free and self-trapped excitons, with the latter resulting from strong electron/hole-lattice coupling owing to the more distorted structures.³⁴⁻³⁵ As shown in **Figure 7.12**, the CIE coordinates of the emission are (0.64, 0.36), which corresponds to red light emission (**Figure 7.13**).

Figure 7.12 Chromaticity coordinates (0.64, 0.36) for the photoluminescence (PL) emission of ImEA[SnI₄] at room temperature (black circle).

Figure 7.13 Images of ImEA[SnI₄] single crystal a) without and b) with exposure of laser of 573 nm excitation wavelength at room temperature. The laser spot size is around 2 μm .

7.2.3 Low excitonic binding energy and application in photodetector

The good visible light absorption capability of ImEA[SnI₄], which spans up to 650 nm, prompted us to study the behaviour of its photogenerated charge carriers. To that end, temperature-dependent PL measurements were performed between 133 and 293 K. The resulting spectra are presented in **Figure 7.11b**. For clarity, emission intensities have been normalized (see **Figure 7.14** for PL spectra retaining relative intensity information).

Plotting emission intensity against the inverse of temperature and fitting the data to the Arrhenius equation (**Figure 7.11c**) provides an estimated excitonic activation energies (E_a) of 83(10) meV. This value, for ImEA[SnI₄], is much lower than those typically reported

for 2D perovskites. For examples, 2D perovskites based on alkyl ammonium cations have E_a above 300 meV, while those with more polarizable aromatic cations such as phenyl ethyl ammonium exhibit E_a of ca. 200 meV.³⁶⁻³⁷ It is proposed that it stems from a combination of the short separation between the Sn-I layers and the relatively high polarizability of the aromatic dication ImEA^{2+} , effectively, rendering $\text{ImEA}[\text{SnI}_4]$ more ‘3D-like’ in character. More importantly, it also indicates the ease of photogenerated charge carriers separations within the material.

Figure 7.14 Temperature-dependent photoluminescence (PL) spectra of single crystal $\text{ImEA}[\text{SnI}_4]$ under excitation of a 573 nm continuous-wave laser beam.

In response, the photoresponsivity of $\text{ImEA}[\text{SnI}_4]$ was probed by fabricating thin film lateral devices with interdigitated electrodes, on the FTO-patterned (100 μm spaced) substrates (see **Figure 7.15** for details). Measurements were conducted, under vacuum, in the dark and upon illumination 445-nm light-emitting diode lamp (445 nm, 1400 W/m^2). Ohmic behavior was observed under both conditions (**Figure 7.16a**) but, despite the generation of significant photocurrents as high as 600 nA at voltage application of 1.0 V, the on-off ratio of the device was observed to be only approximately 4. In comparison, on-off ratio of almost two order of magnitude can be harvested from device based on $\text{ImEA}[\text{PbI}_4]$, though the photocurrent generated is only 1.2 nA (**Figure 7.17**). This reflects the relatively high dark currents seen and, presumably, arises from partial oxidation of Sn^{2+}

to Sn^{4+} , which self-dopes $\text{ImEA}[\text{SnI}_4]$ and increases the background carrier density.³⁸⁻³⁹ More importantly, this also precludes us from getting working, high efficiency solar cells out of the materials.

Figure 7.15 Schematic of the device configuration used for photoresponse study of $\text{ImEA}[\text{SnI}_4]$.

Figure 7.16 a) Current-voltage (I - V) curves for the lateral devices with interdigitated electrodes containing $\text{ImEA}[\text{SnI}_4]$ (film on 100 μm spaced FTO electrodes; see SI for device configuration), before poling, measured in the dark (black circles) and upon illumination by a 445 nm LED light, with a power of 1.4 mW mm^{-2} (red circles). b) I - V curve of the device after 2 $\text{V}/\mu\text{m}$ poling, under illumination of light. c) Current-time (I - t) characteristic of the device after poling at 2 $\text{V}/\mu\text{m}$ under pulsed light.

Figure 7.17 Current-voltage (I - V) curves for the lateral devices with interdigitated electrodes containing ImEA[PbI₄]. Currents generated at 1.0 V in the absence and presence of light illumination are 0.013 nA and 1.183 nA, respectively.

Figure 7.18 Response of the material during application of a field of pulsed 2 V/ μ m.

Interestingly, however, repeated application of voltage across the device (i.e. poling) containing ImEA[SnI₄] caused a drift of the current vs. voltage (I - V) curve from origin. In particular, upon application of a pulsed field of 2 V/ μ m (**Figure 7.18**), an open circuit

voltage of about 200 mV was induced inside the material (**Figure 7.16b**). This observation resembles the switchable photovoltaic behavior reported for 3D lead-halide perovskites, wherein an intrinsic p-n junction is born from the charge imbalance created by ion migration.⁴⁰ Current vs time measurements, shown in **Figure 7.16c**, further show sharp decay and rise of the photocurrent as a response to pulsed light (445 nm, 1400 W/m²), which is indicative of fast carrier extraction as a consequence of the previously discussed low excitonic binding energy. The effect is not as reversible in ImEA[SnI₄] as it is for 3D lead-halide perovskites,⁴⁰ which can be attributed to slower ionic migration of the organic cations in the former due to their larger size and greater charge.⁴¹⁻⁴² However, the results show that permanent doping can also be induced in ImEA[SnI₄] by simple application of electric fields.

7.3 Summary

In conclusion, ImEA[SnI₄] is the first example of a 2D '3 × 3' (110)-oriented tin-iodide perovskite. The main driving force to formation of the unusual structure is attributed to the presence of a coulombic interaction that occurs perpendicular to the plane of the heterocyclic ring. ImEA[SnI₄] features good visible light absorption range (up to 650 nm), low exciton activation energies (E_a) of 83(10) meV, and photoresponsivity with on-off ratio of 4 fold. Moreover, the material can be permanently doped *via* simple application of voltage. This work should spur further exploration of extended solid materials possessing unique architectures, while retaining interesting properties suitable for optoelectronic applications.

7.4 Bibliography

1. Kagan, C. R., Mitzi, D. B., Dimitrakopoulos, C. D., *Science* **1999**, 286 (5441), 945.
2. Mitzi, D. B.; Dimitrakopoulos, C. D.; Kosbar, L. L. *Chem. Mater.* **2001**, 13 (10), 3728-3740.
3. Knutson, J. L.; Martin, J. D.; Mitzi, D. B. *Inorg. Chem.* **2005**, 44 (13), 4699-4705.

4. Takahashi, Y.; Obara, R.; Nakagawa, K.; Nakano, M.; Tokita, J.; Inabe, T. *Chem. Mater.* **2007**, *19* (25), 6312-6316.
5. Stoumpos, C. C.; Mao, L.; Malliakas, C. D.; Kanatzidis, M. G. *Inorg Chem* **2017**, *56* (1), 56-73.
6. Takahashi, Y.; Obara, R.; Lin, Z. Z.; Takahashi, Y.; Naito, T.; Inabe, T.; Ishibashi, S.; Terakura, K. *Dalton Trans.* **2011**, *40* (20), 5563-5568.
7. Mitzi, D. B.; Liang, K. *J. Solid State Chem.* **1997**, *134*, 376-381.
8. Mitzi, D. B. *Chem. Mater.* **1996**, *8* (3), 791-800.
9. Xu, Z.; Mitzi, D. B.; Dimitrakopoulos, C. D.; Maxcy, K. R. *Inorg. Chem.* **2003**, *42* (6), 2031-2039.
10. Willett, R. D.; Maxcy, K. R.; Twamley, B. *Inorg. Chem.* **2002**, *41* (26), 7024-7030.
11. Xu, Z.; Mitzi, D. B. *Inorg. Chem.* **2003**, *42* (21), 6589-6591.
12. Xu, Z.; Mitzi, D. B.; Medeiros, D. R. *Inorg. Chem.* **2003**, *42* (5), 1400-1402.
13. Liao, Y.; Liu, H.; Zhou, W.; Yang, D.; Shang, Y.; Shi, Z.; Li, B.; Jiang, X.; Zhang, L.; Quan, L. N.; Quintero-Bermudez, R.; Sutherland, B. R.; Mi, Q.; Sargent, E. H.; Ning, Z. *J. Am. Chem. Soc.* **2017**, *139* (19), 6693-6699.
14. Ramirez, D.; Schutt, K.; Wang, Z.; Pearson, A. J.; Ruggeri, E.; Snaith, H. J.; Stranks, S. D.; Jaramillo, F. *ACS Energy Lett.* **2018**, *3* (9), 2246-2251.
15. Zimmermann, I.; Aghazada, S.; Nazeeruddin, M. K. *Angew. Chem. Int. Ed.* **2019**, *58* (4), 1072-1076.
16. Lanzetta, L.; Marin-Beloqui, J. M.; Sanchez-Molina, I.; Ding, D.; Haque, S. A. *ACS Energy Lett.* **2017**, *2* (7), 1662-1668.
17. Mitzi, D. B.; Dimitrakopoulos, C. D.; Rosner, J.; Medeiros, D. R.; Xu, Z.; Noyan, C. *Adv. Mater.* **2002**, *14* (23), 1772-1776.
18. Mitzi, D. B.; Feild, C. A.; Harrison, W. T. A.; Guloy, A. M. *Nature* **1994**, *369*, 467-469.
19. Mao, L.; Tsai, H.; Nie, W.; Ma, L.; Im, J.; Stoumpos, C. C.; Malliakas, C. D.; Hao, F.; Wasielewski, M. R.; Mohite, A. D.; Kanatzidis, M. G. *Chem. Mater.* **2016**, *28* (21), 7781-7792.
20. Zhang, X.; Wang, C.; Zhang, Y.; Zhang, X.; Wang, S.; Lu, M.; Cui, H.; Kershaw, S. V.; Yu, W. W.; Rogach, A. L. *ACS Energy Lett.* **2018**, *4* (1), 242-248.

21. Xu, Z.; Mitzi, D. B. *Chem. Mater.* **2003**, *15* (19), 3632-3637.
22. Mitzi, D. B.; Medeiros, D. R.; Malenfant, P. R. L. *Inorg. Chem.* **2002**, *41* (8), 2134-2145.
23. Hong, Z.; Chong, W. K.; Ng, A. Y. R.; Li, M.; Ganguly, R.; Sum, T. C.; Soo, H. S. *Angew. Chem. Int. Ed.* **2019**, *58* (11), 3456-3460.
24. Cheng, Z.; Lin, J. *CrystEngComm* **2010**, *12* (10).
25. Saparov, B.; Mitzi, D. B. *Chem. Rev.* **2016**, *116* (7), 4558-96.
26. Guan, J.; Tang, Z.; Guloy, A. M. *Chem. Commun.* **1999**, 1833-1834.
27. Tang, Z.; Guan, J.; Guloy, A. M. *J. Mater. Chem.* **2001**, *11* (2), 479-482.
28. Zimmermann, I.; Keene, T. D.; Hauser, J.; Decurtins, S.; Liu, S. X. *Acta Crystallogr. Sect. E Struct. Rep. Online* **2014**, *70* (pt. 10), 178-182.
29. Robinson, K.; Gibbs, G. V.; Ribbe, P. H. *Science* **1971**, *172* (3983), 567-570.
30. Cortecchia, D.; Neutzner, S.; Srimath Kandada, A. R.; Mosconi, E.; Meggiolaro, D.; De Angelis, F.; Soci, C.; Petrozza, A. *J. Am. Chem. Soc.* **2016**, *139* (1), 39-42.
31. Mao, L.; Wu, Y.; Stoumpos, C. C.; Wasielewski, M. R.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2017**, *139* (14), 5210-5215.
32. Febriansyah, B.; Koh, T. M.; Lekina, Y.; Jamaludin, N. F.; Bruno, A.; Ganguly, R.; Shen, Z. X.; Mhaisalkar, S. G.; England, J. *Chem. Mater.* **2019**, *31* (3), 890-898.
33. Chen, Q.; De Marco, N.; Yang, Y.; Song, T.-B.; Chen, C.-C.; Zhao, H.; Hong, Z.; Zhou, H.; Yang, Y. *Nano Today* **2015**, *10* (3), 355-396.
34. Dohner, E. R.; Hoke, E. T.; Karunadasa, H. I. *J. Am. Chem. Soc.* **2014**, *136* (5), 1718-1721.
35. Smith, M. D.; Karunadasa, H. I. *Acc. Chem. Res.* **2018**, *51* (3), 619-627.
36. Hong, X.; Ishihara, T.; Nurmikko, A. V. *Phys. Rev. B*, **1992**, *45* (12), 6961-6964.
37. Tanaka, K.; Kondo, T. *Sci. Tech. Adv. Mater.* **2004**, *4* (6), 599-604.
38. Koh, T. M.; Krishnamoorthy, T.; Yantara, N.; Shi, C.; Leong, W. L.; Boix, P. P.; Grimsdale, A. C.; Mhaisalkar, S. G.; Mathews, N. *J. Mater. Chem. A*, **2015**, *3* (29), 14996-15000.
39. 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. *Adv. Mater.* **2014**, *26* (41), 7122-7127.

40. Xiao, Z.; Yuan, Y.; Shao, Y.; Wang, Q.; Dong, Q.; Bi, C.; Sharma, P.; Gruverman, A.; Huang, J. *Nat. Mat.* **2014**, *14* (2), 193-198.
41. Lin, Y.; Bai, Y.; Fang, Y.; Wang, Q.; Deng Y.; Huang, J. *ACS Energy Lett.* **2017**, *2* (7), 1571-1572.
42. Xiao, X.; Dai, J.; Fang, Y.; Zhao, J.; Zheng, X.; Tang, S.; Rudd, P. N.; Zeng, X. C.; Huang, J. *ACS Energy Lett.* **2018**, *3* (3), 684-688.

7.5 Instrumentations and additional data

Nuclear Magnetic Resonance (NMR) spectroscopy. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of organic compounds were recorded in DMSO- d_6 solution using a Bruker Avance 400 spectrometer. Chemical shift values (ppm) are referenced against residual protic solvent peaks.

Solid state (SS) NMR spectroscopy. All solid state NMR experiments in this study were completed on a Bruker Avance III HD 600 MHz spectrometer with a Bruker 4 mm HXY MAS probe. Spectral simulation of all NMR spectra was achieved via *dmfit*. The ImEA[SnI₄] sample was found to be conductive and hence was mixed with a powdered insulator (50 wt% MgO) in the NMR rotor to avoid the detuning effects of conductive samples.

The ^{119}Sn NMR experiments were completed at 14.1 T ($\nu_0(^{119}\text{Sn}) = 223.81$ MHz) under static conditions and resulting data was referenced with respect to SnO_{2(s)} ($\delta_{\text{iso}} = -604.3$ ppm). A ^{119}Sn $\pi/2$ pulse length of 4 μs , determined on SnO_{2(s)}, was utilised throughout. A one-pulse experiment was employed for 3-PyrEA[SnI₄], whereas a VOCS hahn-echo sequence was required to uniformly excite the wider line-shape for ImEA[SnI₄]. Recycle delays of 1 s and 30 s were used for the ImEA[SnI₄] and 3-PyrEA[SnI₄] samples, respectively. The significantly faster relaxation observed in the ImEA[SnI₄] sample is attributed to the conductive nature of the material.

The ^{13}C NMR experiments were completed at 14.1 T ($\nu_0(^{13}\text{C}) = 150.92$ MHz) with an MAS frequency of 6 KHz and 12 KHz for ImEA[SnI₄] and (3-PyrEA[SnI₄]) samples, respectively (a lower spinning speed was desirable for the former sample to reduce spectral overlap of the ^{13}C resonances and neighbouring spinning sidebands). Resulting data was referenced with respect to adamantane (C₁₀H_{16(s)}; $\delta_{\text{iso}} = 38.48, 40.49$ ppm). A ^{13}C CPMAS pulse sequence was employed throughout utilising a ^1H $\pi/2$ pulse length of $2.3\ \mu\text{s}$ (determined on adamantine), a contact pulse length of $4000\ \mu\text{s}$, a recycle delay of 30 s and high-power proton decoupling.

UV-Vis spectroscopy spectroscopy and field-emission scanning electron microscopy (FE-SEM). UV-vis absorption spectra were recorded using a SHIMADZU UV-3600 spectrophotometer, with an integrating sphere (ISR-3100) in the wavelength range 300-800 nm. Surface morphology images of the 2D perovskite thin film samples for photoresponse study were recorded using a JEOL JSM-7600F field emission scanning electron microscope (FESEM), with an accelerating voltage of 5 kV.

X-ray single crystallography. Crystals were mounted on a Bruker X8 Quest CPAD area detector diffractometer and data was collected using I μ S 3.0 Microfocus Mo-K α radiation ($\lambda = 0.71073\ \text{\AA}$) at cryogenic temperatures (100 K). Data reduction and absorption corrections were performed using the SAINT and SADABS software packages, respectively. All structures were solved by direct methods and refined by full-matrix least squares procedures on F^2 , using the Bruker SHELXTL-2014 software package. Non-hydrogen atoms were anisotropically refined before hydrogen atoms were introduced at calculated positions for further refinement of data. The graphical illustrations of crystal structures used throughout the main paper and supporting information were created using the programs Mercury and VESTA.

Temperature- and power-dependent photoluminescence spectroscopies. A WITec alpha 300RAS confocal Raman microscope was used to record the photoluminescence (PL) spectra. The red line of a linearly polarized CW solid laser (573 nm) was chosen for PL measurement. For steady-state and temperature-dependent PL measurements, the

excitation power was kept below $0.8 \mu\text{W}$ on sample to avoid photo degradation and saturation of the detector. A long working distance $20\times$ microscope objective (spot size of $\sim 2 \mu\text{m}$) was used for the low temperature experiments. Temperature dependent measurement was conducted in the range between 293 K and 133 K using a nitrogen gas flow cryostat. Power dependent measurement was conducted by varying laser power between $0.017 - 5 \mu\text{W}$.

Switchable photovoltaic effect measurements. Interdigitated FTO electrodes (3 Fingers) with lateral spacing of $100 \mu\text{m}$ and total effective length of 3.17 cm was used in fabrication of lateral device as shown in **Figure 3.8**. Perovskite active material (200 nm thick) was spincoated as reported in the thin film formation section. The measurements were conducted in a probe station chamber under vacuum of 10^{-6} mbar with the light incident through a quartz window. A monochromatic blue LED of wavelength 445 nm and power 1400 W/m^2 was used for the photocurrent measurements. Electrical properties were measured using a Keithley 4200-SCS semiconductor characterization system. The electric field applied on the perovskite film is $2 \text{ V}/\mu\text{m}$ in dark. After poling, the current-voltage (I - V) and current-time (I - t) curves were measured using the Keithley 4200-SCS.

1-(2-Ammonioethyl)pyridin-1-ium (4) diiodide (referred to as pyridinium ethyl ammonium diiodide, PyrEAI). Isolated as a beige solid (2.39g, 90% yield). ^1H NMR (400 MHz, DMSO-*d*₆): δ 9.06 (d, J = 5.6 Hz, 2 H, ArH), 8.67 (t, J = 7.8 Hz, 1 H, ArH), 8.23 (t, J = 7.0 Hz, 2 H, ArH), 7.97 (bs, 3 H, NH_3^+), 4.86 (t, J = 5.8 Hz, 2 H, CH_2), 3.56 (t, J = 5.8 Hz, 2 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO-*d*₆): δ 146.2, 145.3, 128.2, 57.9, 38.9.

1-(2-Ammonioethyl)-1*H*-imidazol-3-ium diiodide (referred to as imidazolium ethyl ammonium diiodide, ImEAI). Isolated as a white solid (1.52g; 84% yield). ^1H NMR (400 MHz, DMSO-*d*₆): δ 9.13 (s, 1 H, ArH), 7.89 (bs, 3 H, NH_3), 7.79 (t, J = 1.4 Hz, 1 H, ArH), 7.72 (t, J = 1.4 Hz, 1 H, ArH), 4.44 (t, J = 5.8 Hz, 2 H, CH_2), 3.38 (t, J = 5.9 Hz, 2 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO-*d*₆): δ 136.0, 122.1, 120.2, 46.2, 38.6.

2-(2-Ammonioethyl)pyridin-1-ium (5) diiodide (referred to as 2-pyridinium ethyl ammonium diiodide, 2-PyrEAI). Isolated as a beige solid (1.61g; 85% yield). ^1H NMR (400 MHz, DMSO-*d*₆): δ 8.88 (d, 1 H, ArH), 8.50 (t, 1 H, ArH), 8.13 (bs, 3 H, NH_3^+), 7.99 (d, 1 H, ArH), 7.92 (t, 1 H, ArH), 3.39-3.32 (m, 4 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO-*d*₆): δ 152.7, 145.4, 142.7, 127.2, 125.2, 37.3, 31.0.

3-(2-Ammonioethyl)pyridin-1-ium (6) diiodide (referred to as 3-pyridinium ethyl ammonium diiodide, 3-PyrEAI). Isolated as a beige solid (0.84g; 92% yield). ^1H NMR (400 MHz, DMSO-*d*₆): δ 8.92 (s, 1 H, ArH), 8.86 (d, 1 H, ArH), 8.53 (d, 1 H, ArH), 8.04 (t, 2 H, ArH), 7.98 (bs, 1 H, NH_3^+), 3.23-3.20 (m, 2 H, CH_2), 3.16-3.12 (m, 2 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO-*d*₆): δ 146.3, 142.5, 140.7, 137.1, 126.8, 38.8, 29.6.

4-(2-Ammonioethyl)pyridin-1-ium (7) diiodide (referred to as 4-pyridinium ethyl ammonium diiodide, 4-PyrEAI). Isolated as a beige solid (1.20g; 83% yield). ^1H NMR (400 MHz, DMSO-*d*₆): δ 8.92 (d, 2 H, ArH), 8.05 (bs, 3 H, NH_3^+), 8.04 (d, 2 H, ArH), 3.25-3.20 (m, 4 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO-*d*₆): δ 157.9, 141.7, 127.6, 38.1, 32.6.

Table 7.2 Crystallographic and structure refinement data for ImEA[SnI₄].^a

	Compound
	ImEA[SnI ₄]
Empirical formula	C ₅ H ₁₁ I ₄ N ₃ Sn
Formula weight	739.46 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.020 x 0.040 x 0.060 mm
Crystal habit	black plate
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 12.4594(4) Å
	α = 90°
	b = 19.6278(7) Å
	β = 96.2023(16)°
	c = 12.4690(6) Å
	γ = 90°
Volume	3031.5(2) Å ³
Z	8
Density	3.240 g/cm ³
Absorption coefficient	9.805 mm ⁻¹
F(000)	2592
Theta range for data collection	2.43 to 29.16°
Reflections collected	26259
Coverage of independent reflections	99.5%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8280 and 0.5910
Function minimized	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	8119 / 371 / 314
Goodness-of-fit on F ²	1.015
Δ/σ _{max}	0.001
Final R indices	5618 data
	R1 = 0.0476,
[I > 2σ(I)]	wR2 = 0.0739
R indices [all data]	R1 = 0.0817,
	wR2 = 0.0867
Largest diff. peak and hole	1.231 and -1.047 eÅ ⁻³
R.M.S. deviation from mean	0.275 eÅ ⁻³

^aR = Σ||F_o| - |F_c||/Σ|F_o|, wR = {Σ[w(|F_o|² - |F_c|²)²]/Σ[w(|F_o|⁴)]}^{1/2} and ImEA[SnI₄], w = 1/[σ²(F_o²) + (0.0167P)²]; where P = (F_o² + 2F_c²)/3.

Table 7.3 Crystallographic and structure refinement data for **3**[SnI₄] and **4**[SnI₄].^a

	Compound	
	3 [SnI ₄]	4 [SnI ₄]
Empirical formula	C ₇ H ₁₂ I ₄ N ₂ Sn	C ₇ H ₁₂ I ₄ N ₂ Sn
Formula weight	750.48 g/mol	750.48 g/mol
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal size	0.020 x 0.100 x 0.120 mm	0.040 x 0.050 x 0.120 mm
Crystal habit	black plate	black needle
Crystal system	orthorhombic	monoclinic
Space group	P b c a	P 1 21/n 1
Unit cell dimensions	a = 17.9119(4) Å	a = 6.3456(6) Å
	α = 90°	α = 90°
	b = 8.6987(2) Å	b = 12.4593(11) Å
	β = 90°	β = 93.2113(19)°
	c = 20.3708(5) Å	c = 19.8832(19) Å
	γ = 90°	γ = 90°
Volume	3173.98(13) Å ³	1569.5(3) Å ³
Z	8	4
Density	3.141 g/cm ³	3.176 g/cm ³
Absorption coefficient	9.365 mm ⁻¹	9.470 mm ⁻¹
F(000)	2640	1320
Theta range for data collection	2.30 to 30.99°	3.27 to 33.77°
Reflections collected	36743	6189
Coverage of independent reflections	100.00%	99.00%
Absorption correction	Multi-Scan	Multi-Scan
Max. and min. transmission	0.8350 and 0.3990	0.7030 and 0.3960
Function minimized	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	5056 / 0 / 128	6189 / 0 / 117
Goodness-of-fit on F ²	1.053	1.056
Δ/σ _{max}	0.002	0.001
Final R indices [I > 2σ(I)]	4090 data	4578 data
	R1 = 0.0351,	R1 = 0.0518,
	wR2 = 0.0755	wR2 = 0.1183
R indices [all data]	R1 = 0.0484,	R1 = 0.0799,
	wR2 = 0.0830	wR2 = 0.1369
Largest diff. peak and hole	1.977 and -1.094 eÅ ⁻³	3.048 and -2.346 eÅ ⁻³
R.M.S. deviation from mean	0.205 eÅ ⁻³	0.444 eÅ ⁻³

^aR = Σ||F_o| - |F_c||/Σ|F_o|, wR = {Σ[w(|F_o|² - |F_c|²)²/Σ[w(|F_o|⁴)]}^{1/2} and **3**[SnI₄], w = 1/[σ²(F_o²) + (0.0287P)²+16.7852P]; **4**[SnI₄], w = 1/[σ²(F_o²) + (0.0599P)²+ 4.7802P]; where P = (F_o²+2F_c²)/3.

Table 7.4 Crystallographic and structure refinement data for **5**[SnI₄] and **6**[SnI₄].^a

	Compound	
	5 [SnI ₄]	6 [SnI ₄]
Empirical formula	C ₇ H ₁₂ I ₄ N ₂ Sn	C ₇ H ₁₂ I ₄ N ₂ Sn
Formula weight	750.48 g/mol	750.48 g/mol
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal size	0.060 x 0.100 x 0.120 mm	0.020 x 0.060 x 0.200 mm
Crystal habit	black block	black needle
Crystal system	orthorhombic	monoclinic
Space group	P b c a	P 1 2 ₁ /n 1
Unit cell dimensions	a = 17.5926(4) Å	a = 6.2823(3) Å
	α = 90°	α = 90°
	b = 8.7826(2) Å	b = 12.4595(5) Å
	β = 90°	β = 95.176(2)°
	c = 20.6542(5) Å	c = 20.1704(8) Å
	γ = 90°	γ = 90°
Volume	3191.26(13) Å ³	1572.39(12) Å ³
Z	8	4
Density	3.124 g/cm ³	3.170 g/cm ³
Absorption coefficient	9.315 mm ⁻¹	9.452 mm ⁻¹
F(000)	2640	1320
Theta range for data collection	2.29 to 37.08°	2.60 to 33.74°
Reflections collected	49796	6184
Coverage of independent reflections	99.70%	99.40%
Absorption correction	Multi-Scan	Multi-Scan
Max. and min. transmission	0.6050 and 0.4010	0.8330 and 0.2540
Function minimized	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	8135 / 404 / 197	6184 / 0 / 129
Goodness-of-fit on F ²	1.042	1.051
Δ/σ _{max}	0.001	0.001
Final R indices [I > 2σ(I)]	5280 data	4820 data
	R1 = 0.0442,	R1 = 0.0516,
	wR2 = 0.0901	wR2 = 0.1159
R indices [all data]	R1 = 0.0806,	R1 = 0.0780,
	wR2 = 0.1067	wR2 = 0.1322
Largest diff. peak and hole	1.898 and -1.645 eÅ ⁻³	2.677 and -2.455 eÅ ⁻³
R.M.S. deviation from mean	0.233 eÅ ⁻³	0.451 eÅ ⁻³

^aR = Σ||F_o| - |F_c||/Σ|F_o|, wR = {Σ[w(|F_o|² - |F_c|²)²]/Σ[w(|F_o|⁴)]}^{1/2} and (**5**[SnI₄], w = 1/[σ²(F_o²) + (0.0367P)² + 5.3113P]; **6**[SnI₄], w = 1/[σ²(F_o²) + (0.0636P)²]; where P = (F_o² + 2F_c²)/3.

Chapter 8

Inducing formation of a corrugated, white-light emitting 2D lead-bromide perovskite *via* subtle changes in templating cation

This chapter describes about a rare 2×2 (110)-oriented two-dimensional (2D) perovskite based on dicationic 1-(2-ammonioethyl)-1H-imidazol-3-ium organic. Single crystal structure investigation points to the importance of the 5-membered ring size as well as relative position of -NH^+ functionality within the ring in templating the corrugated lattice. In the absence of either one of the two factors, much more common (100) 2D perovskites are formed instead. Upon excitation by UV-light, the resulting corrugated 2D perovskite generates white-light emission covering the entire visible spectrum with the peak maxima at 537 nm and features a large Stoke-shift (of ca. 1.05 eV) and full widths at half maximum (FWHM) of ca. 810 meV. As the consequence, color rendering index (CRI) and correlated color temperature (CCT) of 73 and 5824 K, respectively, can be obtained. It corresponds to ‘colder’ white light emission in comparison to those of reported compounds of the same class where CCTs were of below 5000 K. While adding another list to the limited library of (110) 2D perovskites, this work demonstrates that with a judiciously chosen organic species, goldilocks templating requirement in inducing a particular rare structure possessing desirable properties can be fulfilled.

8.1 Background

Lighting accounts for one-fifth of global electricity consumption.¹ Owing to their low power consumption and high reliability, white light-emitting diodes (WLEDs) are ubiquitously used for this purpose.² Two-dimensional (2D) hybrid Pb-Br perovskites displaying broadband white-light emission are a particularly promising class of materials for WLED applications.³⁻⁴ This is because they are able to function as single-source down-converting white-light-emitting phosphors that display good colour rendition and comparatively stable emission colours.⁵ Additionally, these materials can be evenly deposited from solution over large surface areas, without the need of additives, making them attractive in terms of cost and ease of fabrication.⁶⁻⁷

Mechanistically, it has been proposed that broadband photoluminescence (PL) exhibited by 2D lead-bromide perovskites originates from excited electron-hole pairs stabilized by strong coupling to a deformable inorganic lattice (i.e. self-trapped excitons; STEs).⁸⁻¹⁰ As the white-light emission comes from a single-phase bulk material and its structure is highly dependent upon the cation incorporated, it should be possible to engineer PL properties at a molecular level.¹¹ However, although desirable, relatively few compounds have been reported to exhibit such broadband PL.^{7, 12-19}

Whereas (100)-oriented 2D perovskites consist of flat inorganic sheets, their (110)-oriented congeners have corrugated layers. The aforementioned orientations refer to the different crystallographic planes along which the nominal parent 3D inorganic lattice has been sliced. The inherently more distorted inorganic lattice of the corrugated structure would be expected to result in stronger exciton-phonon coupling and, thereby, manifest in broadband photoluminescence (PL). Indeed, there are only seven examples of lead-bromide hybrid perovskites possessing (110)-oriented inorganic architecture and all of them have been reported to exhibit broadband white-light emission.^{12-17, 20} By comparison, only a handful of (100)-oriented structures (out of the more than 50 examples reported in the Cambridge Structural Database) feature this property.^{7, 9, 11, 17-18} Thus, any work that contributes to the understanding of the molecular design criteria required for successful formation of (110)-

oriented structures, which would enable rapid expansion of this library of compounds, is of significant value.

Figure 8.1 The organic dications used in this study.

In previous work, it has been shown that organic cations containing cyclic ammonium ions bearing various substituents template lead-halide perovskites displaying unusual, often highly distorted, structures.²¹⁻²² Such a molecular design is modular and highly flexible. Thus, a homologous series of organic cations can be readily synthesized and their impact upon the structure of the inorganic lattice can be systematically investigated. In this chapter, a family of dications composed of imidazolium or pyridinium cores substituted at various positions by a 2-ethylammonium chain (**Figure 8.1**) have been employed in preparation of new 2D lead-bromide perovskites.

8.2 Results and discussions

8.2.1 Formability and structure of (110)-lattice

Dication **1** was previously shown (Chapters 6 and 7) to template formation of the first example of a corner-sharing ‘3 × 3’ (110) Pb-I 2D perovskite, **1**[PbI₄].²² Replacement of iodide by the smaller bromide anion, to give **1**[PbBr₄], leads to a 2D material that adopts ‘2 × 2’ corrugation (**Figure 8.2a**). (Summary of crystallographic refinement data can be found in **Section 8.5**) The level of corrugation, ‘n × n’, refers to the number (n) of contiguous Pb octahedra comprising each ridge/groove. Compound **1**[PbBr₄] is only the seventh example of a 2D bromoplumbate framework demonstrated to possess 2 × 2

corrugation. After Lin and co-workers published two structures of this type in 2006 and 2008,¹²⁻¹³ it took more than 5 years before Karunadasa's group reported a further two.¹⁴⁻¹⁵ Recently, Kanatzidis and co-workers also reported two new compounds.^{17, 20}

Figure 8.2 Single crystal X-ray structures of the 2D perovskites a) **1**[PbBr₄], b) **2**[PbBr₄], c) **3**[PbBr₄], d) **4**[PbBr₄] and e) **5**[PbBr₄]. Black, maroon, brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.

Intriguingly, the 2D perovskites **2**[PbBr₄] and **3**[PbBr₄], which are templated by dicationic species that are isomers of **1** (**Figure 8.1**), display more common (100)-oriented structures (**Figures 8.2b-c**). The most obvious difference between the aforementioned dicationic species is that the endocyclic N-atoms of the imidazolium rings in **2** and **3** all bear protons (i.e., are NH⁺ functional groups), whereas that is true for only one of the two endocyclic N-atoms in **1**. In the latter, the other is alkylated. The greater steric bulk of this alkylated endocyclic N-atom inhibits interaction with the bromide ions of the inorganic layers and manifests in a significantly elongated N $\cdots$ Br interaction distance of 3.736 Å (**Figures 8.3 and 8.4**). For reference, the longest endocyclic N $\cdots$ Br distances in **2**[PbBr₄] and **3**[PbBr₄] are 3.392 Å and 3.320 Å, respectively (**Figures 8.5-8.8**). Furthermore, the N $\cdots$ Br coulombic interaction of the alkylated endocyclic N-atom of **1** is perpendicular to the plane of the imidazolium ring. Interactions with the endocyclic NH⁺ functional groups in **1** – **3** are exclusively in the plane of the ring. The aforementioned factors strongly disfavor

penetration of the imidazolium rings of **1** into the cuboctahedral cavities of (100)-oriented 2D inorganic layers, which are comprised of four nearest neighbour, axial, terminally-bound bromide ions. This limitation is most easily accommodated in a 2D structure by corrugation.

Figure 8.3 Depicted as dashed lines are shortest distances between N atoms of primary ammonium group (red) and, NH⁺ functional group (group), and endocyclic N-atoms (blue) of the imidazolium ring of **1** and bridging or terminal Br atoms in cuboctahedral cavity of bromoplumbate lattice in **1**[PbBr₄]. Grey, brown, light brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.

Figure 8.4 Depicted as dashed lines are shortest distances between N atoms of primary ammonium group (red) and, NH⁺ functional group (group), and endocyclic N-atoms (blue) of the imidazolium ring of **1** and terminal Br atoms, leading to ‘*cis* two vacant vertices’ in the inorganic lattice. Grey, brown, light brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.

Figure 8.5 Depicted as dashed lines are shortest distances between N atoms of primary ammonium group (red) and imidazolium ring (green) of **2** and surrounding bridging or terminal Br atoms of (100) oriented bromoplumbate lattice in **2**[PbBr₄]. Grey, brown, light brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.

Figure 8.6 Depicted as dashed lines are shortest distances between N atoms of primary ammonium group (red) and imidazolium ring (green) of **2** and terminal Br atoms, leading to ‘*trans* two vacant vertices’ in the inorganic lattice. Grey, brown, light brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.

Figure 8.7 Depicted as dashed lines are shortest distances between N atoms of primary ammonium group (red) and imidazolium ring (green) of **3** and surrounding bridging or terminal Br atoms of (100) oriented bromoplumbate lattice in $3[\text{PbBr}_4]$. Grey, brown, light brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.

Figure 8.8 Depicted as dashed lines are shortest distances between N atoms of primary ammonium group (red) and imidazolium ring (green) of **3** and terminal Br atoms, leading to ‘*trans* two vacant vertices’ in the inorganic lattice. Grey, brown, light brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.

In the hope of reproducing the H-bond configuration of **1**, required for formation of a corrugated structure, the pyridinium-containing dications **4** and **5** were used. Unfortunately, the resulting perovskites **4**[PbBr₄] and **5**[PbBr₄] still exhibit flat, (100)-oriented, bromoplumbate sheets (**Figures 8.2d-e**). Although it is possible that the larger ring size or pyridinium (relative to imidazolium) rings is a contributing factor, it is believed the primary reason for this observation is the absence of an additional coulombic interaction perpendicular to plane of the heterocyclic ring (**Figures 8.9-8.12**). As such, the ammonium N-atoms can intrude into the cuboctahedral cavities of the (100)-oriented 2D layers and there is no driving force for corrugation of the structure.

Figure 8.9 Depicted as dashed lines are shortest distances between N atoms of primary ammonium group (red) and imidazolium ring (green) of **4** and surrounding bridging or terminal Br atoms of (100) oriented bromoplumbate lattice in $4[\text{PbBr}_4]$. Grey, brown, light brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.

Figure 8.10 Depicted as dashed lines are shortest distances between N atoms of primary ammonium group (red) and imidazolium ring (green) of **4** and terminal Br atoms, leading to ‘*trans* two vacant vertices’ in the inorganic lattice. Grey, brown, light brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.

Figure 8.11 Depicted as dashed lines are shortest distances between N atoms of primary ammonium group (red) and imidazolium ring (green) of **5** and surrounding bridging or terminal Br atoms of (100) oriented bromoplumbate lattice in **5**[PbBr₄]. Grey, brown, light brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.

Figure 8.12 Depicted as dashed lines are shortest distances between N atoms of primary ammonium group (red) of **4** and terminal Br atoms, leading to ‘*trans* two vacant vertices’ in the inorganic lattice. Grey, brown, light brown and blue spheres represent Pb, Br, C and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.

8.2.2 Effects of corrugated structure to optical properties

The degree of distortion *within* the $[\text{PbBr}_6]^{4-}$ octahedra (i.e., intra-octahedral) that comprise the inorganic layers was assessed for the compounds reported herein using the octahedral bond length distortion parameter Δ_{oct} .^{16, 23-24}

$$\Delta_{oct} = \frac{1}{6} \sum_{i=1}^6 \left[\frac{d_i - d_m}{d_m} \right]^2 \quad (\text{Eqn. 8.1})$$

where d_i corresponds to Pb–Br bond length, d_m to average bond length. Larger values correspond to greater deviation from ideal octahedral symmetry. From the average Δ_{oct} values calculated for each structure, listed in **Table 8.1**, it is clear that the degree of distortion experienced by the $[\text{PbBr}_6]^{4-}$ octahedra is the largest for **1**[PbBr₄] ($\Delta_{oct} = 22.93 \times 10^{-4}$). This is mainly due to its corrugated structure. Based upon literature precedent,¹⁶ one would expect this compound to be a good candidate for broadband white-light emission.

Table 8.1 Calculated intra-octahedral distortion (Δ_{oct}) of **1**[PbBr₄] – **5**[PbBr₄].

Compound	$\Delta_{oct} (\times 10^{-4})^a$
1 PbBr ₄	22.93
2 PbBr ₄	5.82
3 PbBr ₄	11.37
4 PbBr ₄	2.63
5 PbBr ₄	4.73

^aOctahedral bond-length distortion.

More detailed comparison of intra-octahedral distortion of the structure of **1**[PbBr₄] with that of published 2×2 (110) 2D perovskites can be obtained using the additional parameters octahedral elongation (λ_{oct}) and octahedral angle variance (σ_{oct}^2):

$$\lambda_{oct} = \frac{1}{6} \sum_{i=1}^6 \left[\frac{d_i}{d_0} \right]^2 \quad (\text{Eqn. 8.2})$$

$$\sigma_{oct}^2 = \frac{1}{11} \sum_{i=1}^{12} (\alpha_i - 90)^2 \quad (\text{Eqn. 8.3})$$

These two parameters quantify the deviation from O_h symmetry originating from Pb–Br bond lengths (d) and Br–Pb–Br angles (α), *via* changes in edge length (Br–Br distances)

and O_h volume (V) relative to an ideal structure.²³⁻²⁴ Interestingly, while the Δ_{oct} values for all of the corrugated Pb-Br perovskites are of a similar magnitude, the λ_{oct} and σ^2_{oct} are much larger in **1**[PbBr₄] (**Table 8.2**). This can be attributed to the asymmetry nature of dicationic **1**. More specifically, it contains multiple ammonium ions that significantly differ in terms of their steric profiles (i.e., endocyclic NH and alkylated N atoms, plus an exocyclic primary ammonium cation). As a result, the lead-bromide octahedral are presented with an inherently asymmetric charge environment.

Table 8.2 Summary of distortion parameters comparison of **1**[PbBr₄], with other 2×2 (110) 2D perovskites.

Compound	λ_{oct}^a	$\sigma^2_{oct}^b$	$\Delta_{oct}(\times 10^{-4})^c$
1 [PbBr ₄]	1.0177	53.67	22.93
ImPA [PbBr ₄] ^d	1.0088	20.80	26.02
IsEA [PbBr ₄] ^e	1.0123	38.89	9.67
N-MEDA [PbBr ₄] ^f	1.0080	24.51	8.20
EDBE [PbBr ₄] ^g	1.0090	23.91	24.00
EPZ [PbBr ₄] ^h	1.0164	40.26	38.07
3APr [PbBr ₄] ⁱ	1.0180	43.64	35.24

^aOctahedral elongation. ^bOctahedral angle variance. ^cOctahedral bond-length distortion.

^dImidazolium propyl ammonium,¹² ^eIsothiourethylammonium,¹³ ^fN¹-methylethane-1,2-diammonium,¹⁴ ^g2,2'-(ethylenedioxy)bis(ethylammonium),¹⁵ ^h1-ethylpiperazinium,¹⁷ ⁱ3-aminopyrrolidinium.²⁰

Physically, **1**[PbBr₄] – **5**[PbBr₄] appear colourless and the UV-vis absorption spectra of these materials confirm their high bandgap nature (**Figure 8.13a**). Their features are similar to those of other 2D lead-halide perovskites, inasmuch as the dielectric mismatch between organic and inorganic layers leads to strongly bound excitons, which results in sharp excitonic absorption bands in the region 370 – 420 nm.³⁻⁵ Significant bathochromic shifts of the absorption spectra are observed in **4**[PbBr₄] and **5**[PbBr₄] relative to **1**[PbBr₄]. This is due to both the (100) structure of the former compounds and the closer approach of their

Pb-(μ -Br)-Pb bond angles to ideal values (180°), which stabilizes the conduction band and, consequently, narrows the band gap.^{22, 25-26}

Figure 8.13 Room temperature (RT) a) UV-vis absorption and b) photoluminescence (PL) spectra of **1[PbBr₄]** – **5[PbBr₄]**. c) Plot and linear fit of the dependence of PL intensity upon laser fluence for **1[PbBr₄]**, measured at 293 K, in the range 5 - 50 $\mu\text{J}/\text{cm}^2$. d) PL spectrum of **1[PbBr₄]** at RT (red line) and 77 K (black line). e) Chromaticity coordinates for the PL emission of **1[PbBr₄]**, compared with reported values for previously reported 2×2 (110) 2D perovskites.

Upon excitation with 350 nm UV light, **1[PbBr₄]** – **5[PbBr₄]** all exhibit PL emission in the visible region comprised of a narrow band and a lower energy, broad feature (**Figure 8.13b**). The maxima of the former are located at similar energies ranging from 408 – 434 nm, close to their excitonic transitions. Thus, it can be assumed that the narrow emission originates from direct relaxation of free excitons.^{5, 11} As with other non-corrugated 2D Pb-Br perovskites,^{7, 16} the broad emission bands in **2[PbBr₄]** – **5[PbBr₄]** are red-shifted by only ca. 25 - 30 nm relative to their respective exciton bands. In contrast, a dramatic shift of ca. 124 nm and extensive broadening of the low energy band is observed for **1[PbBr₄]**. This is consistent with expectations based upon the large intra-octahedral distortions observed for this compound (**Tables 8.2 and 8.3**) and can, in particular, be attributed to its (110)-oriented inorganic framework.

8.2.3 Self-trapped excitons and cold white-light emission

Several studies have concluded that such broadband white-light emission occurs intrinsically and it is ascribed to the self-trapped excitons formed in the disordered crystal lattice.⁸⁻¹⁰ This type of mechanism has also been invoked for hybrid lead-halide systems of lower dimensionality, including those possessing one- and zero-dimensional inorganic lattices.²⁷⁻²⁹ This work's experimental observations concur and, therefore, the mechanism of PL in such systems is not discussed in any depth herein.

For instance, power-dependent PL measurements were performed for **1**[PbBr₄], at 293 K, and it was observed that the PL intensity increases linearly with excitation fluence from 5 to 50 $\mu\text{J}/\text{cm}^2$, with no signs of PL saturation (**Figure 8.13c**). These observations are consistent with an intrinsic, excitonic origin for the broadband PL. In addition, no change in emission band shape is seen throughout the course of the experiment (see **Figure 8.14** for PL evolution with different excitation intensity). This indicates there is no difference in the emissive defect sites accessed at different fluences. Note that **1**[PbBr₄] also displays similar PL features at temperatures ranging from room temperature (RT) to 77 K (**Figures 8.13d and 8.15**). Time-resolved PL was, additionally, conducted (**Figure 8.16**) and it was found that the effective PL lifetime of **1**[PbBr₄] is relatively short at room temperature (ca. 1.43 ns), but moderately increases upon lowering the temperature (to ca. 3.31 ns at 77 K). All of this data is consistent with previous reports of formation of self-trapped excitons in this class of materials.

Figure 8.14 Photoluminescence (PL) evolution of **1**[PbBr₄] as a function of excitation fluence.

Figure 8.15 Photoluminescence (PL) evolution of **1**[PbBr₄] as a function of temperature.

Figure 8.16 Time-resolved photoluminescence (PL) spectra of **1**[PbBr₄] recorded at emission wavelength 550 nm at 293 K and 77 K. PL lifetimes of approximately 1.43 ns and 3.31 ns at 293 K and 77 K, respectively, are obtained by monoexponential fittings.

Figure 8.17 Chromaticity coordinates of the emission of **1**[PbBr₄] – **5**[PbBr₄].

RT emission of **1**[PbBr₄] spans across the entire visible region, is heavily Stokes-shifted (by ca. 1.05 eV), and features a large full width at half maximum (FWHM) of ca. 810 meV. The CIE chromaticity coordinate of its emission is shown in **Figure 8.17**, along with those of the other compounds reported herein. While the emissions of **2**[PbBr₄] – **5**[PbBr₄] are located in the deep blue region, as reflected by CIE coordinates (x, y) of (0.18, 0.14), (0.25,

0.29), (0.19, 0.22) and (0.19, 0.22), respectively, that of **1**[PbBr₄] is shifted much closer to the central white region (**Table 8.3**). Its CIE coordinates of (0.32, 0.41) correspond to a correlated colour temperature (CCT) of 5824 K and colour rendering index (CRI) of 73. In contrast, the 2×2 corrugated compounds (N-MEDA)PbBr₄, (EDBE)PbBr₄, (3APr)PbBr₄, and (EPZ)PbBr₄ possess CCTs below 5000K (4669, 3990, 3456 and 3324 K, respectively).^{14-15, 17, 20} Such values correspond to ‘warm’ white-light emission, whereas the more blue-shifted, intense emission band in **1**[PbBr₄] makes it more suitable for ‘cold’ white-light LEDs (**Figure 8.5e**).

Table 8.3 Calculated Commission Internationale de l’Eclairage (CIE) chromaticity coordinates, Color Rendering Index (CRI) and Correlated Color Temperature (CCT) of **1**[PbBr₄] – **5**[PbBr₄].

Compound	CIE x-coordinate	CIE y-coordinate	Color Rendering Index (CRI)	Correlated Color Temperature (CCT)
1 [PbBr ₄]	0.3223	0.4131	73	5824
2 [PbBr ₄]	0.1765	0.1363	46	N.A.
3 [PbBr ₄]	0.2532	0.2853	85	14223
4 [PbBr ₄]	0.1879	0.2177	57	N.A.
5 [PbBr ₄]	0.1875	0.2201	56	N.A.

8.3 Summary

In conclusion, a rare 2×2 (110) 2D perovskite that is templated by the dication 1-(2-ammonioethyl)-1*H*-imidazol-3-ium (**1**) is studied in this chapter. Its corrugated 2D bromoplumbate layers exhibit a high degree of [PbBr₆]⁴⁻ intra-octahedral distortion, which manifests in broadband white-light emission, associated with large Stokes-shift and FWHM values. Furthermore, it is demonstrated that access to the desired (110)-oriented structure, rather than the (100)-oriented alternative, is a consequence of the organic cation possessing a subtle balance of structural properties. In the case of this study, inclusion of a coulombic interaction perpendicular to the plane of the heterocyclic ring *via* alkylation of an endocyclic *N*-atom. As such, this work adds to the short list of known corrugated 2D

lead-halide perovskites, and provides molecular engineering insights that may contribute to the design of better performing materials in the future. However, as highlighted through the study, designing a cation that can template (110)-type structure is a challenge (thus its rarity). As such, in the next chapter, an attempt in inducing white light emission in the more common (100)-type is described.

8.4 Bibliography

1. Sun, Y.; Giebink, N. C.; Kanno, H.; Ma, B.; Thompson M. E.; Forrest, S. R. *Nature*, **2006**, *440* (7086), 908-912.
2. Xia, Z.; Liu, Q. *Prog. Mater. Sci.*, **2016**, *84*, 59-117.
3. Saparov, B.; Mitzi, D. B. *Chem. Rev.*, **2016**, *116* (7), 4558-4596.
4. Cheng, Z.; Lin, J. *CrystEngComm*, **2010**, *12* (10).
5. Smith, M. D.; Karunadasa, H. I. *Acc. Chem. Res.*, **2018**, *51* (3), 619-627.
6. Wang, S.; Yao, Y.; Kong, J.; Zhao, S.; Sun, Z.; Wu, Z.; Li, L.; Luo, J. *Chem. Commun.*, **2018**, *54* (32), 4053-4056.
7. Hu, H.; Morris, S. A.; Qiao, X.; Zhao, D.; Salim, T.; Chen, B.; Chia, E. E. M.; Lam, Y. M. *J. Mater. Chem. C*, **2018**, *6* (38), 10301-10307.
8. Hu, T.; Smith, M. D.; Dohner, E. R.; Sher, M. J.; Wu, X.; Trinh, M. T.; Fisher, A.; Corbett, J.; Zhu, X. Y.; Karunadasa, H. I.; Lindenberg, A. M. *J. Phys. Chem. Lett.*, **2016**, *7* (12), 2258-2263.
9. Yangu, A.; Garrot, D.; Lauret, J. S.; Lusson, A.; Bouchez, G.; Deleporte, E.; Pillet, S.; Bendeif, E. E.; Castro, M.; Triki, S.; Abid, Y.; Boukheddaden, K. *J. Phys. Chem. C*, **2015**, *119* (41), 23638-23647.
10. Wang, X.; Meng, W.; Liao, W.; Wang, J.; Xiong, R. G.; Yan, Y. *J. Phys. Chem. Lett.*, **2019**, *10* (3), 501-506.
11. Smith, M. D.; Jaffe, A.; Dohner, E. R.; Lindenberg, A. M.; Karunadasa, H. I. *Chem. Sci.*, **2017**, *8* (6), 4497-4504.
12. Li, Y. Y.; Lin, C. K.; Zheng, G. L.; Cheng, Z. Y.; You, H.; Wang, W. D.; Lin, J. *Chem. Mater.*, **2006**, *18*, 3463-3469.
13. Li, Y.; Zheng G.; Lin, J. *Eur. J. Inorg. Chem.*, **2008**, *2008* (10), 1689-1692.

14. Dohner, E. R.; Hoke, E. T.; Karunadasa, H. I. *J. Am. Chem. Soc.*, **2014**, *136* (5), 1718-1721.
15. Dohner, E. R.; Jaffe, A.; Bradshaw, L. R.; Karunadasa, H. I. *J. Am. Chem. Soc.*, **2014**, *136* (38), 13154-13157.
16. Mao, L.; Wu, Y.; Stoumpos, C. C.; Wasielewski, M. R.; Kanatzidis, M. G. *J. Am. Chem. Soc.*, **2017**, *139*, 5210-5215.
17. Mao, L.; Guo, P.; Kepenekian, M.; Hadar, I.; Katan, C.; Even, J.; Schaller, R. D.; Stoumpos, C. C.; Kanatzidis, M. G. *J. Am. Chem. Soc.*, **2018**, *140* (40), 13078–13088.
18. Neogi, I.; Bruno, A.; Bahulayan, D.; Goh, T. W.; Ghosh, B.; Ganguly, R.; Cortecchia, D.; Sum, T. C.; Soci, C.; Mathews, N.; Mhaisalkar, S. G. *ChemSusChem*, **2017**, *10* (19), 3765-3772.
19. Hautzinger, M. P.; Dai, J.; Ji, Y.; Fu, Y.; Chen, J.; Guzei, I. A.; Wright, J. C.; Li, Y.; Jin, S. *Inorg. Chem.*, **2017**, *56* (24), 14991-14998.
20. Li, X.; Guo, P.; Kepenekian, M.; Hadar, I.; Katan, C.; Even, J.; Stoumpos, C. C.; Schaller, R. D.; Kanatzidis, M. G. *Chem. Mater.*, **2019**, *31* (9), 3582-3590.
21. Febriansyah, B.; Koh, T. M.; John, R. A.; Ganguly, R.; Li, Y.; Bruno, A.; Mhaisalkar, S. G.; England, J. *Chem. Mater.*, **2018**, *30* (17), 5827-5830.
22. Febriansyah, B.; Koh, T. M.; Lekina, Y.; Jamaludin, N. F.; Bruno, A.; Ganguly, R.; Shen, Z. X.; Mhaisalkar, S. G.; England, J. *Chem. Mater.*, **2019**, *31* (3), 890–898.
23. Robinson, K.; Gibbs, G. V.; Ribbe, P. H. *Science* **1971**, *172*, 567-570.
24. Cortecchia, D.; Neutzner, S.; Srimath Kandada, A. R.; Mosconi, E.; Meggiolaro, D.; De Angelis, F.; Soci, C.; Petrozza, A. *J. Am. Chem. Soc.*, **2016**, *139* (1), 39-42.
25. Pradeesh, K.; Nageswara Rao, K.; Vijaya Prakash, G. *J. App. Phys.*, **2013**, *113* (8).
26. Takahashi, Y.; Obara, R.; Nakagawa, K.; Nakano, M.; Tokita, J.-Y.; Inabe, T. *Chem. Mater.* **2007**, *19*, 6312-6316.
27. Yuan, Z.; Zhou, C.; Tian, Y.; Shu, Y.; Messier, J.; Wang, J. C.; van de Burgt, L. J.; Kountouriotis, K.; Xin, Y.; Holt, E.; Schanze, K.; Clark, R.; Siegrist, T.; Ma, B. *Nature Commun.*, **2017**, *8*.
28. Zhou, C.; Lin, H.; Tian, Y.; Yuan, Z.; Clark, R.; Chen, B.; van de Burgt, L. J.; Wang, J. C.; Zhou, Y.; Hanson, K.; Meisner, Q. J.; Neu, J.; Besara, T.; Siegrist, T.; Lambers, E.; Djurovich, P.; Ma, B. *Chem. Sci.*, **2018**, *9* (3), 586-593.

29. Zhou, C.; Lin, H.; Shi, H.; Tian, Y.; Pak, C.; Shatruk, M.; Zhou, Y.; Djurovich, P.; Du, M.-H.; Ma, B. *Angew. Chem. Int. Ed.*, **2018**, 57 (4), 1021-1024.

8.5 Instrumentations and additional data

UV-Vis spectroscopy. UV-vis absorption spectra of the thin films samples were recorded using a SHIMADZU UV-3600 spectrophotometer, with an integrating sphere (ISR-3100), in the wavelength range 300 – 800 nm and a scanning resolution of 0.5 nm s⁻¹.

Steady-state, time-resolved, temperature- and power-dependent photoluminescence (PL) spectroscopies. Samples were photoexcited using 325 nm femtosecond laser pulses, generated with an optical parametric amplifier (OPA, Coherent OPerA Solo). The OPA was powered by using Coherent LIBRA laser, with a fundamental wavelength of 800 nm and output pulse-width of ~50 fs, at a repetition rate of 1 kHz. The PL signal was collected using a lens pair and sent to a spectrometer (Princeton Instrument, SP-2500 series), where it was detected in steady-state and TRPL measurements by a CCD (Pixis-400) and streak camera (Optronis), respectively. The power-dependent measurements were obtained in this configuration using a set of variable density filters to change the excitation fluence in the range of *ca.* 5 – 50 $\mu\text{J}/\text{cm}^2$. For temperature-dependent measurements, the samples were mounted onto a liquid nitrogen-cooled Janis st-300 cryostat, adjusted to the optical plane of the inverted microscope, and measured within the temperature range 77 – 293 K.

X-ray single crystallography. Crystals were mounted on a Bruker X8 Quest CPAD area detector diffractometer and data was collected using a I μ S 3.0 Microfocus Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$), at cryogenic temperatures (100 K). Data reduction and absorption corrections were performed using the SAINT and SADABS software packages, respectively. All structures were solved by direct methods and refined by full-matrix least squares procedures on F², using the Bruker SHELXTL-2014 software package. Non-hydrogen atoms were anisotropically refined, after which hydrogen atoms were introduced at calculated positions and further refinement of data was performed. Graphical depictions

of the crystal structures used throughout the manuscript were created using the program VESTA.

1-(2-Ammonioethyl)-1*H*-imidazol-3-ium dibromide. Isolated as a white solid (1.52g; 84% yield). ^1H NMR (400 MHz, DMSO- d_6): δ 9.13 (s, 1 H, ArH), 7.89 (bs, 3 H, NH_3), 7.79 (t, $J = 1.4$ Hz, 1 H, ArH), 7.72 (t, $J = 1.4$ Hz, 1 H, ArH), 4.44 (t, $J = 5.8$ Hz, 2 H, CH_2), 3.38 (t, $J = 5.9$ Hz, 2 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 136.0, 122.1, 120.2, 46.2, 38.6.

2-(2-Ammonioethyl)pyridin-1-ium dibromide. Isolated as a beige solid (1.44g; 83% yield). ^1H NMR (400 MHz, DMSO- d_6): δ 8.88 (d, 1 H, ArH), 8.50 (t, 1 H, ArH), 8.13 (bs, 3 H, NH_3^+), 7.99 (d, 1 H, ArH), 7.92 (t, 1 H, ArH), 3.39-3.32 (m, 4 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 152.7, 145.4, 142.7, 127.2, 125.2, 37.3, 31.0.

3-(2-Ammonioethyl)pyridin-1-ium dibromide. Isolated as a white solid (0.76g; 91% yield). ^1H NMR (400 MHz, DMSO- d_6): δ 8.92 (s, 1 H, ArH), 8.86 (d, 1 H, ArH), 8.53 (d, 1 H, ArH), 8.04 (t, 2 H, ArH), 7.98 (bs, 1 H, NH_3^+), 3.23-3.20 (m, 2 H, CH_2), 3.16-3.12 (m, 2 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 146.3, 142.5, 140.7, 137.1, 126.8, 38.8, 29.6.

4-(2-Ammonioethyl)pyridin-1-ium dibromide. Isolated as a beige solid (1.14g; 86% yield). ^1H NMR (400 MHz, DMSO- d_6): δ 8.92 (d, 2 H, ArH), 8.05 (bs, 3 H, NH_3^+), 8.04 (d, 2 H, ArH), 3.25-3.20 (m, 4 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 157.9, 141.7, 127.6, 38.1, 32.6.

Table 8.4 Crystallographic and structure refinement data for **1[PbBr₄]**, **2[PbBr₄]**, and **3[PbBr₄]**.^a

	Compound		
	1[PbBr₄]	2[PbBr₄]	3[PbBr₄]
Empirical formula	C ₅ H ₁₀ Br ₄ N ₃ Pb	C ₅ H ₅ Br ₄ N ₃ Pb	C ₅ H ₁₀ Br ₄ N ₃ Pb
Formula weight	638.99 g/mol	633.95 g/mol	638.99 g/mol
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal size	0.080 x 0.100 x 0.120 mm	0.020 x 0.040 x 0.120 mm	0.020 x 0.060 x 0.200 mm
Crystal habit	colorless block	colorless plate	colorless plate
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	P b c a	P 1 21/c 1	P 1 21/c 1
Unit cell dimensions	a = 9.5053(2) Å	a = 10.5249(7) Å	a = 10.0629(6) Å
	α = 90°	α = 90°	α = 90°
	b = 11.7946(2) Å	b = 11.4885(7) Å	b = 11.6838(8) Å
	β = 90°	β = 109.985(2)°	β = 108.486(4)°
	c = 23.5189(4) Å	c = 11.9069(7) Å	c = 11.9306(10) Å
	γ = 90°	γ = 90°	γ = 90°
Volume	2636.73(8) Å ³	1353.03(15) Å ³	1330.34(17) Å ³
Z	8	4	4
Density	3.219 g/cm ³	3.112 g/cm ³	3.190 g/cm ³
Absorption coefficient	24.886 mm ⁻¹	24.248 mm ⁻¹	24.662 mm ⁻¹
F(000)	2264	1112	1132
Theta range for data collection	2.88 to 31.00°	2.54 to 30.00°	2.51 to 31.04°
Reflections collected	30720	15540	4187
Coverage of independent reflections	99.9%	99.9%	99.3%
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan
Max. and min. transmission	0.2410 and 0.1540	0.6430 and 0.1590	0.6380 and 0.0830
Function minimized	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	4193 / 0 / 119	3944 / 0 / 119	4187 / 0 / 120
Goodness-of-fit on F ²	1.069	1.036	1.042
Δ/σ _{max}	0.001	0.001	0.001
Final R indices [I > 2σ(I)]	3378 data	2902 data	2941 data
	R1 = 0.0251,	R1 = 0.0451,	R1 = 0.0650,
	wR2 = 0.0430	wR2 = 0.0902	wR2 = 0.1279
R indices [all data]	R1 = 0.0396,	R1 = 0.0708,	R1 = 0.1061,
	wR2 = 0.0471	wR2 = 0.1018	wR2 = 0.1503
Largest diff. peak and hole	1.060 and -1.188 eÅ ⁻³	2.091 and -1.623 eÅ ⁻³	3.031 and -2.676 eÅ ⁻³
R.M.S. deviation from mean	0.263 eÅ ⁻³	0.301 eÅ ⁻³	0.491 eÅ ⁻³

^aR = Σ||F_o| - |F_c||/Σ|F_o|, wR = {Σ[w(|F_o|² - |F_c|²)²]/Σ[w(|F_o|⁴)]}^{1/2} and **1[PbBr₄]**, w = 1/[σ²(F_o²) + (0.0150P)² + 0.2316P]; **2[PbBr₄]**, w = 1/[σ²(F_o²) + (0.0298P)² + 3.1350P]; **3[PbBr₄]**, w = 1/[σ²(F_o²) + (0.0472P)² + 21.4593P]; where P = (F_o² + 2F_c²)/3.

Table 8.5 Crystallographic and structure refinement data for **4[PbBr₄]** and **5[PbBr₄]**.^a

	Compound	
	4[PbBr₄]	5[PbBr₄]
Empirical formula	C ₇ H ₁₂ Br ₄ N ₂ Pb	C ₇ H ₁₂ Br ₄ N ₂ Pb
Formula weight	651.02 g/mol	651.02 g/mol
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal size	0.020 x 0.040 x 0.220 mm	0.040 x 0.080 x 0.120 mm
Crystal habit	yellow needle	yellow plate
Crystal system	orthorhombic	monoclinic
Space group	P b c a	P 1 21/n 1
Unit cell dimensions	a = 16.8270(7) Å	a = 5.9837(2) Å
	α = 90°	α = 90°
	b = 8.3941(3) Å	b = 11.8526(4) Å
	β = 90°	β = 93.9990(14)°
	c = 19.8920(9) Å	c = 19.4795(6) Å
	γ = 90°	γ = 90°
Volume	2809.7(2) Å ³	1378.17(8) Å ³
Z	8	4
Density	3.078 g/cm ³	3.138 g/cm ³
Absorption coefficient	23.355 mm ⁻¹	23.808 mm ⁻¹
F(000)	2320	1160
Theta range for data collection	2.38 to 27.00°	2.71 to 34.00°
Reflections collected	18962	24583
Coverage of independent reflections	100.00%	99.90%
Absorption correction	Multi-Scan	Multi-Scan
Max. and min. transmission	0.6520 and 0.0790	0.4490 and 0.1620
Function minimized	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	3065 / 411 / 211	5625 / 0 / 128
Goodness-of-fit on F ²	1.058	1.027
Δ/σ _{max}	0.001	0.001
Final R indices	2253 data	4466 data
[I > 2σ(I)]	R1 = 0.0433,	R1 = 0.0328,
	wR2 = 0.0937	wR2 = 0.0580
R indices [all data]	R1 = 0.0676,	R1 = 0.0503,
	wR2 = 0.1089	wR2 = 0.0637
Largest diff. peak and hole	2.133 and -1.832 eÅ ⁻³	1.289 and -2.076 eÅ ⁻³
R.M.S. deviation from mean	0.254 eÅ ⁻³	0.339 eÅ ⁻³

^aR = Σ||F_o| - |F_c||/Σ|F_o|, wR = {Σ[w(|F_o|² - |F_c|²)²]/Σ[w(|F_o|⁴)]}^{1/2} and **4[PbBr₄]**, w = 1/[σ²(F_o²) + (0.0346P)² + 42.7986P]; **5[PbBr₄]**, w = 1/[σ²(F_o²) + (0.0167P)²]; where P = (F_o² + 2F_c²)/3.

Chapter 9

Two-dimensional hybrid lead-bromide perovskite broadband emitters with highly deformed metal coordination spheres

Published studies of layered (2D) (100)-oriented hybrid lead-bromide perovskites evidence a correlation between increased inter-octahedral (Pb-Br-Pb) distortions and the appearance of broadband white light emission. However, the impact of distortions within their constituent $[\text{PbBr}_6]^{4-}$ octahedra (intra-octahedral) has yet to be assessed. Herein, two new (100)-oriented 2D Pb-Br perovskites, whose structures display unusually high intra-octahedral distortions, whilst retaining minimal inter-octahedral distortions are investigated. Using a combination of temperature-dependent, power-dependent and time-resolved photoluminescence spectroscopic measurements, it is shown that increased intra-octahedral distortion induces exciton localization processes and leads to formation of multiple photoinduced emissive colour centres. Ultimately, this leads to highly Stokes-shifted, ultrabroad white light emission at room temperature.

9.1 Background

Metal halide perovskites that exhibit broadband emission, upon near-ultraviolet (UV) excitation, are an intensely studied class of materials.^{1, 2} The interest in them originates from their potential as single-source down-converting white-light-emitting phosphors, displaying good color rendition and stable emission color.^{3, 4} Furthermore, they can be deposited on large area substrates from solution, at relatively low temperatures, and without the need of additives, which makes them attractive in terms of cost and ease of fabrication.⁵ Recently, very high luminescence quantum yields up to 86% have been achieved in metal halide perovskites exhibiting warm white-light emission, such as Bi-doped $\text{Cs}_2(\text{Ag}_{0.60}\text{Na}_{0.40})\text{InCl}_6$.⁶ This has spurred efforts intended to develop further broadband emitters and obtain an understanding of how these properties can be induced by synthetic design.

Two-dimensional (2D) hybrid Pb-Br perovskites are a focal point of such research and recent work has allowed compilation of a library of these compounds that exhibit broadband luminescence. However, despite this surge in the synthesis of new Pb-Br perovskites, the photophysical origins of the observed photoluminescence broadening are still under investigation. Several studies have highlighted the formation of self-trapped excitons, involving localization of electrons and holes at specific crystal sites by their own lattice distortion field, as the key mechanism leading to ultrabroadband, highly Stokes shifted emission.^{5, 7} Most evidence for this proposition comes from theoretical works, and rigorous experimental support is lacking.⁸⁻¹¹ Alternatively, it has also been suggested that permanent color centers (e.g., positive and negative ion vacancies, and atoms in interstitial sites) play a role in mediating the observed trapping and luminescence processes.^{12, 13}

Regardless, it is widely accepted that the structural properties of a perovskite, including (electronic) dimensionality, control the energetic landscape and defectivity, and, thereby, directly affect emission energy and bandwidth.^{5, 8, 14-16} This has important synthetic implications, since the desired level and type of structural distortion can be tailored by incorporation of carefully selected organic cations. Correspondingly, several recent reports

have attempted to establish correlations between structural and optical properties, of two-dimensional (2D) perovskites.¹⁶⁻¹⁸

Structurally, 2D Pb-halide perovskites can be seen as being derived from their 3D counterparts by slicing the inorganic lattice of the latter along either the (100), (110), or (111) crystallographic planes.^{19, 20} Early on, broadband emission was linked to Pb-Br perovskites bearing rare corrugated (110) structures.^{1, 2, 17, 21, 22} Later, more common (100)-variants, which typically emit narrow free-excitonic (FE) blue or near-UV PL, were also found to exhibit similar broad PL features, albeit with a strong dependence on temperature. In particular, Smith et al. suggested a correlation between greater out-of-plane inter-octahedra distortions of the crystal lattice in (100) Pb-Br perovskites with increased relative intensity of broadband emission.¹⁶ Subsequent reports by Neogi,¹⁸ Wang,³ and Hu⁴ further supported this conclusion. In contrast to the high out-of-plane tilt angles, the PbBr_6 units in all of these reports retain a ‘close-to-ideal’ octahedral coordination geometry.^{3, 4, 18}

Figure 9.1 The organic dications, **1** and **2**, used in this study.

The influence of structural distortion within the coordination sphere of the lead ions (i.e. ‘intra-octahedral distortion’), rather than between the Pb-Br octahedra (‘inter-octahedral distortion’), upon broadband emission has not been investigated. In response, bromide salts of the ethylammonium-appended cyclic dications **1** and **2** (**Figure 9.1**), which had previously been found to template 2D Pb-I perovskites displaying large intra-octahedral distortions,²⁴ were combined with stoichiometric PbBr_2 in hot hydrobromic acid. Slow cooling yielded single crystals of the desired materials **1** $[\text{PbBr}_4]$ and **2** $[\text{PbBr}_4]$ suitable for high resolution X-ray crystallography. Purity of the bulk materials was confirmed using powder X-ray diffraction (**Figures 9.2a-b**).

Figure 9.2 Powder X-ray diffraction (PXRD) patterns of powdered 2D hybrid perovskites **1**[PbBr₄] (a) and **2**[PbBr₄] (b). The simulated room temperature (RT) PXRD patterns are also provided for comparison.

9.2 Results and discussions

9.2.1 2D (100) perovskites based on sterically demanding organic cation

The crystal structures of **1**[PbBr₄] and **2**[PbBr₄] (**Figure 9.3**, see **Section 9.5** for summary of crystallographic refinement data) confirm that the 2D inorganic lattice was obtained. Topologically, both materials feature a conventional (100) structure, with single-layer-thick corner-shared octahedral [PbBr₆]⁴⁻ units separated by monolayers of dications **1** and **2**. The latter leads to very small distances between the inorganic layers of ca. 4.169 and 4.069 Å, respectively.

The degree of structural distortion of the inorganic layers was assessed quantitatively by calculation of octahedral elongation (λ_{oct}), octahedral angle variance (σ_{oct}^2), and octahedral bond-length distortion (Δ_{oct}) parameters:^{14, 17, 23}

$$\text{Bond length distortion: } \Delta_{oct} = \frac{1}{6} \sum_{i=1}^6 \left[\frac{d_i - d_m}{d_m} \right]^2 \quad (\text{Eqn. 9.1})$$

$$\text{Octahedral elongation: } \lambda_{oct} = \frac{1}{6} \sum_{i=1}^6 \left[\frac{d_i}{d_0} \right]^2 \quad (\text{Eqn. 9.2})$$

$$\text{Octahedral angle variance: } \sigma_{oct}^2 = \frac{1}{11} \sum_{i=1}^{12} (\alpha_i - 90)^2 \quad (\text{Eqn. 9.3})$$

where d_i represents Pb–Br bond length, d_m to average bond length, d_0 to center-to-vertex distance of a regular polyhedron of the same volume, and α_i to individual Br–Pb–Br angle. Δ_{oct} , λ_{oct} and σ^2_{oct} provide a quantitative measure of polyhedral distortion independent of the polyhedron effective size.

Figure 9.3 Single crystal X-ray structures of a) $1[\text{PbBr}_4]$ and b) $2[\text{PbBr}_4]$ at room temperature. Penetration of the organic dications into the ‘bay regions’ of the 2D perovskites, built from four neighbouring $[\text{PbBr}_6]^{4-}$ octahedra, are depicted in c) $1[\text{PbBr}_4]$ and d) $2[\text{PbBr}_4]$. The approximate degree of penetration of the ethylammonium groups, (illustrated by a dotted orange line) are given in the figure. ‘Top view’ of (e) $1[\text{PbBr}_4]$ and (f) $2[\text{PbBr}_4]$, presented with their respective crystallographic axes. Pb-(μ -Br)-Pb bond angles are included. Black, brown, grey, and blue spheres represent Pb, Br, C, and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.

Larger values correspond to greater distortion. The intra-octahedral distortions exhibited by $1[\text{PbBr}_4]$ and $2[\text{PbBr}_4]$ are in overall large compared with other examples of (100) perovskites (**Table 9.1**). Instead, they are of a similar order of magnitude to those reported for (110) perovskites (**Table 9.2**). In addition, due to lattice contraction, the high degree of

intra-octahedral distortion of the inorganic lattice gets even more pronounced in low temperature (100 K) where **2** was found to enforce much more severe octahedral elongation and angle variance values relative to **1** (Figure 9.4, Table 9.3).

Figure 9.4 Single crystal X-ray structures of a) **1**[PbBr₄] and b) **2**[PbBr₄] at 100 K. Penetration of the organic dications into the ‘bay regions’ of the 2D perovskites, built from four neighbouring [PbBr₆]⁴⁻ octahedra, are depicted in c) **1**[PbBr₄] and d) **2**[PbBr₄]. The approximate degree of penetration of the ethylammonium groups, (illustrated by a dotted orange line) are given in the figure. ‘Top view’ of (e) **1**[PbBr₄] and (f) **2**[PbBr₄], presented with their respective crystallographic axes. Pb-(μ-Br)-Pb bond angles are included. Black, brown, grey, and blue spheres represent Pb, Br, C, and N atoms, respectively. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability.

The large intra-octahedral distortions in the compounds in this study can be attributed to the inherently asymmetric environment of their constituent [PbBr₆]⁴⁻ octahedra. More specifically, the organic dications within a monolayer alternate in terms of their orientation, with either their cyclic heads or ethylammonium tails pointing into the cuboctahedral cavities (‘bay regions’) formed by the terminal bromide ligands of four neighbouring Pb-Br octahedra (Figures 9.3c-d). In addition, the bay region on the other face of the 2D

inorganic layer formed from the same Pb-Br octahedra hosts the other end (heads or tails) of the dication. This asymmetry is exacerbated in the great difference in penetration of the heads and tails of the dications into the ‘bay regions’ of the perovskites.

Table 9.1 Summary of distortion parameters for **1**[PbBr₄], **2**[PbBr₄] and other selected 2D perovskites.

Compound	$\lambda_{\text{oct}}^{\text{a}}$	$\sigma_{\text{oct}}^2{}^{\text{b}}$	Δ_{oct} ($\times 10^{-4}$) ^c	D_{tilt} (°)	D_{out} (°)	D_{in} (°)
1 [PbBr ₄]	1.0104	30.09	13.655	7.9	6.0	5.1
2 [PbBr ₄]	1.0109	33.99	9.460	12.2	10.5	6.2
DMABA [PbBr ₄] ^d	1.0094	32.64	4.300	17.1	16.7	3.9
AEA [PbBr ₄] ^e	1.0060	20.72	0.852	35.7	22.4	28.5
MPenDA [PbBr ₄]	1.0007	2.58	0.004	32.6	17.9	27.7
CyDMA [PbBr ₄] ^h	1.0016	5.09	0.855	32.3	23.2	23.0
(PEA) ₂ [PbBr ₄] ^f	1.0056	16.35	9.770	29.2	10.4	27.9
(BA) ₂ [PbBr ₄] ^g	1.0027	9.43	0.067	25.2	2.8	25.0

^aOctahedral elongation. ^bOctahedral angle variance. ^cOctahedral bond-length distortion.

^dButylammonium,¹⁶ ^e4-(*N*¹,*N*¹-dimethylammonio)butylammonium,¹⁷ ^fphenylethylammonium,²⁴ ^g3-(2-ammonioethyl)anilinium.¹⁶ (**PEA**)₂[PbBr₄] and (**BA**)₂[PbBr₄] are not broadband emitters at room temperature.

Whereas the bulky ring moieties in **1**[PbBr₄] and **2**[PbBr₄] display minimal penetration of ca. 0.319 and 0.374 Å, respectively, the appended ethylammonium chains are found to insert quite deeply, by ca. 1.095 Å and 1.346 Å, respectively. The greater penetration of the piperidinium ring of **2**, compared with the pyridinium ring of **1**, is likely a consequence of its lesser ability to delocalize positive charge and this, combined with its greater steric bulk, leads to greater distortion in **2**[PbBr₄] relative to **1**[PbBr₄]. In contrast, in conventional 2D perovskites (RNH₃)₂PbX₄, all cuboctahedral cavities are occupied by primary ammonium functionality, so the environments of their Pb-Br octahedra are inherently more symmetrical. Furthermore, the penetrations of their primary ammonium moieties into the perovskite ‘bay regions’ are also significantly smaller, where

corresponding distances of ca. 0.7 Å and below are normally seen, which results in much smaller intra-octahedral distortions.¹⁵

Table 9.2 Summary of distortion parameters of 2D perovskites **1**[PbBr₄] and **2**[PbBr₄] in comparison to (110) Pb-Br perovskites.

No.	Organic cation	Δd (x10 ⁻⁴)	λ_{oct}	σ_{oct}^2	Ref.
1.		26.02	1.0088	20.80	21
2.		9.67	1.0123	38.89	22
3.		8.20	1.0080	24.51	1
4.		24.00	1.0090	23.91	2
5.		17.40	1.0068	17.35	17
6.		13.66	1.0104	30.09	This work
7.		9.46	1.0109	33.99	This work

Table 9.3 Summary of distortion parameters for **1**[PbBr₄] and **2**[PbBr₄] at different temperatures.

No.	Compound	Δd (x10 ⁻⁴)	λ_{oct}	σ_{oct}^2	D_{tilt} (°)	D_{out} (°)	D_{in} (°)
1.	1 [PbBr ₄] at 100 K	1.0131	36.41	19.59	6.7	6.1	2.8
2.	2 [PbBr ₄] at 100 K	1.0205	62.32	16.57	7.7	4.9	5.9
3.	1 [PbBr ₄] at RT	1.0104	30.09	13.65	7.9	6.0	5.1
4.	2 [PbBr ₄] at RT	1.0109	33.99	9.46	12.2	10.5	6.2

Conversely, **1**[PbBr₄] and **2**[PbBr₄] exhibit minimal inter-octahedral distortions with the latter exhibits slightly higher distortion than the former (**Table 9.1**). This is evident in their Pb-(μ-Br)-Pb bond angles, which are as high as 180 and 175°, respectively (θ_{tilt} ; **Figures 9.3e-f**). As a frame of reference, the highest Pb-(μ-Br)-Pb bond angles reported, thus far, for (100) 2D Pb-Br perovskites range between 144 and 153°. ^{16, 18, 24, 25} More thorough

quantification of the inter-octahedral distortions is provided by their respective in-plane (D_{in}) and out-of-plane (D_{out}) distortion parameters (as a convolution of the compound's D_{tilt} where $D_{tilt} = 180^\circ - \theta_{tilt}$), which can be calculated using the methodology employed in ref. 16. Small values of 5.1 and 6.0° were obtained for **1**[PbBr₄] and 6.2 and 10.5° for **2**[PbBr₄], confirming the presence of very mild inter-octahedral distortions. For comparison, inter-octahedral distortion angles of reported white light emitting (100) 2D bromoplumbates exceed 15°. ^{3, 4, 16, 18} Furthermore, the minimal inter-octahedral distortions features of the two compounds are also retained even at low temperature (100 K; **Figure 9.4** and **Table 9.3**).

The small inter-octahedral distortions observed for **1**[PbBr₄] and **2**[PbBr₄] are likely due to the relatively diffuse, sterically hindered positive charges of the cyclic rings present in the templating dications. By comparison, primary ammonium groups have highly localized and accessible positive charges. One would anticipate that the latter cations would exert a greater driving force for bringing the negatively charged lead-halide octahedra into close proximity with them, thereby distorting the inorganic lattice. This would manifest as a compression of the Pb-(μ-X)-Pb bond angles (in-plane and/or out-of-plane) between neighboring octahedra. The reduced prominence of primary ammonium cations in these materials, therefore, leads to reduced inter-octahedral distortions. ^{26, 27}

Figure 9.5 Raman spectra of (PipEA)PbBr₄ (upper panel) and (PyrEA)PbBr₄ (lower panel).

Thus far, dications **1** and **2** template (100) 2D Pb-Br perovskites that exhibit large intra-octahedral distortions of the inorganic lattice, but without enforcing appreciable inter-octahedral tilting. The mutual interaction between the structural properties of the organic cation and those of the inorganic lattice is further corroborated by Raman measurements (**Figure 9.5**). In particular, the mode at 123 cm^{-1} in **2**[PbBr₄], which can be attributed to the lurching of the ammonium moieties,²⁸ shifts to significantly higher wavenumbers ($\sim 136\text{ cm}^{-1}$) in **1**[PbBr₄]. This is likely due to the interaction of the [PbBr₄]²⁻ lattice with the positively charged aromatic ring of dication **1**.

9.2.2 Generation of broadband emission

The structural properties of the two perovskites **1**[PbBr₄] and **2**[PbBr₄] have significant impacts upon their single crystal optical properties. **Figures 9.6a and 9.6b** show the transformed Kubelka–Munk function $F(R) = (1-R)^2/2R$ obtained from the reflectance R measured on ground crystals, which gives a spectrum proportional to the absorption coefficient of the material. The excitonic peak of the layered perovskites appears as a sharp band located at 434 nm and 422 nm for **1**[PbBr₄] and **2**[PbBr₄], respectively. The absorption blue-shift of **2**[PbBr₄] correlates well with the slightly smaller average Pb-(μ -Br)-Pb angle of this compound relative to **1**[PbBr₄]. This is because greater deviation from the linearity results in poorer orbital overlap (Pb-6s and Br-4p orbitals) and causes widening of the band-gap, as previously observed in similar compounds.^{26, 29}

On the whole, **2**[PbBr₄] features higher degree of both intra-octahedral and inter-octahedral distortions than **1**[PbBr₄]. As the consequence, the two materials have striking differences in their steady-state photoluminescence (PL). At room temperature, the emission of the less-distorted compound **1**[PbBr₄] features a predominant narrowband, blue emission between 430–500 nm, followed by a broad and unstructured tail. The high energy emission shows a double-peaked structure which results from the self-absorption of the excitonic emission, which is particularly strong in single crystals of compounds that exhibit a very small Stokes-shift.³⁰ This is also confirmed by the fact that PL measured from thin films,

where the influence of luminescence self-absorption is much less severe, shows a single-peaked excitonic emission (**Figure 9.7**).

Figure 9.6 Absorption (blue line) and luminescence (red line) spectra of (a) 1[PbBr₄] and (b) 2[PbBr₄], at room temperature. Temperature-dependent photoluminescence of (c) 1[PbBr₄] and (d) 2[PbBr₄]. PL spectra were recorded on single crystals using an excitation wavelength (λ_{exc}) of 405 nm.

Figure 9.7 Absorption (blue line) and photoluminescence (red line) spectra of a) 1[PbBr₄] and b) 2[PbBr₄] measured on perovskite thin films.

On the other hand, the more distorted compound $2[\text{PbBr}_4]$ has an ultrabroad (full width at half maximum, FWHM, = 292 nm, 1.1 eV), heavily Stokes shifted emission (203 nm) peak at 607 nm, which partially overlaps with the free excitonic emission peak at 452 nm. Similar optical properties are retained also when the perovskite is spin-coated in form of thin film (**Figure 9.7**), indicating the morphology-independent nature of the emission. Such broadband emission results in nearly pure white-light, with a correlated colour temperature (CCT) = 4088, Commission Internationale de l'Eclairage (CIE) chromaticity coordinate (0.38; 0.38) and colour rendering index (CRI) = 96 (**Figure 9.8**). This CRI value is higher than that of fluorescent light sources (about 65) and surpasses the values reported for other 2D white-light emitting perovskites.^{5, 31} Such behaviour is noteworthy because, to date, room temperature broadband emission has only been observed for (100) 2D Pb-Br perovskites with strong inter-octahedral distortions. However, $2[\text{PbBr}_4]$ displays significant intra-octahedral distortion of its $[\text{PbBr}_6]^{4-}$ octahedra, but only mild inter-octahedral tilting (**Table 9.1**).

Figure 9.8 CIE chromaticity diagram and coordinates for the room temperature emission of $1[\text{PbBr}_4]$ (0.19;0.17) and $2[\text{PbBr}_4]$ (0.38;0.38) under excitation wavelength $\lambda_{\text{exc}} = 405$ nm.

9.2.3 Formation of multiple photoinduced emissive colour centres

As is typically observed in similar layered perovskites,⁵ broadband emission becomes dominant in both **1**[PbBr₄] and **2**[PbBr₄] at low temperatures, increasing in intensity by about two orders of magnitude upon moving from 298 to 77 K (**Figures 9.6c,d and Figure 9.9**). This increase is accompanied by narrowing of the band and a redshift of the peak in the temperature (T) range 298 to ~150 K, followed by a blue-shift upon decreasing T < 150 K (**Figure 9.10**).

Figure 9.9 Temperature dependent photoluminescence ($\lambda_{\text{exc}} = 405 \text{ nm}$) of a) **1**[PbBr₄] and b) **2**[PbBr₄].

The dependence of the integrated PL intensity upon temperature follows Arrhenius-type behaviour, with at least two non-radiative thermally activated channels being present. This results in two distinct activation energies for each material:^{32, 33} $E_{a1} = 41 \text{ meV}$ and $E_{a2} = 122 \text{ meV}$ for **1**[PbBr₄]; $E_{a1} = 43 \text{ meV}$ and $E_{a2} = 140 \text{ meV}$ for **2**[PbBr₄]. In both materials, E_{a2} is the dominant component (see **Table 9.4 and Figure 9.11**). The less distorted structure of **1**[PbBr₄] results in lower de-trapping energies (E_{a2} in particular) and causes faster quenching of the broadband PL with temperature. The presence of two thermally activated channels suggests the formation of at least two emissive species, although it is possible that more emissive intra-gap states with wide energy distribution, stemming from exciton trapping at different sites of the perovskite lattice, might actually be involved in the radiative decay leading to ultrabroad PL.

Figure 9.10 Temperature dependence of a) full width at half maximum (FWHM) and b) peak maximum of broadband emission.

Table 9.4 Fitting results for the Arrhenius plots in **Figure 9.11**.

	I_0 [$\times 10^7$]	Ea_1 [meV]	C_1	Ea_2 [meV]	C_2 [$\times 10^4$]	R^2
1[PbBr ₄]	2.3 ± 0.1	41 ± 1	388 ± 48	122 ± 16	2.9 ± 2.3	0.999
2[PbBr ₄]	1.3 ± 0.4	43 ± 1	216 ± 32	140 ± 17	5.2 ± 4.8	0.999

Figure 9.11 Arrhenius plots of the integrated PL intensity (I) as a function of temperature. The fitting was done with the Arrhenius formula including two competitive nonradiative recombination channels $I = I_0 / [1 + C_1 \exp(-Ea_1/kT) + C_2 \exp(-Ea_2/kT)]$, where Ea_1 , Ea_2 are the activation energies for the thermal de-trapping process, k is the Boltzmann constant, I_0 is the zero-temperature PL intensity and C_1 , C_2 represent the strength of the quenching processes. The fitting results are summarized in **Table 9.4**.

To probe the broadband emission from both samples, power-dependent photoluminescence measurements were performed at 78 K. The resulting data, presented in **Figure 9.12** in double- logarithmic scale, exhibit power law dependence $I = P^K$, where I is PL intensity and P is excitation power. As expected for an excitonic transition, the intensity of the excitonic emission peak in **1[PbBr₄]**, at 430 nm, increases linearly with increasing excitation power and, thus, $K \sim 1$ (**Figure 9.12a**).³⁴ On the other hand, the accompanying band in the spectral range 435 – 460 nm demonstrates a sublinear dependence, with $K = 0.85 \pm 0.01$ (**Figure 9.12b**). A sublinear trend is also observed for the broadband component (460 - 900 nm) in both **1[PbBr₄]** and **2[PbBr₄]**, with $K = 0.89 \pm 0.01$ and 0.95 ± 0.01 , respectively (**Figure 9.12c**). A similar trend was also previously observed for the broadband emission of Cs₃Sb₂I₉.³⁵ However, such behaviour is contrary to the majority of similar broadband emitting perovskites, for which PL intensity exhibits a linear dependence upon excitation density and does not show saturation behavior. The latter has been interpreted as a signature trait of the formation of self-trapped excitons.⁵

Figure 9.12 Integrated PL intensity, at 77 K, as function of excitation fluence. a) **1[PbBr₄]** (integration range 428 nm – 435 nm); b) **1[PbBr₄]** (integration range 435 nm – 460 nm); c) broadband emission of **1[PbBr₄]** (red line) and **2[PbBr₄]** (blue line) with integration range of 460 - 900 nm for both. PL spectra were recorded for single crystals, using an excitation wavelength (λ_{exc}) of 405 nm.

PL excitation-power dependence in semiconductors with $K < 1$ was shown to be characteristic of emission of excitons bound to donor-acceptor pairs (DAP recombination)³⁴. It has been suggested that the various defects that hybrid perovskites are prone to,^{36, 37} owing to their soft metal halide lattice, can offer sites for the DAP luminescence process.³⁸ However, strong electron-phonon interactions characteristic of 2D perovskites have also been shown to promote exciton trapping at specific sites of the crystal lattice, induced by its own lattice distortion field. Such localization effects pose additional restrictions upon the rate of radiative recombination. These are not taken into account in the derivation of the power law model and might render it inaccurate for the analysis of self-trapped exciton emission.^{34, 35} Therefore, exciton self-trapping cannot be completely ruled-out.

Time-resolved PL was used to investigate the charge carriers relaxation dynamics upon photoexcitation (see **Equation 4** used to analyze the temporal PL profile where t_f and t_s are the fast and slow decay components.). Contrary to the nonexponential t^{-1} (t = time, ns) decay characteristic of DAP recombination,^{38, 39} double-exponential PL decay was observed.

$$I_{PL} = A * \exp\left(-\frac{t}{t_f}\right) + B * \exp\left(-\frac{t}{t_s}\right) \quad (\text{Eqn. 9.3})$$

Figure 9.13 Time-resolved photoluminescence (TRPL) of 1[PbBr₄] and 2[PbBr₄]. a) Excitonic emission of 1[PbBr₄] (in the range 420 - 435 nm) and broadband emission of 2[PbBr₄] (in the range 450 nm - 750 nm) at 298 K; b) broadband emission of 1[PbBr₄] and 2[PbBr₄] (in the range 470 - 750 nm) at 77 K. Data was recorded for single crystals, using an excitation wavelength (λ_{exc}) of 368 nm.

While the excitonic emission of **1**[PbBr₄] almost completely decays within the first 30 ps, the broadband emission of **2**[PbBr₄] (integrated over the range 450 - 750 nm) undergoes a much slower decay, with lifetimes t_f (fast decay component) = 100 ps and t_s (slow decay component) = 400 ps (**Figure 9.13a**). These lifetimes increase to t_f = 12 ns and t_s = 27 ns at 78 K (**Figure 9.13b**). Similarly, at 78K the low-energy broadband emission of **1**[PbBr₄] also shows double-exponential decay, with t_f = 2 ns and t_s = 95 ns. In concordance with the temperature-dependent PL data analysis, the two lifetimes are attributed to two different emissive species, whose relative contribution is convoluted in the broadband luminescence. The differences in lifetime signatures of the two compounds at low temperature indicate that the different structural properties directly affect the recombination dynamics of the materials, which might arise from coupling with different phonon modes or stabilization of different luminescent color centers.

Table 9.5 Fitting results of TRPL decays.

		A ₁	t ₁	B ₁	t ₂	C ₁	t ₃
Exciton	1 [PbBr ₄] (293 K)	78%	10 ps	3%	156 ps	19%	28 ps
Broad component	1 [PbBr ₄] (293 K)	69%	100 ps	31%	480 ps		
Broad component	1 [PbBr ₄] (77 K)	77%	2 ns	23%	95 ns		
Broad component	2 [PbBr ₄] (77 K)	52%	13 ns	48%	28 ns		

9.3 Summary

In summary, the ditopic dications **1** and **2** are employed to template the (100)-oriented 2D perovskites **1**[PbBr₄] and **2**[PbBr₄]. Uniquely, their bromoplumbate layers feature high levels of intra-octahedral distortion, but with only minimal inter-octahedral tilting. Such contrasts get more pronounced at low temperature (100 K). This enables us to study the independent effect of distortion within the [PbBr₆]⁴⁻ octahedra upon the perovskite optical properties. Highly Stokes-shifted, ultra-broadband white light emission is observed in both compounds at low temperature (78 K), but it is retained at room temperature only in the case of the more distorted case **2**[PbBr₄] (CRI = 96 and FWHM = 292 nm). To date, such

room temperature emissive behaviour in (100)-oriented 2D Pb-Br perovskites has been observed exclusively for structures displaying very large inter-octahedral distortions. Unambiguous assignment of the mechanism by which PL occurs in **1**[PbBr₄] and **2**[PbBr₄] has not been possible. However, based upon power- and temperature-dependent PL studies, the presence of multiple emissive centres is favoured, rather than a trapped exciton model. Regardless, given that large-scale intra-octahedral distortions can be induced by judicious selection of dications containing 2 sterically divergent ammonium ions, it is clear that this work offers a new avenue by which ultra-broadband white light emitting Pb-Br perovskites can be designed. In the next chapter, abilities to induce broadband emission that is achieved by modulating the inorganic structures *via* similar targeted molecular approach are further demonstrated and discussed.

9.4 Bibliography

1. Dohner, E. R.; Hoke, E. T.; Karunadasa, H. I., *J. Am. Chem. Soc.* **2014**, *136* (5), 1718-1721.
2. Dohner, E. R.; Jaffe, A.; Bradshaw, L. R.; Karunadasa, H. I., *J. Am. Chem. Soc.* **2014**, *136* (38), 13154-13157.
3. Wang, S.; Yao, Y.; Kong, J.; Zhao, S.; Sun, Z.; Wu, Z.; Li, L.; Luo, J., *Chem. Commun.* **2018**, *54* (32), 4053-4056.
4. Hu, H.; Morris, S. A.; Qiao, X.; Zhao, D.; Salim, T.; Chen, B.; Chia, E. E. M.; Lam, Y. M., *J. Mater. Chem. C* **2018**, *6* (38), 10301-10307.
5. Smith, M. D.; Karunadasa, H. I., *Acc. Chem. Res.* **2018**, *51* (3), 619-627.
6. Luo, J.; Wang, X.; Li, S.; Liu, J.; Guo, Y.; Niu, G.; Yao, L.; Fu, Y.; Gao, L.; Dong, Q.; Zhao, C.; Leng, M.; Ma, F.; Liang, W.; Wang, L.; Jin, S.; Han, J.; Zhang, L.; Etheridge, J.; Wang, J.; Yan, Y.; Sargent, E. H.; Tang, J., *Nature* **2018**, *563* (7732), 541-545.
7. Williams, R. T.; Song, K. S., *J. Phys. Chem. Solids* **1990**, *51* (7) 679-716.
8. Wang, X.; Meng, W.; Liao, W.; Wang, J.; Xiong, R. G.; Yan, Y., *J. Phys. Chem. Lett.* **2019**, *10* (3), 501-506.

9. Cortecchia, D.; Yin, J.; Bruno, A.; Lo, S.-Z. A.; Gurzadyan, G. G.; Mhaisalkar, S.; Brédas, J.-L.; Soci, C., *J. Mat. Chem. C* **2017**, 5 (11), 2771-2780.
10. Yin, J.; Li, H.; Cortecchia, D.; Soci, C.; Brédas, J.-L., *ACS Energy Lett.* **2017**, 2 (2), 417-423.
11. Katan, C.; Mercier, N.; Even, J., *Chem. Rev.* **2019**, 119 (5), 3140-3192.
12. Booker, E. P.; Thomas, T. H.; Quarti, C.; Stanton, M. R.; Dashwood, C. D.; Gillett, A. J.; Richter, J. M.; Pearson, A. J.; Davis, N. J. L. K.; Sirringhaus, H.; Price, M. B.; Greenham, N. C.; Beljonne, D.; Dutton, S. E.; Deschler, F., *J. Am. Chem. Soc.* **2017**, 139 (51), 18632-18639.
13. Paternò, G. M.; Mishra, N.; Barker, A. J.; Dang, Z.; Lanzani, G.; Manna, L.; Petrozza, A., *Adv. Funct. Mater.* **2018**, 1805299, 1-6.
14. Cortecchia, D.; Neutzner, S.; Srimath Kandada, A. R.; Mosconi, E.; Meggiolaro, D.; De Angelis, F.; Soci, C.; Petrozza, A., *J. Am. Chem. Soc.* **2016**, 139 (1), 39-42.
15. Du, K. Z.; Tu, Q.; Zhang, X.; Han, Q.; Liu, J.; Zauscher, S.; Mitzi, D. B., *Inorg. Chem.* **2017**, 56 (15), 9291-9302.
16. Smith, M. D.; Jaffe, A.; Dohner, E. R.; Lindenberg, A. M.; Karunadasa, H. I., *Chem. Sci.* **2017**, 8 (6), 4497-4504.
17. Mao, L.; Wu, Y.; Stoumpos, C. C.; Wasielewski, M. R.; Kanatzidis, M. G., *J. Am. Chem. Soc.* **2017**, 139 (14), 5210-5215.
18. Neogi, I.; Bruno, A.; Bahulayan, D.; Goh, T. W.; Ghosh, B.; Ganguly, R.; Cortecchia, D.; Sum, T. C.; Soci, C.; Mathews, N.; Mhaisalkar, S. G., *ChemSusChem* **2017**, 10 (19), 3765-3772.
19. Cheng, Z.; Lin, J., *CrystEngComm* **2010**, 12 (10).
20. Saparov, B.; Mitzi, D. B., *Chem. Rev.* **2016**, 116 (7), 4558-96.
21. Li, Y.Y.; Lin, C. K.; Zheng, G. L.; Cheng, Z. Y.; You, H.; Wang, W. D.; Lin, J., *Chem. Mater.*, **2006**, 18, 3463-3469.
22. Li, Y.; Zheng, G.; Lin, J., *Eur. J. Inorg. Chem.* **2008**, 2008 (10), 1689-1692.
23. Robinson, K.; Gibbs, G. V.; Ribbe, P. H., *Science* **1971**, 172, 567-570.
24. Shibuya, K.; Koshimizu, M.; Nishikido, F.; Saito, H.; Kishimoto, S., *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2009**, 65 (11), m1323-m1324.

25. Li, X.-N.; Li, P.-F.; Liao, W.-Q.; Ge, J.-Z.; Wu, D.-H.; Ye, H.-Y., *Eur. J. Inorg. Chem.* **2017**, 2017 (5), 938-942.
26. Febriansyah, B.; Koh, T. M.; Lekina, Y.; Jamaludin, N. F.; Bruno, A.; Ganguly, R.; Shen, Z. X.; Mhaisalkar, S. G.; England, J., *Chem. Mater.* **2019**, 31 (3), 890-898.
27. Knutson, J. L.; Martin J. D.; Mitzi, D. B., *Inorg. Chem.* **2005**, 44 (13), 4699-4705.
28. Leguy, A. M.; Goni, A. R.; Frost, J. M.; Skelton, J.; Brivio, F.; Rodriguez-Martinez, X.; Weber, O. J.; Pallipurath, A.; Alonso, M. I.; Campoy-Quiles, M.; Weller, M. T.; Nelson, J.; Walsh, A.; Barnes, P. R., *Phys Chem Chem Phys* **2016**, 18 (39), 27051-27066.
29. Cortecchia, D.; Neutzner, S.; Yin, J.; Salim, T.; Srimath Kandada, A. R.; Bruno, A.; Lam, Y. M.; Martí-Rujas, J.; Petrozza, A.; Soci, C., *APL Mater.* **2018**, 6 (11).
30. Gong, X.; Voznyy, O.; Jain, A.; Liu, W.; Sabatini, R.; Piontkowski, Z.; Walters, G.; Bappi, G.; Nokhrin, S.; Bushuyev, O.; Yuan, M.; Comin, R.; McCamant, D.; Kelley, S. O.; Sargent, E. H., *Nat. Mater.* **2018**, 17 (6), 550-556.
31. Wang, G. E.; Xu, G.; Wang, M. S.; Cai, L. Z.; Li, W. H.; Guo, G. C., *Chem. Sci.* **2015**, 6 (12), 7222-7226.
32. Friel, I.; Thomidis, C.; Fedyunin, Y.; Moustakas, T. D., *J. Appl. Phys.* **2004**, 95 (7), 3495-3502.
33. Luckert, F.; Yakushev, M. V.; Faugeras, C.; Karotki, A. V.; Mudryi, A. V.; Martin, R. W., *J. Appl. Phys.* **2012**, 111 (9).
34. Schmidt, T.; Lischka, K.; Zulehner, W., *Phys. Rev. B* **1992**, 45 (16), 8989-8994.
35. McCall, K. M.; Stoumpos, C. C.; Kostina, S. S.; Kanatzidis, M. G.; Wessels, B. W., *Chem. Mater.* **2017**, 29 (9), 4129-4145.
36. Meggiolaro, D.; Motti, S. G.; Mosconi, E.; Barker, A. J.; Ball, J.; Andrea Riccardo Perini, C.; Deschler, F.; Petrozza, A.; De Angelis, F., *Energy & Environ. Sci.* **2018**, 11 (3), 702-713.
37. Martiradonna, L., *Nat. Mater.* **2018**, 17 (5), 377.
38. Martinez, A. D.; Warren, E. L.; Gorai, P.; Borup, K. A.; Kuciauskas, D.; Dippo, P. C.; Ortiz, B. R.; Macaluso, R. T.; Nguyen, S. D.; Greenaway, A. L.; Boettcher, S. W.; Norman, A. G.; Stevanović, V.; Toberer, E. S.; Tamboli, A. C., *Energy & Environ. Sci.* **2016**, 9 (3), 1031-1041.

39. Guo, B.; Qiu, Z. R.; Wong, K. S., *Appl. Phys. Lett.* **2003**, 82 (14), 2290-2292.

9.5 Instrumentations and additional data

Nuclear Magnetic Resonance (NMR) spectroscopy. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of organic compounds were recorded in DMSO- d_6 solution, using a Bruker Avance 400 spectrometer. Chemical shift values (ppm) are referenced against residual protic solvent peaks.

X-ray single crystallography. Crystals were mounted on a Bruker X8 Quest CPAD area detector diffractometer and data was collected using I μ S 3.0 Microfocus Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$), at both cryogenic and ambient temperatures (100 and 296 K, respectively). Data reduction and absorption corrections were performed using the SAINT and SADABS software packages, respectively. All structures were solved by direct methods and refined by full-matrix least squares procedures on F^2 , using the Bruker SHELXTL-2014 software package. Non-hydrogen atoms were anisotropically refined, after which hydrogen atoms were introduced at calculated positions and the data was further refined. Graphical representations of the crystal structures used throughout the main paper and supporting information were created using the programs Mercury and VESTA.

Analysis of penetration of the organic cations into the cuboctahedral cavities of the inorganic lattices. All analysis was performed using the software package Mercury. The boundary of the perovskite cuboctahedral cavities or ‘bay region’ was defined as being the mean plane comprised of the terminal bromide ions, on the same side of the 2D planes, of four nearest neighbour $[\text{PbBr}_6]^{4-}$ octahedra. The degree of penetration of the aromatic ring moieties (pyridinium and piperidinium) were quantified by measuring the distance between the “para”-carbon atom in the ring and the aforementioned mean planes (see **Figures 9.4c and 2d**). Meanwhile, penetration of the exocyclic primary ammonium is obtained by measuring the distances between the N atoms of the primary ammonium heads and the mean planes.

UV-vis spectroscopy. UV-vis absorption spectra were recorded using a SHIMADZU UV-3600 spectrophotometer, with an integrating sphere (ISR-3100), in the wavelength range 200 – 800 nm, a step size of 0.5 nm, and a slow scan speed.

Raman spectroscopy. The measurements were performed upon single crystals of perovskite, using a inVia Raman Microscope Renishaw micro-Raman confocal microscope (with a 10 x objective and a 785 nm excitation wavelength). All measurements were performed in air.

Steady-state temperature- and power-dependent photoluminescence (PL) spectroscopies. PL was excited at different fluences with a 405 nm Oxixus laser and collected with a Maya 2000 Spectrometer. All measurements were conducted under vacuum, at 77 K. All temperature-dependent measurements were performed using an Oxford Instruments cold finger cryostat.

Time-resolved photoluminescence (TRPL) spectroscopy. TRPL measurements were performed at 293 and 77 K, using a Hamamatsu streak camera and Chameleon laser from Coherent. Excitation at 368 nm, with a fluence 2.5 nJ/cm², and different repetition rates of 80 and 2 MHz were used. Lifetimes of individual decay components and their contributions to the overall decay are listed in **Table 9.5**. The following equation was used to analyze the temporal PL profile:

$$I = I_0 * \exp(-t/\tau)^\beta$$

Where τ and β are the decay constant and lifetime distribution parameter, respectively.

Powder X-ray diffraction. Powder X-ray diffraction measurements were conducted using a Bruker AXS D8 ADVANCE system containing a Cu K α radiation source ($\lambda = 1.5418$ Å). The XRD spectra were recorded with an incident angle of 5°, a step size of 0.05°, and a delay time of 1 s for each step.

1-(2-Ammonioethyl)pyridin-1-ium (1) dibromide. Isolated as a beige solid (1.52 g, 85 % yield). ^1H NMR (400 MHz, DMSO- d_6): δ 9.14 (d, 2 H, ArH), 8.67 (t, 1 H, ArH), 8.23 (t, 2 H, ArH), 8.18 (bs, 3 H, NH_3^+), 4.95 (t, 2 H, CH_2), 3.53 (t, 2 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 146.2, 145.4, 128.3, 57.7, 39.1.

1-(2-Ammonioethyl)piperidin-1-ium (2) dibromide. Isolated as a white solid (1.28 g; 88 % yield). ^1H NMR (400 MHz, DMSO- d_6): δ 9.51 (bs, H, NH^+), 8.08 (bs, 3 H, NH_3^+), 3.49 (m, 2 H, CH_2), 3.30 (m, 4 H, CH_2), 3.02 (m, 2 H, CH_2), 1.80-1.67 (m, 5 H, CH_2), 1.42-1.39 (m, H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 52.8, 52.7, 33.4, 22.5, 20.9.

Table 9.6 Crystallographic and structure refinement data for **1**[PbBr₄] and **2**[PbBr₄] at room temperature.^a

	Compound	
	1 [PbBr ₄] RT	2 [PbBr ₄] RT
Empirical formula	C ₇ H ₁₂ Br ₄ N ₂ Pb	C ₇ H ₁₈ Br ₄ N ₂ Pb
Formula weight	651.02 g/mol	657.06 g/mol
Temperature	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal size	0.020 x 0.040 x 0.060 mm	0.020 x 0.120 x 0.200 mm
Crystal habit	pale yellow block	pale yellow plate
Crystal system	monoclinic	monoclinic
Space group	P 1 21/c 1	P 1 21/c 1
Unit cell dimensions	a = 10.339(5) Å	a = 6.1592(2) Å
	α = 90°	α = 90°
	b = 17.223(9) Å	b = 19.9946(8) Å
	β = 105.29(2)°	β = 95.2440(10)°
	c = 8.346(4) Å	c = 12.1402(4) Å
	γ = 90°	γ = 90°
Volume	1433.6(13) Å ³	1488.82(9) Å ³
Z	4	4
Density	3.016 g/cm ³	2.931 g/cm ³
Absorption coefficient	22.887 mm ⁻¹	22.039 mm ⁻¹
F(000)	1160	1184
Theta range for data collection	2.36 to 31.11°	2.64 to 32.13°
Reflections collected	4563	17677
Coverage of independent reflections	99.0%	99.6%
Absorption correction	Multi-Scan	Multi-Scan
Max. and min. transmission	0.6570 and 0.3410	0.6670 and 0.0960
Function minimized	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	4563 / 62 / 122	5206 / 403 / 211
Goodness-of-fit on F ²	1.006	1.000
Δ/σ _{max}	0.001	0.001
Final R indices	2481 data	2431 data
	R1 = 0.0633,	R1 = 0.0572,
	wR2 = 0.1302	wR2 = 0.1047
R indices [all data]	R1 = 0.1340,	R1 = 0.1551,
	wR2 = 0.1615	wR2 = 0.1389
Largest diff. peak and hole	3.197 and -1.596 eÅ ⁻³	1.865 and -2.121 eÅ ⁻³
R.M.S. deviation from mean	0.274 eÅ ⁻³	0.306 eÅ ⁻³

^a $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR = \{ \Sigma [w(|F_o|^2 - |F_c|^2)] / \Sigma [w(|F_o|^4)] \}^{1/2}$ and **1**[PbBr₄], $w = 1 / [\sigma^2(F_o^2) + (0.0615P)^2]$; **2**[PbBr₄], $w = 1 / [\sigma^2(F_o^2) + (0.0485P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 9.7 Crystallographic and structure refinement data for **1**[PbBr₄] and **2**[PbBr₄] at 100 K.^a

	Compound	
	1 [PbBr ₄] 100 K	2 [PbBr ₄] 100 K
Empirical formula	C ₇ H ₁₂ Br ₄ N ₂ Pb	C ₇ H ₁₈ Br ₄ N ₂ Pb
Formula weight	651.02 g/mol	657.06 g/mol
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal size	0.020 x 0.040 x 0.120 mm	0.040 x 0.120 x 0.320 mm
Crystal habit	yellow needle	colorless plate
Crystal system	orthorhombic	monoclinic
Space group	P b c a	P 1 21/c 1
Unit cell dimensions	a = 17.0426(4) Å	a = 6.1025(2) Å
	α = 90°	α = 90°
	b = 8.2800(2) Å	b = 19.6991(8) Å
	β = 90°	β = 97.1920(14)°
	c = 19.7640(5) Å	c = 12.2289(5) Å
	γ = 90°	γ = 90°
Volume	2788.95(12) Å ³	1458.52(10) Å ³
Z	8	4
Density	3.101 g/cm ³	2.992 g/cm ³
Absorption coefficient	23.529 mm ⁻¹	22.497 mm ⁻¹
F(000)	2320	1184
Theta range for data collection	2.38 to 30.00°	2.66 to 32.00°
Reflections collected	29677	32046
Coverage of independent reflections	100.00%	100.00%
Absorption correction	Multi-Scan	Multi-Scan
Max. and min. transmission	0.6500 and 0.1650	0.4660 and 0.0520
Function minimized	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	4071 / 0 / 128	5064 / 0 / 128
Goodness-of-fit on F ²	1.040	1.022
Δ/σ _{max}	0.002	0.001
Final R indices	3076 data	3524 data
	R1 = 0.0319,	R1 = 0.0371,
	[I > 2σ(I)] wR2 = 0.0600	wR2 = 0.0626
R indices [all data]	R1 = 0.0551,	R1 = 0.0682,
	wR2 = 0.0679	wR2 = 0.0747
Largest diff. peak and hole	1.272 and -1.594 eÅ ⁻³	1.649 and -1.947 eÅ ⁻³
R.M.S. deviation from mean	0.290 eÅ ⁻³	0.297 eÅ ⁻³

^aR = Σ||F_o| - |F_c||/Σ|F_o|, wR = {Σ[w(|F_o|² - |F_c|²)²]/Σ[w(|F_o|⁴)]}^{1/2} and **1**[PbBr₄], w = 1/[σ²(F_o²) + (0.0240P)² + 6.4233P]; **2**[PbBr₄], w = 1/[σ²(F_o²) + (0.0143P)² + 6.5277P] where P = (F_o² + 2F_c²)/3.

Chapter 10

Selective generation of trimeric organic-bromoplumbate hybrids that display intrinsic, highly Stokes-shifted, efficient broadband emission

*Molecular, low-dimensionality hybrid organic lead halides are an interesting class of materials that have significant potential for artificial illumination applications. Through systematic variation of templating N-alkyl pyridinium cations, a series of bromoplumbates have been prepared. Whereas comparatively short and flexible N-alkyl substituents (ethyl, hydroxy ethyl, and pentyl) yield one-dimensional (1D) inorganic chains, more rigid substituents (benzyl, acetamidyl, and cyanomethyl) afford hybrids composed of rare lead-bromide face-sharing trimers. Of the rigid substituents studied, benzyl groups were found to enforce the highest level of distortion of the individual $[\text{PbBr}_6]^-$ octahedra, comprising their trimeric structures. Upon exposure to ultra-violet (UV) light, benzyl pyridinium lead-bromide (**1**)₂ $[\text{PbBr}_4]$ exhibits a broadband emission, centered at 571 nm, which spans from 400 to 800 nm. More specifically, it displays a large Stokes shift of ca. 1.39 eV and a full width at half maximum (FWHM) of ca. 540 meV. The reduced size and dimensionality of its inorganic lattice also results in a photoluminescence quantum yield (at least 10%) that is approximately one order magnitude higher than that of 1D congeners. Mechanistically, broadband emission in (**1**)₂ $[\text{PbBr}_4]$ is deduced to be due to self-trapped excitons, originating from exciton-phonon coupling in the quantumically-confined bromoplumbate lattice.*

10.1 Background

In recent years, organic-inorganic p-block metal halide hybrids have received much attention due to the exceptional versatility of their structural and optoelectronic properties.¹⁻³ When appropriate organic and inorganic components are chosen, the connectivity of the metal halide polyhedra can be tuned to provide three- (3D), two- (2D), one- (1D), or zero-dimensional (0D) anionic inorganic architectures, surrounded by organic cations.⁴⁻⁸ Such structural variety implies that there is a vast parameter space in which to explore novel structures that exhibit new and useful features. For example, lowering the dimensionality of the inorganic lattice leads to more localized electronic states and, consequently, narrower conduction and valence bands. This promotes self-trapping of excitons and stronger exciton emission. As a result, unlike the narrow emission bands with small Stokes shifts, typically, observed in 3D metal halide hybrids, corrugated-2D, 1D and 0D materials have been shown to display efficient and heavily Stokes-shifted luminescence, centred at a wide range of wavelengths.⁹⁻¹³

Moreover, 0D p-block metal halide compounds, generally, exhibit broadband emission that is highly efficient, with high to near-unity photoluminescence quantum efficiencies having been reported for such materials.^{6, 8, 11, 12} This, coupled with their color tunability and ease of processing, renders them promising luminescent materials for solid state lighting, luminescent solar concentrators and radiation detection applications. However, despite comprehensive characterization of the mechanistic features of their luminescence behavior and their applicability in light emitting devices,^{6, 12, 14, 15} the number of distinct 0D hybrids that have been reported is small (less than 10) relative to their 1D and 2D congeners.^{4, 10, 16-25} Furthermore, the reported 0D compounds are templated by a wide-range of, largely, unrelated organic cations. For example, Ma and co-workers used 1-butyl-1-methylpyrrolidinium, *N,N'*-dimethylethylenedi-ammonium and tetraphenylphosphonium to induce different tin bromide,^{6, 8} tin iodide,⁶ antimony chloride,^{6, 11} and lead chloride⁷ monomeric structures. Meanwhile Smith and Zhou utilized butane-1,4-bis(dimethylsulfonium) and 1-butyl-1-methylpyrrolidinium, respectively, to synthesize

materials containing lead bromide trimers.^{5, 26} Thus, systematic study of the impact of organic cation structure upon the formability of 0D architectures is still underexplored.

This thesis is interested in investigating the impact of systematic variation of templating organic cation upon the structure of self-assembled low-dimensionality lead halide inorganic lattices, and its concomitant influence upon their photophysical properties. For instance, it has been shown that appending hydrogen bonding functionalities to viologens can induce their dimerization and endow the resulting 1D materials with photoconductivity.² In addition, by using compact organic dications it was possible to form 2D lead iodide perovskites with very short inorganic layer separations, which led to improved charge carrier generation and enhanced photovoltaic efficiencies.³ The unifying theme across these studies is the use of cyclic cations, such as pyridiniums, with appended alkyl substituents, which are straightforward to prepare and structurally vary.

Figure 10.1 The *N*-alkyl pyridinium cations used in this work.

Utilizing this general molecular design approach, this study sought to access comparably rare trimeric bromoplumbate compounds. To this end, a series of *N*-alkyl pyridyl cations were prepared and used to template formation of new low dimensional organic lead bromide hybrids (**1 – 6**; **Figure 10.1**). Based upon literature precedent,^{27, 28} it was anticipated that inclusion of flexible and short *N*-alkyl substituents, such as ethyl (**4**), pentyl (**5**) and 2-hydroxyethyl (**6**), would result in assembly of 1D inorganic chains. In such systems, coulombic interactions between the pyridinium rings and inorganic lattice cause the former to orientate parallel to the latter. These interactions are distinct from those that dominate in 2D perovskites, where hydrogen bonding interactions associated with the ammonium functionality of the cations are a controlling factor.^{18, 29, 30} By extension, it was

postulated that relatively rigid *N*-alkyl substituents, such as benzyl (**1**), acetamidyl (**2**) and cyanomethyl (**3**), would increase the steric impact of the organic cation and, thereby, cause a further reduction of the dimensionality of the bromoplumbate. In addition to synthesizing low-dimensional hybrids containing rare trimeric bromoplumbates, detailed studies of the optical properties of one of them, (**1**)₂[PbBr₄] were performed, and it is shown that it displays efficient, heavily Stokes-shifted, broadband emission.

10.2 Results and discussions

10.2.1 Lattice confinement by rigid organic cations

X-ray crystal structures of the *N*-alkyl pyridinium templated compounds containing 1D bromoplumbate chains and trimeric bromoplumbate units are shown in **Figures 10.2** and **10.3**, respectively. (Crystallographic and refinement data are provided in **Section 10.5**) As anticipated, employing flexible *N*-alkyl substituents leads to formation of 1D polymeric chains of the monomer [PbBr₃][−]. This is exemplified by the cation *N*-ethyl pyridinium (**4**), where the 1D chains in **4**[PbBr₃] (**Figure 10.2a**) result from face-sharing of its constituent [PbBr₆]^{4−} octahedra. The coordination sphere of Pb is distorted, with large differences between the Pb–Br distances (ranging from 2.8185(13) to 3.3633(13) Å) *trans* to one another along two of the three axes. Despite the potential existence of several C–H⋯Br intermolecular interactions between the bromoplumbate chains and pyridinium cations, the main driving force for crystal packing is likely to be Coulombic interactions. This notion is supported by the tendency of the pyridinium rings to align parallel to the inorganic lattices, which minimizes separation of the opposing charges of these two components. Furthermore, the structures of **5**[PbBr₃] and **6**[PbBr₃] (**Figures 10.2b and 10.2c**), whose cations contain pentyl and 2-hydroxyethyl substituents, respectively, show similar properties. This suggests that long-chain linear *N*-alkyl functional groups and those with the potential to disrupt H-bonding interactions, do not interfere with self-assembly of the 1D Pb–Br polymeric chains.

Figure 10.2 Single crystal X-ray structures of the one-dimensional (1D) lead-bromide hybrids a) $4[\text{PbBr}_3]$, b) $5[\text{PbBr}_3]$ and c) $6[\text{PbBr}_3]$. Dark gray, brown, gray, blue and red spheres represent Pb, Br, C, N and O atoms, respectively. H atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

Figure 10.3 Single crystal X-ray structures of trimeric lead-bromide hybrids a) $(\mathbf{1})_2[\text{PbBr}_4]$, b) $(\mathbf{2})_2[\text{PbBr}_4]$ and c) $(\mathbf{3})_2[\text{PbBr}_4]$. Dark gray, brown, gray, blue, red, and yellow spheres represent Pb, Br, C, N, O and S atoms, respectively. H atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

In contrast, distinct bromoplumbate architectures can be obtained (**Figure 10.3**), using the same crystallization conditions, with the substituents **1**, **2**, and **3**. More specifically, the resulting hybrids $(\mathbf{1})_2[\text{PbBr}_4]$, $(\mathbf{2})_2[\text{PbBr}_4]$ and $(\mathbf{3})_2[\text{PbBr}_4]$ are comprised of isolated molecular $[\text{Pb}_3\text{Br}_{12}]^{6-}$ trimers that are separated by, and appear at regular intervals in, a matrix of organic counteranions. The trimers are built from monomeric lead bromide octahedra that link to one another in a face-sharing fashion. Their constituent Pb–Br bond lengths vary from 2.9219(7) to 3.1666(7) Å in $(\mathbf{1})_2[\text{PbBr}_4]$, 2.8764(5) to 3.2722(6) Å in $(\mathbf{2})_2[\text{PbBr}_4]$, and 2.8423(17) to 3.3350(2) Å in $(\mathbf{3})_2[\text{PbBr}_4]$. Such inorganic motifs are very rare, relative to 1D and 2D hybrids, and are distinct to the so-called ‘0D’ compounds that are composed of more common monometallic halides.^{6–8, 11} In fact, there are only four compounds containing trimeric Pb–Br units.^{5, 26, 31, 32} The major difference between cations

1 – 3 and **4 – 6**, used in this study, is that the *N*-alkyl substituents in the former group contain sp or sp² hybridized C atoms. This endows them with a degree of rigidity that, possibly, inhibits ideal packing around the inorganic octahedra and, thereby, prevents assembly of infinite 1D [PbBr₃][−] chains.

Interestingly, the tendency to form inorganic trimers, rather than 1D structures, is also influenced by the identity of the halide used. Whereas replacement of the bromide ions in (1)₂[PbBr₄] with chloride provided the isostructural, trimer-containing compound (1)₂[PbCl₄], combination of PbI₂ with (1)I afforded the 1D iodoplumbate (1)[PbI₃] (**Figure 10.4**). Presumably, the larger Pb-halide cuboctahedral cavities formed by the bigger iodide anions are better able to accommodate close packing with the *N*-benzyl pyridinium cation.

Figure 10.4 Single crystal X-ray structures of a) (1)₂[PbCl₄] and b) (1)[PbI₃] containing trimeric and one-dimensional chain of inorganic bromoplumbate lattice, respectively. Dark gray, green, purple, brown and blue spheres represent Pb, Cl, I, C, and N atoms, respectively. H atoms are omitted for clarity.

The breaking of 1D bromoplumbate chains into trimeric structures is readily apparent in single crystal, low-frequency Raman measurements (**Figure 10.5**). Close similarity to vibrations (at 142 cm^{−1}) in published bromoplumbate 1D compounds with face-sharing linkages,^{4, 33} allows assignment of the vibration in 4[PbBr₃] at 143 cm^{−1} as symmetric stretching of comparatively strong Pb-Br bonds. In (1)₂[PbBr₄] this Raman mode shifts to lower energy (132 cm^{−1}) and decreases in intensity by a factor of ~3. The former indicates weakening of the Pb-Br bonds and an increase in Pb-Br bond lengths, while the latter

reflects a decrease of the overall rigidity of bonding. This is consistent with their X-ray crystal structures, wherein $(\mathbf{1})_2[\text{PbBr}_4]$ has six terminally-bound halides in each of their trimeric inorganic components, while $4[\text{PbBr}_3]$ has none (i.e., all are bridging). The peaks below 100 cm^{-1} , contributed by vibrations involving scissoring modes of Pb-Br-Pb and Br-Pb-Br, differ as well. However, precise assignment of these features is not straightforward because of the large number of overlapping vibrational modes in this region.

Figure 10.5 Low-frequency Raman spectra of hybrid $4[\text{PbBr}_3]$ and $(\mathbf{1})_2[\text{PbBr}_4]$ single crystals showing a shift in Pb–Br stretching to lower wavenumber from one-dimensional bromoplumbate chain (142 cm^{-1}) to the trimeric structure (132 cm^{-1}).

10.2.2 Distorted structures and broadband emission generations

Overall, the bulky benzyl pyridium cations in $(\mathbf{1})_2[\text{PbBr}_4]$ impose greater structural distortion of their constituent $[\text{PbBr}_6]^{4-}$ octahedra than the corresponding cations in the other trimeric structures, $(\mathbf{2})_2[\text{PbBr}_4]$ and $(\mathbf{3})_2[\text{PbBr}_4]$ (**Table 10.1**). The degree of intraoctahedral distortion is assessed *via* the parameters octahedral elongation (λ_{oct}), octahedral angle variance (σ^2_{oct}), and octahedral bond-length distortion (Δ_{oct})^{34, 35} which are calculated using the following equations:

$$\lambda_{oct} = \frac{1}{6} \sum_{i=1}^6 \left[\frac{d_i}{d_0} \right]^2 \quad (\text{Eqn. 10.1})$$

$$\sigma_{oct}^2 = \frac{1}{11} \sum_{i=1}^{12} (\alpha_i - 90)^2 \quad (\text{Eqn. 10.2})$$

$$\Delta_{oct} = \frac{1}{6} \sum_{i=1}^6 \left[\frac{d_i - d_m}{d_m} \right]^2 \quad (\text{Eqn. 10.3})$$

where d_i corresponds to Pb–Br bond length, d_0 to center-to-vertex distance of a regular polyhedron of the same volume, d_m to average bond length, and α_i to individual Br–Pb–Br angle. λ_{oct} and σ_{oct}^2 provide a quantitative measure of polyhedral distortion independent of the effective size of the polyhedron, with larger values equating to greater distortion.

Table 10.1 Distortion parameters derived from the single crystal X-ray structures of the trimeric bromoplumbates (1)₂[PbBr₄], (2)₂[PbBr₄] and (3)₂[PbBr₄]^a

Compound	$\lambda_{oct} \text{ (avg)}^b$	$\sigma_{oct}^2 \text{ (avg)}^c$	$\Delta_{oct} (\times 10^{-4})^d$
(1) ₂ [PbBr ₄]	1.0120	39.07	10.79
(2) ₂ [PbBr ₄]	1.0058	13.04	27.66
(3) ₂ [PbBr ₄]	1.0114	31.93	21.93

^aAveraged distortion parameters are given because X-ray structures of (1)₂[PbBr₄], (2)₂[PbBr₄] and (3)₂[PbBr₄] contain two, two and three geometrically distinct octahedra, respectively. ^bOctahedral elongation. ^cOctahedral angle variance. ^dOctahedral bond length distortion.

It was previously reported, and is generally accepted, that the tendency of 2D bromoplumbate perovskites to undergo broadband photo-luminescence increases with increasing distortion of their constituent lead-bromide octahedra.^{4, 19} Thus, it is noteworthy that the levels of intra-octahedral structural distortion displayed by (1)₂[PbBr₄] – (3)₂[PbBr₄] are very large, even relative to broadband-emitting 2D perovskites.^{19, 20, 23} This could be attributed to uneven charge and steric environments provided by the surrounding organic matrixes at which the inorganic trimers are embedded. In particular, the diffuse character of pyridinium cores and the rigidity of the *N*-substituents lead to different interactions with bridging and terminal bromide ions. As a result, the trimeric face-sharing [PbBr₆]⁴⁻ octahedra have to adopt ‘non-ideal’ Pb-Br bond length and bond angle in order to accommodate such disturbances in the crystal packing. Consistent with expectations, all of

the trimeric hybrids reported herein were found to exhibit broadband emission (**Figure 10.6**). This validates the approach pursued in this study. Optical characterization of the hybrid trimers was performed and in this thesis, $(1)_2[\text{PbBr}_4]$ is selected as representative due to the greater distortion that the bromoplumbate lattice experiences.

Figure 10.6 Photoluminescence spectra of $(1)_2[\text{PbBr}_4]$, $(2)_2[\text{PbBr}_4]$, and $(3)_2[\text{PbBr}_4]$ at room temperature with an excitation wavelength of 350 nm.

Single crystals of $(1)_2[\text{PbBr}_4]$ appear colorless and transparent under ambient light, which is indicative of little-to-no light absorption in the visible region and a large HOMO-LUMO energy gap. Consistent with this, its pseudoabsorption spectrum, converted from diffuse-reflectance measurements using the Kubelka–Munk function, shows an absorption band with a maxima of 318 nm (**Figure 10.7a**). Upon photoexcitation by ≤ 375 nm UV light, $(1)_2[\text{PbBr}_4]$ exhibits strong photoluminescence (PL) at room temperature. The emission band is broad, with a maxima at 571 nm, an emission width of ca. 1.45 eV, and a full width at half-maximum (FWHM) of ca. 0.54 eV (**Figure 10.7a**). Relative to its absorption onset, the observed PL exhibits a large Stokes shift of ca. 1.39 eV. The photoluminescence quantum efficiency (PLQE) of $(1)_2[\text{PbBr}_4]$ is also determined to be at least 10% (**Figure 10.8**), which is similar to that reported for other trimeric bromoplumbates.²⁶ As a frame of reference, the prototypical 1D compound $4[\text{PbBr}_3]$ exhibits a PLQE of ca. 1.0%, which is

of a similar magnitude to values reported for other 1D lead-bromide hybrids (0.4-0.6%).⁴ Thus, although the 1D materials templated by **4** – **6** also exhibit broadband emission (**Figure 10.9**), moving to a 0D trimer can yield a ten-fold enhancement of PLQE. This is a straightforward consequence of increased quantum-confinement and illustrates why a decrease in dimensionality is advantageous.

Figure 10.7 a) Room temperature UV-vis diffuse reflectance (DRS), transformed using Kubelka-Munk (K-M) function, and photoluminescence (PL, $\lambda_{\text{ex}} = 350$ nm) spectra of **(1)**₂[PbBr₄]. b) Laser fluence-dependent integrated PL intensity of **(1)**₂[PbBr₄], recorded in the range 0.08 – 1.43 $\mu\text{J}/\text{cm}^2$ at 293 K, plus a linear fit of the data. c) Integrated PL intensity as a function of temperature (red triangles), and a fit of the data to **Eqn. 10.5** (black line). The experiment was conducted using 350 nm excitation and 0.08 $\mu\text{J}/\text{cm}^2$ laser fluence. d) Time-resolved PL spectra of **(1)**₂[PbBr₄], recorded at an emission wavelength of 570 nm, at temperatures of 77 and 293 K. e) Full-width at half-maxima (FWHM, blue circles) and PL lifetime (red squares) as a function of temperature. Similarly coloured solid lines correspond to fits of the experimental data to **Eqns. 10.4** and **10.5**, respectively.

Figure 10.8 Excitation line of reference and emission spectrum of $(\mathbf{1})_2[\text{PbBr}_4]$ collected by an integrating sphere. The photoluminescence quantum efficiency (PLQE) is calculated using the equation: $\eta_{QE} = \frac{I_S}{(E_R - E_S)}$.

Figure 10.9 Photoluminescence spectrum of $4[\text{PbBr}_3]$, $5[\text{PbBr}_3]$, and $6[\text{PbBr}_3]$ at room temperature with an excitation wavelength of 350 nm.

Identical broad PL features were obtained for $(\mathbf{1})_2[\text{PbBr}_4]$ when excitation wavelengths shorter than 375 nm were used (**Figure 10.10**). Such invariance suggests that the broadband emission is an intrinsic feature of this material. In addition, photoluminescence excitation (PLE) spectra probing the emission band from 450 to 700 nm retain the same shape and features (**Figure 10.11**). This implies that the entirety of the observed emission originates from a common set of excited states. Moreover, the PLE spectra exhibit similar onsets of ca. 390–400 nm as the UV-vis data, which further evidences the intrinsic origin of the broadband PL. This conclusion is also supported by intensity-dependent continuous-wave PL measurements. If the emission arises from permanent defects, PL would be expected to saturate as these traps become filled. Instead, PL intensity is found to increase linearly with fluence from 0.08 to $1.43 \mu\text{J}/\text{cm}^2$ at 293 K (**Figures 10.7b** and **10.12**), with no signs of saturation.

Figure 10.10 Excitation-wavelength-dependent photoluminescence (PL) spectra of $(\mathbf{1})_2[\text{PbBr}_4]$ at room temperature.

Figure 10.11 Emission-wavelength-dependent photoluminescence excitation (PLE) spectra of $(\mathbf{1})_2[\text{PbBr}_4]$ at room temperature.

Figure 10.12 Photoluminescence (PL) evolution of $(\mathbf{1})_2[\text{PbBr}_4]$ as a function of excitation power at room temperature.

10.2.3 Self-trapped excitons mechanism

Possible origins of the highly Stokes-shifted broadband emission seen for $(\mathbf{1})_2[\text{PbBr}_4]$ are as follows:³⁶ (1) energy transfer from the inorganic to a broadband emitting organic

component; (2) broadband phosphorescence, which would require a spin-forbidden transition; (3) deep-trap emission; and (4) self-trapped excitons (STE). These possibilities were investigated *via* temperature-dependent PL experiments (**Figure 10.13**).

Figure 10.13 Photoluminescence (PL) evolution of (1)₂[PbBr₄] as a function of temperature.

The first can be dismissed because the organic component does not display broadband emission. Meanwhile, the second option can be ruled out due to the observed inverse relationship between temperature and PL intensity (**Figure 10.7c**). For phosphorescence, PL intensity would be expected to increase with increasing temperature.³⁷ The third possibility can also be excluded, as none of its signature features are observed. More specifically, neither saturation of PL intensity, blue-shift of PL spectra with increasing excitation fluence (**Figures 10.7b and 10.12**), nor a significant variation of PL lifetime across different emission wavelengths (**Figure 10.14**) are observed. Thus, the most plausible origin of the large Stokes-shifted broadband emission is STE.^{5, 13, 36} This assignment is supported by the temperature-dependent behaviors of its PL full-width at half-maxima (FWHM), lifetime, and intensity, which are discussed in the following paragraph.

Figure 10.14 Room temperature time-resolved photoluminescence (PL) spectra of (1)₂[PbBr₄] at emission wavelengths 500 nm, 570 nm, and 600 nm.

Figure 10.15 Temperature-dependent time-resolved photoluminescence (PL) spectra of (1)₂[PbBr₄] (see Table 10.2 for the summary of the PL lifetime at each temperature).

In typical semiconductors, the temperature-dependent behavior of the FWHM of a PL peak can be described by the following equation:

$$\text{FWHM} = 2.36\sqrt{S}\hbar\omega_{\text{phonon}}\sqrt{\coth\left(\frac{\hbar\omega_{\text{phonon}}}{2k_B T}\right)} \quad (\text{Eqn. 10.4})$$

where the Huang-Rhys factor (S) describes the strength of exciton-photon coupling. In the case of $(\mathbf{1})_2[\text{PbBr}_4]$, fitting of the experimental data yields a large value of $S = 24 \pm 2$ (**Figure 10.7e**; blue curve), which falls within the typical range of materials with STEs ($\sim 20 - 80$).³⁸ For comparison, similar lead bromide perovskite direct bandgap semiconductors without broadband emission have S values of ~ 3.2 .³⁹

Table 10.2 Summary of photoluminescence lifetime of $(\mathbf{1})_2[\text{PbBr}_4]$ at different temperature.

Temperature (K)	Lifetime (ns)
77	2520.80 ± 5.52
100	2183.90 ± 5.39
120	1936.70 ± 4.38
140	1702.00 ± 3.73
160	1459.70 ± 3.29
180	1191.00 ± 2.42
200	914.35 ± 1.76
220	688.14 ± 1.41
250	416.94 ± 0.95
280	240.91 ± 0.73
293	185.25 ± 0.55

The temperature-dependent behavior of the PL lifetime $\tau(T)$ and intensity for $(\mathbf{1})_2[\text{PbBr}_4]$ also shows behavior characteristic of STE. As shown in **Figure 10.7d**, monoexponential fitting of the decay of its broadband emission gives a long lifetime of approximately 426 ns at room temperature, which increases to around 5.8 μs upon lowering the temperature to 77 K. (See **Figure 10.15** for the complete time-resolved photoluminescence (PL) spectra evolution as a function of temperature from 77 K to 293 K.) The temperature-dependent lifetime of a STE system can be described by **Eqn. 10.5**.⁴⁰

$$\tau(T) = \left[\tau_R^{-1} + \nu_0 \exp\left(-\frac{E_B}{k_B T}\right) \right]^{-1} \quad (\text{Eqn. 10.5})$$

where τ_R is the radiative decay rate, while ν_0 and E_B are the branching rate and the energy barrier to a non-radiative channel, respectively. Similarly, the PL intensity of STE can be described by **Eqn. 10.6**:

$$I(T) = I_0 \frac{\tau(T)}{\tau_R} \quad (\text{Eqn. 10.6})$$

Using these equations, good fits of the experimental data can be obtained (**Figure 10.7e**, **Table 10.2**). This serves to further validate the assignment of STE as the mechanism by which broadband fluorescence proceeds.

10.3 Summary

In summary, the selective formation of trimeric bromoplumbates by engineering the molecular structure of the pyridinium cation was attempted. This was successfully achieved through incorporation of comparatively rigid benzyl, acetamidyl, and cyanomethyl substituents, which contain sp^2 or sp hybridized C atoms. The resulting ‘0D’ $[\text{Pb}_3\text{Br}_{12}]^{6-}$ trimers are very rare with only four compounds of this type having been published prior to this study. Of the trimers detailed herein, the *N*-benzyl pyridinium containing compound (**1**)₂ $[\text{PbBr}_4]$ exhibits the most severe distortions of the constituent lead-bromide octahedra (i.e., coordination spheres). Its highly confined inorganic lattice and strong intraoctahedral distortions result in PL emission that is efficient (at least 10% PLQE), ultra-broad (ca. 540 meV), and highly Stokes-shifted (1.39 eV). Mechanistically, the broadband emission is deduced to be due to self-trapped excitons, which are the result of exciton-phonon coupling in the quantumically-confined bromoplumbate lattice. Thus, this work demonstrates a method that can be used to tailor the Pb-halide inorganic structure at a molecular level and, thereby, induce desirable photophysical properties. Utilization of even more sterically hindered and rigid *N*-alkyl substituents would be expected to induce a further reduction in dimensionality, which would provide further improvements in emissive behaviour.

10.4 Bibliography

1. Manser, J. S.; Christians, J. A.; Kamat, P. V. *Chem. Rev.* **2016**, *116* (21), 12956-13008.
2. Febriansyah, B.; Koh, T. M.; John, R. A.; Ganguly, R.; Li, Y.; Bruno, A.; Mhaisalkar, S. G.; England, J. *Chem. Mater.* **2018**, *30* (17), 5827-5830.
3. Febriansyah, B.; Koh, T. M.; Lekina, Y.; Jamaludin, N. F.; Bruno, A.; Ganguly, R.; Shen, Z. X.; Mhaisalkar, S. G.; England, J. *Chem. Mater.* **2019**, *31* (3), 890-898.
4. Mao, L.; Guo, P.; Kepenekian, M.; Hadar, I.; Katan, C.; Even, J.; Schaller, R. D.; Stoumpos, C. C.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2018**, *140* (40), 13078-13088.
5. Smith, M. D.; Watson, B. L.; Dauskardt, R. H.; Karunadasa, H. I. *Chem. Mater.* **2017**, *29* (17), 7083-7087.
6. Zhou, C.; Lin, H.; Tian, Y.; Yuan, Z.; Clark, R.; Chen, B.; van de Burgt, L. J.; Wang, J. C.; Zhou, Y.; Hanson, K.; Meisner, Q. J.; Neu, J.; Besara, T.; Siegrist, T.; Lambers, E.; Djurovich, P.; Ma, B. *Chem. Sci.* **2018**, *9* (3), 586-593.
7. Zhou, C.; Lin, H.; Worku, M.; Neu, J.; Zhou, Y.; Tian, Y.; Lee, S.; Djurovich, P.; Siegrist, T.; Ma, B. *J. Am. Chem. Soc.* **2018**, *140* (41), 13181-13184.
8. Zhou, C.; Lin, H.; Shi, H.; Tian, Y.; Pak, C.; Shatruk, M.; Zhou, Y.; Djurovich, P.; Du, M.-H.; Ma, B. *Angew. Chem. Int. Ed.* **2018**, *57* (4), 1021-1024.
9. Wu, X.; Trinh, M. T.; Niesner, D.; Zhu, H.; Norman, Z.; Owen, J. S.; Yaffe, O.; Kudisch, B. J.; Zhu, X. Y. *J. Am. Chem. Soc.* **2015**, *137* (5), 2089-96.
10. Yuan, Z.; Zhou, C.; Tian, Y.; Shu, Y.; Messier, J.; Wang, J. C.; van de Burgt, L. J.; Kountouriotis, K.; Xin, Y.; Holt, E.; Schanze, K.; Clark, R.; Siegrist, T.; Ma, B. *Nat. Comm.* **2017**, *8*.
11. Zhou, C.; Worku, M.; Neu, J.; Lin, H.; Tian, Y.; Lee, S.; Zhou, Y.; Han, D.; Chen, S.; Hao, A.; Djurovich, P. I.; Siegrist, T.; Du, M.-H.; Ma, B. *Chem. Mater.* **2018**, *30* (7), 2374-2378.
12. Zhou, C.; Tian, Y.; Yuan, Z.; Lin, H.; Chen, B.; Clark, R.; Dilbeck, T.; Zhou, Y.; Hurley, J.; Neu, J.; Besara, T.; Siegrist, T.; Djurovich, P.; B. Ma, *ACS Appl. Mater. Interfaces* **2017**, *9* (51), 44579-44583.
13. Smith, M. D.; Karunadasa, H. I. *Acc. Chem. Res.* **2018**, *51* (3), 619-627.

14. Han, D.; Shi, H.; Ming, W.; Zhou, C.; Ma, B.; Saparov, B.; Ma, Y.-Z.; Chen, S.; Du, M.-H. *J. Mater. Chem. C* **2018**, *6* (24), 6398-6405.
15. Wang, X.; Meng, W.; Liao, W.; Wang, J.; Xiong, R. G.; Yan, Y. *J. Phys. Chem. Lett.* **2019**, *10* (3), 501-506.
16. Dohner, E. R.; Hoke, E. T.; Karunadasa, H. I. *J. Am. Chem. Soc.*, **2014**, *136* (5), 1718-1721.
17. Dohner, E. R.; Jaffe, A.; Bradshaw, L. R.; Karunadasa, H. I. *J. Am. Chem. Soc.*, **2014**, *136* (38), 13154-13157.
18. Cheng, Z.; Lin, J. *CrystEngComm*, **2010**, *12* (10).
19. Mao, L.; Wu, Y.; Stoumpos, C. C.; Wasielewski, M. R.; Kanatzidis, M. G. *J. Am. Chem. Soc.*, **2017**, *139*, 5210-5215.
20. Neogi, I.; Bruno, A.; Bahulayan, D.; Goh, T. W.; Ghosh, B.; Ganguly, R.; Cortecchia, D.; Sum, T. C.; Soci, C.; Mathews, N.; Mhaisalkar, S. G. *ChemSusChem*, **2017**, *10* (19), 3765-3772.
21. Smith, M. D.; Jaffe, A.; Dohner, E. R.; Lindenberg, A. M.; Karunadasa, H. I. *Chem. Sci.*, **2017**, *8* (6), 4497-4504.
22. Hu, H.; Morris, S. A.; Qiao, X.; Zhao, D.; Salim, T.; Chen, B.; Chia E. E. M.; Lam, Y. M. *J. Mater. Chem. C*, **2018**, *6* (38), 10301-10307.
23. Wang, S.; Yao, Y.; Kong, J.; Zhao, S.; Sun, Z.; Wu, Z.; Li, L.; Luo, J. *Chem. Commun.*, **2018**, *54* (32), 4053-4056.
24. Wu, G.; Zhou, C.; Ming, W.; Han, D.; Chen, S.; Yang, D.; Besara, T.; Neu, J.; Siegrist, T.; Du, M.-H.; Ma, B.; Dong, A. *ACS Energy Lett.*, **2018**, *3* (6), 1443-1449.
25. Lin, H.; Zhou, C.; Neu, J.; Zhou, Y.; Han, D.; Chen, S.; Worku, M.; Chaaban, M.; Lee, S.; Berkwits, E.; Siegrist, T.; Du, M. H.; Ma, B. *Adv. Opt. Mater.*, **2019**, *7* (6).
26. Zhou, J.; Li, M.; Ning, L.; Zhang, R.; Molokeev, M. S.; Zhao, J.; Yang, S.; Han, K.; Xia, Z. *J. Phys. Chem. Lett.*, **2019**, *10* (6), 1337-1341.
27. Duan, H. B.; Yu, S. S.; Liu, S. X.; Zhang, H. *Dalton Trans*, **2017**, *46* (7), 2220-2227.
28. Duan, H. B.; Yu, S. S.; Tong, Y. B.; Zhou, H.; Ren, X. M. *Dalton Trans*, **2016**, *45* (11), 4810-4818.
29. Mitzi, D. B. *Dalton Trans.* **2001**, (1), 1-12.
30. Saparov, B.; Mitzi, D. B. *Chem. Rev.* **2016**, *116* (7), 4558-96.

31. Thirumurugan, A.; Rao, C. N. R. *Cryst. Growth Des.* **2008**, *8*, 1640-1644.
32. Pan, J.; Sun, A.-H.; Han, S.-D.; Wei, L.; Li, J.-H.; Wang, G.-M. *J. Clust. Sci.* **2017**, *28* (5), 2669-2679.
33. Niemann, R. G.; Kontos, A. G.; Palles, D.; Kamitsos, E. I.; Kaltzoglou, A.; Brivio, F.; Falaras, P.; Cameron, P. J. *J. Phys. Chem. C* **2016**, *120* (5), 2509-2519.
34. Robinson, K.; Gibbs, G. V.; Ribbe, P. H. *Science* **1971**, *172*, 567-570.
35. Cortecchia, D.; Neutzner, S.; Srimath Kandada, A. R.; Mosconi, E.; Meggiolaro, D.; De Angelis, F.; Soci, C.; Petrozza, A. *J. Am. Chem. Soc.* **2016**, *139* (1), 39-42.
36. Chong, W. K.; Giovanni, D.; Sum, T. Excitonics in 2D Perovskites. In *Halide Perovskites: Photovoltaics, Light Emitting Devices, and Beyond*; Sum, T., Mathews, N.; Wiley-VCH Verlag GmbH & Co. KGaA, 2019; 55-79.
37. Tsuboi, T.; Aljaroudi, N. *Phys. Rev. B* **2005**, *72* (12).
38. Luo, J.; Wang, X.; Li, S.; Liu, J.; Guo, Y.; Niu, G.; Yao, L.; Fu, Y.; Gao, L.; Dong, Q.; Zhao, C.; Leng, M.; Ma, F.; Liang, W.; Wang, L.; Jin, S.; Han, J.; Zhang, L.; Etheridge, J.; Wang, J.; Yan, Y.; Sargent, E. H.; Tang, J. *Nature* **2018**, *563* (7732), 541-545.
39. Lao, X.; Yang, Z.; Su, Z.; Wang, Z.; Ye, H.; Wang, M.; Yao, X.; Xu, S. *Nanoscale* **2018**, *10* (21), 9949-9956.
40. Williams, R. T.; Song, K. S. *J. Phys. Chem. Solids* **1990**, *51*, 679-716.
41. Benek, O.; Musilek, K.; Horova, A.; Dohnal, V.; Dolezal, R.; Kuca, K. *Med. Chem.* **2015**, *11* (1), 21-29.
42. Boobalana, R.; Chen, C. *Tetrahedron Lett.*, **2016**, *57* (17), 1930-1934.
43. Allgäuer, D. S.; Mayr, H. *Eur. J. Org. Chem.*, **2013**, *28*, 6379-6388.
44. Kanitskaya, L. V.; Elokhina, V. N.; Fedorov, S. V.; Shulunova, A. M.; Nakhmanovich, A. S.; Turchaninov, V. K.; Lopyrev, V. A. *Russ. J. Gen. Chem.* **2002**, *72*, 778-784.
45. Katritzky, A. R.; Dega-Szafran, Z. *Mag. Res. Chem.* **1989**, *27*, 1090-1105.
46. Lukáč, M.; Mrva, M.; Garajová, M.; Mojžišová, G.; Varinská, L.; Mojžiš, J.; Sabol, M.; Kubincová, J.; Haragová, H.; Ondriska, F.; Devínsky, F. *Eur. J. Med. Chem.*, **2013**, *66*, 46-55.

10.5 Instrumentations and additional data

Nuclear Magnetic Resonance (NMR) spectroscopy. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of organic compounds were recorded in DMSO- d_6 solution using a Bruker AV400 spectrometer. Chemical shift values (ppm) are referenced against residual protic solvent peaks.

UV-vis spectroscopy. UV-vis spectra of polycrystalline samples were collected using a Shimadzu UV-3600 UV-VIS-NIR Spectrophotometer, with BaSO_4 as the 100% reflectance reference. The measurements were conducted over a 300 – 800 nm wavelength range, in the diffuse reflectance mode, using an integrating sphere, and a scanning resolution of 0.5 nm s^{-1} . Relative absorbance was obtained from Kubelka–Munk transformation of the reflectance spectra: $\alpha/S = (1 - R)^2(2R)^{-1}$, where R is the reflectance, and α and S are the absorption and scattering coefficients, respectively.

Steady-state, time-resolved, temperature- and power-dependent photoluminescence (PL) spectroscopies. Samples were photoexcited with 325 nm femtosecond laser pulses, generated using an optical parametric amplifier (OPA, Coherent OPerA Solo). The OPA was powered by a Coherent LIBRA laser, with a fundamental wavelength of 800 nm and output pulse-width of $\sim 50 \text{ fs}$, at a repetition rate of 1 kHz. The PL signal was collected using a lens pair and sent to a spectrometer (Princeton Instrument, SP-2500 series) where it was detected by a CCD camera (Pixis-400) or a streak camera (Optronis) in steady-state and TRPL measurements, respectively. The power-dependent measurements were obtained in this configuration by changing the excitation power in the range of 2.5 – 40 μW , using a set of variable density filters. For temperature-dependent studies, the samples were mounted onto a liquid nitrogen-cooled Janis cryostat st-300, adjusted to the optical plane of the inverted microscope, and measured within the temperature range 77 – 293 K.

Raman spectroscopy. Raman scattering measurements were performed using a WITec alpha 300RAS confocal Raman microscope. An Acton spectrometer with a diffraction grating of $1800 \text{ grooves mm}^{-1}$ (1.3 cm^{-1} resolution) and a thermoelectrically cooled Andor

CCD detector were used to collect data. To avoid absorption by the samples, which could lead to photoluminescence and degradation, the 633 nm (red) line from a He–Ne gas laser with a power of 5 mW was chosen, while the laser spot area was $\sim 1 \mu\text{m}^2$. The backscattered Raman signal passed through two 633 nm BragGrate Notch Filters (BNF). Measurements at 80 K were conducted under a nitrogen gas flow cryostat.

X-ray crystallography. Crystals were mounted on a Bruker X8 Quest CPAD area detector diffractometer and data was collected using a I μ S 3.0 Microfocus Mo-K α radiation source ($\lambda = 0.71073 \text{ \AA}$), at cryogenic temperatures (100 K). Data reduction and absorption corrections were performed using the SAINT and SADABS software packages, respectively. All structures were solved by direct methods and refined by full-matrix least squares procedures on F^2 , using the Bruker SHELXTL-2014 software package. Non-hydrogen atoms were anisotropically refined, after which hydrogen atoms were introduced at calculated positions and the data was further refined. The graphical illustrations of crystal structures used throughout the main paper and supporting information were created using the program VESTA.

1-(benzyl)pyridin-1-ium bromide (1Br). Isolated as a brown solid (1.37g; 90% yield). ^1H NMR (400 MHz, DMSO- d_6): δ 9.36 (d, 2 H, ArH), 8.65 (dd, 1 H, ArH), 8.20 (dd, 2 H, ArH), 7.60 (dd, 2 H, ArH), 7.41 (dt, 3 H, ArH), 6.00 (s, 2 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 146.0, 144.8, 134.3, 129.3, 129.2, 128.8, 128.4, 63.0. The NMR spectroscopic data match the reported values.⁴¹

1-(acetamidy)pyridin-1-ium bromide (2Br). Isolated as a white solid (1.11g; 91% yield). ^1H NMR (400 MHz, DMSO- d_6): δ 8.97 (d, 2 H, ArH), 8.65 (dd, 1 H, ArH), 8.18 (dd, 2 H, ArH), 8.02 (s, 1 H, $\text{C}(\text{O})\text{NH}_2$), 7.69 (s, 1 H, $\text{C}(\text{O})\text{NH}_2$), 5.41 (s, 2 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 166.0, 146.2, 146.0, 127.4, 61.5. The NMR spectroscopic data match the reported values.⁴²

1-(cyanomethyl)pyridin-1-ium bromide (3Br). Isolated as a white solid (0.78g; 83% yield). ^1H NMR (400 MHz, DMSO- d_6): δ 9.16 (d, 2 H, ArH), 8.71 (dd, 1 H, ArH), 8.23 (dd, 2 H, ArH), 5.99 (s, 2 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 147.6, 145.5, 128.6, 114.3, 47.7. The NMR spectroscopic data match the reported values.⁴³

1-(ethyl)pyridin-1-ium bromide (4Br). Isolated as a white solid (1.25g; 84% yield). ^1H NMR (400 MHz, DMSO- d_6): δ 9.28 (d, 2 H, ArH), 8.63 (dd, 1 H, ArH), 8.17 (dd, 2 H, ArH), 4.72 (q, 2 H, CH_2), 1.52 (t, 3 H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 146.0, 145.2, 128.6, 56.8, 16.9. The NMR spectroscopic data match the reported values.^{44,45}

1-(pentyl)pyridin-1-ium bromide (5Br). Isolated as a yellow solid (1.22g; 91% yield). ^1H NMR (400 MHz, DMSO- d_6): δ 9.20 (d, 2 H, ArH), 8.63 (dd, 1 H, ArH), 8.18 (dd, 2 H, ArH), 4.66 (t, 2 H, CH_2), 1.92 (m, 2 H, CH_2), 1.33 (m, 4 H, CH_2), 0.85 (t, 3 H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 145.5, 144.7, 127.9, 60.2, 30.4, 27.2, 21.4, 13.5.

1-(2-hydroxyethyl)pyridin-1-ium bromide (6Br). Isolated as a brown solid (0.94g; 88% yield). ^1H NMR (400 MHz, DMSO- d_6): δ 9.09 (d, 2 H, ArH), 8.63 (dd, 1 H, ArH), 8.17 (dd, 2 H, ArH), 4.73 (t, 2 H, CH_2), 3.86 (t, 2 H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO-

d6): δ 145.7, 145.2, 127.7, 63.1, 60.0. The NMR spectroscopic data match the reported values.⁴⁶

1-benzylpyridin-1-ium chloride (1Cl). Isolated as pale yellow oil (1.12; 85% yield). ¹H NMR (400 MHz, DMSO-d6): δ 9.29 (d, 2 H, ArH), 8.63 (dd, 1 H, ArH), 8.19 (dd, 2 H, ArH), 7.59–7.40 (m, 5 H, ArH), 5.91 (s, 2 H, CH₂). ¹³C{¹H} NMR (100 MHz, DMSO-d6): δ 146.0, 144.9, 134.3, 129.4, 129.2, 128.8, 128.5, 63.2. The NMR spectroscopic data match the reported values.⁴¹

1-benzylpyridin-1-ium iodide (1I). Isolated as brown solid (1.17; 83% yield). ¹H NMR (400 MHz, DMSO-d6): δ 9.20 (d, 2 H, ArH), 8.64 (dd, 1 H, ArH), 8.19 (dd, 2 H, ArH), 7.58–7.38 (m, 5 H, ArH), 5.88 (s, 2 H, CH₂). ¹³C{¹H} NMR (100 MHz, DMSO-d6): δ 146.0, 144.8, 134.3, 129.4, 129.2, 128.8, 128.5, 63.3. The NMR spectroscopic data match the reported values.⁴¹

Table 10.3 Crystallographic and structure refinement data for (1)₂[PbBr₄], (2)₂[PbBr₄] and (3)₂[PbBr₄].^a

	Compound		
	(1) ₂ [PbBr ₄]	(2) ₂ [PbBr ₄]	(3) ₂ [PbBr ₄]
Empirical formula	C ₂₄ H ₂₄ Br ₄ N ₂ Pb	C ₁₄ H ₁₈ Br ₄ N ₄ O ₂ Pb	C ₄₆ H ₅₄ Br ₁₂ N ₁₂ O ₂ Pb ₃ S ₂
Formula weight	867.28 g/mol	801.15 g/mol	2451.62 g/mol
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal size	0.010 x 0.080 x 0.100 mm	0.100 x 0.120 x 0.180 mm	0.020 x 0.040 x 0.120 mm
Crystal habit	colorless plate	colorless block	colorless needle
Crystal system	trigonal	trigonal	triclinic
Space group	R -3	R -3	P -1
Unit cell dimensions	a = 17.3480(4) Å	a = 15.4933(3) Å	a = 11.1106(5) Å
	α = 90°	α = 90°	α = 103.424(2)°
	b = 17.3480(4) Å	b = 15.4933(3) Å	b = 15.9420(9) Å
	β = 90°	β = 90°	β = 91.033(2)°
	c = 22.6258(6) Å	c = 24.3672(4) Å	c = 19.7704(10) Å
	γ = 120°	γ = 120°	γ = 93.167(2)°
Volume	5897.0(3) Å ³	5065.5(2) Å ³	3399.2(3) Å ³
Z	9	9	2
Density	2.198 g/cm ³	2.364 g/cm ³	2.395 g/cm ³
Absorption coefficient	12.550 mm ⁻¹	14.607 mm ⁻¹	14.570 mm ⁻¹
F(000)	3636	3312	2256
Theta range for data collection	2.25 to 34.35°	2.26 to 37.79°	2.32 to 27.00°
Reflections collected	22299	24847	59945
Coverage of independent reflections	99.9%	100%	99.90%
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan
Max. and min. transmission	0.8850 and 0.3670	0.3230 and 0.1780	0.7590 and 0.2740
Function minimized	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	5493 / 0 / 141	6043 / 0 / 114	14828 / 993 / 736
Goodness-of-fit on F ²	1.013	1.039	1.023
Δ/σ _{max}	0.001	0.001	0.001
Final R indices [I > 2σ(I)]	3694 data	4786 data	7986 data
	R1 = 0.0452,	R1 = 0.0390,	R1 = 0.0626,
	wR2 = 0.0553	wR2 = 0.0998	wR2 = 0.1009
R indices [all data]	R1 = 0.0924,	R1 = 0.0532,	R1 = 0.1450,
	wR2 = 0.0666	wR2 = 0.1070	wR2 = 0.1327
Largest diff. peak and hole	1.449 and -1.851 eÅ ⁻³	2.326 and -1.396 eÅ ⁻³	1.527 and -1.445 eÅ ⁻³
R.M.S. deviation from mean	0.295 eÅ ⁻³	0.229 eÅ ⁻³	0.263 eÅ ⁻³

^aR = Σ||F_o| - |F_c||/Σ|F_o|, wR = {Σ[w(|F_o|² - |F_c|²)²]/Σ[w(|F_o|⁴)]}^{1/2} and (1)₂[PbBr₄], w = 1/[σ²(F_o²) + (0.0076P)² + 24.9052P]; (2)₂[PbBr₄], w = 1/[σ²(F_o²) + (0.0530P)² + 19.8701P]; (3)₂[PbBr₄], w = 1/[σ²(F_o²) + (0.0263P)² + 9.0353P] where P = (F_o² + 2F_c²)/3.

Table 10.4 Crystallographic and structure refinement data for **4**[PbBr₃], **5**[PbBr₃] and **6**[PbBr₃].^a

	Compound		
	4 [PbBr ₃]	5 [PbBr ₃]	6 [PbBr ₃]
Empirical formula	C ₇ H ₁₀ Br ₃ NPb	C ₂₀ H ₃₂ Br ₅ N ₂ Pb _{1.50}	C ₇ H ₇ Br ₃ NOPb
Formula weight	555.08 g/mol	1010.81 g/mol	568.06 g/mol
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal size	0.020 x 0.040 x 0.080 mm	0.020 x 0.040 x 0.120 mm	0.020 x 0.040 x 0.080 mm
Crystal habit	colorless block	colorless needle	orange block
Crystal system	orthorhombic	triclinic	triclinic
Space group	P 21 21 21	P -1	P -1
Unit cell dimensions	a = 7.8870(3) Å	a = 10.9668(5) Å	a = 7.7918(7) Å
	α = 90°	α = 114.818(2)°	α = 90.295(2)°
	b = 10.0639(3) Å	b = 11.9630(5) Å	b = 11.1156(9) Å
	β = 90°	β = 91.946(2)°	β = 98.934(2)°
	c = 15.1133(5) Å	c = 12.1132(6) Å	c = 14.7794(12) Å
	γ = 90°	γ = 96.673(2)°	γ = 100.308(2)°
Volume	1199.60(7) Å ³	1426.61(12) Å ³	1243.40(18) Å ³
Z	4	2	4
Density	3.073 g/cm ³	2.353 g/cm ³	3.035 g/cm ³
Absorption coefficient	24.010 mm ⁻¹	15.861 mm ⁻¹	23.174 mm ⁻¹
F(000)	984	928	1004
Theta range for data collection	2.91 to 29.99°	2.47 to 29.00°	2.29 to 35.00°
Reflections collected	9678	24979	10746
Coverage of independent reflections	99.8%	99.4%	99.5%
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan
Max. and min. transmission	0.6450 and 0.2500	0.7420 and 0.2520	0.6540 and 0.2590
Function minimized	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	3473 / 0 / 110	7552 / 0 / 261	10746 / 0 / 238
Goodness-of-fit on F ²	0.991	1.008	1.036
Δ/σ _{max}	0.001	0.001	0.001
Final R indices [I > 2σ(I)]	2870 data	5173 data	6773 data
	R1 = 0.0361,	R1 = 0.0462,	R1 = 0.0579,
	wR2 = 0.0678	wR2 = 0.0612	wR2 = 0.1004
R indices [all data]	R1 = 0.0498,	R1 = 0.0857,	R1 = 0.1173,
	wR2 = 0.0727	wR2 = 0.0727	wR2 = 0.1230
Largest diff. peak and hole	1.237 and -1.124 eÅ ⁻³	1.587 and -1.358 eÅ ⁻³	2.234 and -3.517 eÅ ⁻³
R.M.S. deviation from mean	0.211 eÅ ⁻³	0.271 eÅ ⁻³	0.426 eÅ ⁻³

^aR = Σ||F_o| - |F_c||/Σ|F_o|, wR = {Σ[w(|F_o|² - |F_c|²)²]/Σ[w(|F_o|⁴)]}^{1/2} and **4**[PbBr₃], w = 1/[σ²(F_o²) + (0.0236P)²]; **5**[PbBr₃], w = 1/[σ²(F_o²)]; **6**[PbBr₃], w = 1/[σ²(F_o²) + (0.0368P)² + 3.1667P] where P = (F_o² + 2F_c²)/3.

Table 10.5 Crystallographic and structure refinement data for (1)₂[PbCl₄] and (1)[PbI₃].^a

	Compound	
	(1) ₂ [PbCl ₄]	(1)[PbI ₃]
Empirical formula	C ₂₄ H ₂₄ Cl ₄ N ₂ Pb	C ₁₂ H ₁₂ I ₃ NPb
Formula weight	689.44 g/mol	758.12 g/mol
Temperature	100(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal size	0.020 x 0.040 x 0.200 mm	0.010 x 0.020 x 0.120 mm
Crystal habit	colorless needle	yellow needle
Crystal system	trigonal	monoclinic
Space group	R -3	P 1 21/m 1
Unit cell dimensions	a = 17.1827(7) Å	a = 11.7951(11) Å
	α = 90°	α = 90°
	b = 17.1827(7) Å	b = 7.8822(7) Å
	β = 90°	β = 101.304(2)°
	c = 21.6452(12) Å	c = 11.8001(11) Å
	γ = 120°	γ = 90°
Volume	5534.5(5) Å ³	1075.79(17) Å ³
Z	9	2
Density	1.862 g/cm ³	2.340 g/cm ³
Absorption coefficient	7.308 mm ⁻¹	12.132 mm ⁻¹
F(000)	2988	664
Theta range for data collection	2.33 to 26.99°	2.72 to 32.65°
Reflections collected	8529	20470
Coverage of independent reflections	99.9%	99.8%
Absorption correction	Multi-Scan	Multi-Scan
Max. and min. transmission	0.8680 and 0.3230	0.8880 and 0.3240
Function minimized	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	2684 / 0 / 141	4177 / 261 / 118
Goodness-of-fit on F ²	1.039	1.028
Δ/σ _{max}	0.001	0.001
Final R indices	2032 data	1976 data
	R1 = 0.0445,	R1 = 0.0554,
	[I > 2σ(I)]	
R indices [all data]	wR2 = 0.0731	wR2 = 0.1416
	R1 = 0.0694,	R1 = 0.1407,
	wR2 = 0.0839	wR2 = 0.1769
Largest diff. peak and hole	0.913 and -0.778 eÅ ⁻³	1.619 and -1.151 eÅ ⁻³
R.M.S. deviation from mean	0.162 eÅ ⁻³	0.239 eÅ ⁻³

^aR = Σ||F_o| - |F_c||/Σ|F_o|, wR = {Σ[w(|F_o|² - |F_c|²)²]/Σ[w(|F_o|⁴)]}^{1/2} and (1)₂[PbCl₄], w = 1/[σ²(F_o²) + (0.0228P)²]; (1)[PbI₃], w = 1/[σ²(F_o²) + (0.0816P)² + 0.1230P] where P = (F_o² + 2F_c²)/3.

Chapter 11

Conclusions and future outlook

This chapter summarizes the findings and discusses the implication and novelty of the research. It reiterates the extent to which the thesis objectives have been met and what are the outstanding questions left. Finally, opportunities and strategies for future work are suggested.

11.1 Conclusions of thesis

The studies in this thesis focus on the use of targeted molecular design approach to induce optoelectronic properties of low-dimensional organic metal-halide hybrids that are relevant to photovoltaic and solid-state lighting applications. In addition, the studies also aim to understand the formability of inorganic framework with different structures and dimensionalities *via* functional group variation. The conclusions of this thesis are summarized as follows:

- a. Photoconductivity of one- and two-dimensional perovskites may be enhanced via modulation of i) charge transfer interaction between organic and inorganic moieties and/or ii) inter-inorganic framework interaction in the lattices*

In the beginning, it is demonstrated for the first time that 1D lead-iodide materials can be endowed with extended light absorption (up to 800 nm), reduced band gaps (1.74 eV to 1.77 eV) and enhanced photoconductivity. This is achieved by employing viologen (*N,N'*-dialkyl-4,4'-bipyridinium) cations endowed with hydrogen bonding functionalities, which served to induce π - π stacking interactions (3.593 to 3.687 Å). The resulting 'viologen dimers' reinforces charge-transfer (CT) interactions with the 1D lead-iodide chains as a result of further stabilization of the organics lowest unoccupied molecular orbitals (LUMOs).

In addition, a series of new 2D perovskites based on *N*-substituted pyridinium cations are presented. The hybrid materials exhibit reduced band gaps (2.35 – 2.46 eV), relaxed dielectric confinement (excitonic binding energies of 130 – 200 meV), and improved electrical and photoconductivities (more than 10-fold) relative to conventional 2D lead-iodide perovskites. Such features can be realized by reducing their inorganic inter-octahedral distortions (largest Pb-(μ -I)-Pb bond angles of 170 – 179°) and inorganic layers separation (shortest I $\cdots$ I contacts $\leq$ 4.278 – 4.447 Å). The former is attributed to the low charge density and the bulk nature of the pyridine ring, which minimize the

strength of interaction with the iodoplumbate layer, while the latter is due to compact nature of the dications.

On the whole, such properties of the herein studied $n = 1$ perovskites mimic those of their $n = 2$ analogues, where n refers to the number of contiguous 2D inorganic layers (i.e., not separated by organic cations). The origin of the more ‘3D-like’ behaviour of these materials was probed using computational studies and shown to derive from their structural features. At the time of publication, the highest power conversion efficiencies (1.43 and 1.83%) for pure 2D perovskite solar cells were obtained in those studies. Thus, the studies demonstrate that improvement in devices level can be realized through suitable molecular design of the organic cations.

b. Broadband emission can be induced via reinforcement of the inorganic frameworks’ structural distortion and dimensionality

In order to induce a broadband emission from the 2D lead-bromide perovskite, dicationic 1-(2-ammonioethyl)-1*H*-imidazol-3-ium organic were utilized to template a rare 2×2 (110)-oriented structure. Upon excitation by UV-light, the resulting corrugated 2D perovskite generates white-light emission as a consequence of exciton-phonon coupling (i.e. self-trapped excitons). The emission covers the entire visible spectrum with the peak maxima at 537 nm and features a large Stoke-shift (of ca. 1.05 eV) and full widths at half maximum (FWHM) of ca. 810 meV. As the consequence, color rendering index (CRI) and correlated color temperature (CCT) of 73 and 5824 K, respectively, can be obtained. It corresponds to ‘colder’ white light emission in comparison to those of reported compounds of the same class where CCTs were of below 5000 K.

Following that, the study went on to investigate new (100)-oriented 2D Pb-Br perovskites, whose structures display unusually high intra-octahedral distortions (deformed lead-bromide coordination geometry), whilst retaining minimal inter-octahedral distortions. This is achieved by incorporating sterically-demanding organic

cations, such as that with piperidinium core (1-(2-ammonioethyl)piperidin-1-ium). Using a combination of various photoluminescence spectroscopic measurements, it is demonstrated that increased intra-octahedral distortion induces exciton localization processes and leads to formation of multiple photoinduced emissive colour centres. Ultimately, this leads to highly Stokes-shifted, ultrabroad white light emission (CIE coordinates of (0.38, 0.38), CCT of 4088 K and CRI of 96) at room temperature.

Finally, three new compounds containing very rare lead-bromide trimers templated by pyridinium cations functionalized with rigid substituents (benzyl, acetamidyl, and cyanomethyl) are also reported. Upon exposure to ultra-violet (UV) light, prototypical benzyl pyridinium lead-bromide, featuring highest level of distortion of the individual $[\text{PbBr}_6]^-$ octahedra, exhibits a broadband emission, centered at 571 nm, which spans from 400 to 800 nm. More specifically, it displays a large Stokes shift of ca. 1.39 eV and a full width at half maximum (FWHM) of ca. 540 meV. The reduced size and dimensionality of its inorganic lattice also results in a photoluminescence quantum yield (at least 10%) that is approximately one order magnitude higher than that of 1D congeners. Mechanistically, broadband emission in benzyl pyridinium lead-bromide is deduced to be due to self-trapped excitons, originating from exciton-phonon coupling in the quantumically-confined bromoplumbate lattice. As such, the studies demonstrate strategies that can be used to tailor the Pb-halide inorganic structure at a molecular level and, thereby, induce desirable photophysical properties for optoelectronic applications.

c. Understanding the inorganic lattice formability in low-dimensional perovskite

Firstly, using pyridinium core as the framework, empirical understanding of the two-dimensional (2D), one-dimensional (1D), and trimeric lead-halide hybrid materials formation can be gleaned. Primary ammonium groups ($-\text{NH}_3^+$) are found to be a prerequisite for formation of 2D perovskites, presumably due to the highly localized charge density and limited steric bulk of this functionality. In the absence of $-\text{NH}_3^+$, 1D iodoplumbate inorganic architectures are obtained with comparatively short and flexible *N*-alkyl substituents (e.g. ethyl, propyl, and pentyl). The presence of *N*-alkyl

substituents containing neutral hydrogen bond donors (e.g. alcohol, carboxylic acid, and primary amide functionality) did not change this outcome and the 1D structures were retained. When more rigid substituents are employed (e.g. benzyl, acetamidyl, and cyanomethyl), hybrids composed of very rare face-sharing inorganic trimers can be afforded.

Secondly, systematic tuning of the aromatic ring size and position of -NH functionalities lead to the discovery of the unprecedented corrugated ' 3×3 ' (110)-oriented 2D lead-iodide and tin-iodide perovskites (where ' $n \times n$ ' refers to the number (n) of contiguous metal-halide octahedra comprising each ridge). The compact nature of the dications produces super short lead-iodide and tin-iodide sheet separations, with respective iodide-iodide ($I \cdots I$) distances as small as 4.278 Å and 4.174 Å. This eventually results in low exciton activation energies of less than 100 meV. The main driving force to formation of the unusual structure is attributed to the presence of a coulombic interaction that occurs perpendicular to the plane of the heterocyclic ring. With similar approach, a rare white-light emitting ' 2×2 ' (110)-oriented 2D lead-bromide perovskite with significance in solid-state lighting applications can also be obtained. Single crystal structure investigation demonstrates that in the absence of the exact aromatic ring size and positioning of -NH functionalities, much more common (100) 2D perovskites are formed instead.

11.2 Outstanding questions

Holistically, these results demonstrate that with well-designed organic cations, optoelectronic properties of low-dimensional hybrid materials can be modulated such that they can be relevant to photovoltaic and solid-state lighting applications. Furthermore, with appropriate experimental methodology, insights regarding the materials formability can be gleaned, while at the same time, accessing the synthesis of materials featuring rare or unprecedented structures. Nevertheless, there are still some relevant questions left unanswered within the scope of this work. Herein are proposed several questions, which if answered would further improve comprehension of the approach.

a. What is the limit of 2D perovskite formation?

In this study, organic cations containing pyridinium, imidazolium, and piperidinium cores have been shown to be capable of templating 2D metal-halide frameworks. The 2D perovskites formed can be considered unique because the cations possess ‘hindered’ positive charge center in addition to the ammonium functionality. However, such cyclic system is still relatively small and the study was conducted with the fixed number of ammonioalkyl chain of two carbon atoms. Hence it is interesting to investigate how the metal-halide framework can differ by the effects of enlarging the ring size and tuning the alkyl chain length.

b. How influential is halogen bonding in low dimensional material formation?

Throughout the study in this thesis, much of the focus has been paid on the effect of hydrogen bonding and Coulombic interactions in the formation of materials’ inorganic framework. Apart from that, it is also worth-scrutinizing how halogen bonding would perturb the formation of certain structure in the absence or presence of ammonium groups. Although there are a few reported compounds indicating the presence of halogen bonding in low-dimensional perovskites, investigation to deliberately study the effects is non-existent. Thus, incorporating heavy halogen atoms such as bromine (Br) or iodine (I) into the organic cations would be appealing to explore the possible structures.

c. What is the consequence of greater charge-transfer (CT) interaction and can it exhibit superior properties than 2D perovskites with thicker inorganic layer?

These results show that in 2D system studied in this thesis (which contain polarizable organic), as suggested by DFT calculations, there is charge-transfer interaction between the organic and inorganic components. However, unlike in viologen-based hybrids, the effect of CT is still not yet clear in enhancing the optical properties of the materials. Hence, ring modification such as incorporation of electron withdrawing groups (i.e. to

bring down the organics lowest unoccupied molecular orbitals or LUMOs) would be required to enable us scrutinize the effects. In addition, study to compare the device performance between materials with different degree of CT and with that of thicker inorganic layers (i.e. $2 \leq n \leq 5$) would confirm the applicability of the approach.

d. How the formation of monomeric structure can be induced?

These results also demonstrate that with the targeted molecular approach, the inorganic components featuring 2D, 1D and even trimeric structures can be tuned. The trends are that with lower dimensionality, broadband emissions tend to occur as manifestations of more distorted structures. More importantly, moving to lower dimensionality imparts greater confinement to the system and thus, greater photoluminescence quantum yield (PLQY) is normally observed in '0D' system. As such, any method capable of inducing monomeric structure to form will be highly favorable for further development of the materials.

11.3 Implications and future outlook

Herein are put forward some future work which could help either solve the questions left unanswered within the scope of this work or expand the capability of the proposed approach to further enhance the materials' optoelectronic properties that are relevant to photovoltaic and solid-state lighting applications.

11.3.1 Electron withdrawing group incorporation to enhance charge-transfer interaction

As previously mentioned, it is hypothesized that by lowering down the LUMO level of the organic cations, enhanced CT would be expected. This would correspondingly result in better light absorption capability and enhanced charge transport relative to the current system.

In this regard, ring modification of the current organic cation system such as incorporation of electron withdrawing groups, such as fluorine, carboxyl, nitro, nitrile, and trifluoromethyl functionalities would be helpful because their presence is able to stabilize the LUMOs of the overall organic compounds (**Figure 11.1**). However, such functionalization should be carried out systematically at different position, because it would introduce extra steric bulk (especially with groups other than fluorine atom). Thus, it may rupture the whole 2D perovskite framework if the organic structure is incompatible with 2D lattices.

Figure 11.1 Molecular structures of proposed organic cations containing electron withdrawing functionalities.

Another way to enhance the charge-transfer between the organic and inorganic components is by employing aromatic heterocyclic compounds containing multiple nitrogen atoms, such as diazines and triazines (**Figure 11.2**). The presence of extra nitrogen in the ring acts as electron withdrawing groups within the ring and thus, is capable of stabilizing the organics LUMO levels. However, although it may not sterically present a problem to 2D lattice formation, extra care has to be paid on the preparation of divalent organic cation because the extra nitrogen could potentially be protonated as well, especially in the presence of strong acid such as hydroiodic acid, to give higher valent cationic species.

Figure 11.2 Molecular structures of proposed organic cations containing electron diazines and triazines as the aromatic cores.

11.3.2 Halogen bonding for perovskite formability investigation and intermolecular electronic interaction enhancement

The effect of halogen bonding towards perovskite formation and the overall electronic properties has never been systematically investigated. However, separate isolated reports in literature concerning related compounds suggest interesting potential of the interaction. For example, while at room temperature, formamidinium cation induces 1D face-sharing lead-iodide chain (i.e. non-perovskite δ -phase),¹ iodoformamidinium is capable of templating 1D corner-sharing structure.² Directional contact of 3.539 Å between iodine atom of the iodoformamidinium organic and terminal iodide ion in the 1D inorganic lattice ($I_{\text{org}} \cdots I_{\text{inorg}}$) suggests the presence of halogen bonding interaction.³

Another example is concerning pyridinium cation. Similar to the previous example, unsubstituted pyridinium cation tends to result in 1D face-sharing lattices.⁴ Surprisingly, incorporating heavy atoms such as bromine or iodine into the organic aromatic core, formation of 2D perovskites can be induced (although the formability of the structure is found to depend on the position of the atom relative to the NH moiety in the ring).⁵⁻⁶ Directional $I_{\text{org}} \cdots I_{\text{inorg}}$ and $\text{Br}_{\text{org}} \cdots I_{\text{inorg}}$ of 3.560 and 3.581 Å, respectively, evidence of similar interaction. Last insight can be gleaned from anilinium cation. With unsubstituted anilinium alone, a rare 1D material with edge-sharing connectivity was obtained.⁷ However, functionalizing the ring with a Br atom renders the cation capable of templating 2D lattice formation ($\text{Br}_{\text{org}} \cdots I_{\text{inorg}}$ of 3.862 Å).

Figure 11.3 Molecular structures of proposed organic cations containing heavy atoms iodine and bromine to induce halogen bonding interaction with the inorganic lattices.

In summary, glance literature review suggests that there is something unique with this interaction despite its limited exploration. Therefore, by incorporating the heavy atom such bromide and iodide, the formability of certain perovskite structures (**Figure 11.3**) can be investigated. More importantly, the optoelectronic properties of the materials can also concomitantly be modulated. As demonstrated by Karunadasa and co-workers, it is possible to alter the optical and electronic properties of the inorganic layers of 2D perovskites by similar halogen bonding interaction. In their case, this was achieved *via* intercalation of iodine species.⁸

11.3.3 Inducing monomeric lead-halide hybrid with bulky organic cations

These results suggest that rigid functionalities are capable of selectively generating hybrid materials featuring trimeric inorganic lattices (i.e. ‘0D’), when pyridinium cation is used as the core. Apart from the broadband emission (that is a result of distorted inorganic lattices), the most direct consequence of such confinement is a 10-fold enhancement in PLQY relative to that of 1D counterparts that are templated by the more flexible substituents. It has previously reported that near-unity PLQY is possible to achieve with hybrids containing metal-halide monomers. As such, confining the inorganic lattice from trimeric form to the monomeric forms would improve the PLQY even further.

Figure 11.4 Molecular structures of proposed organic cations where the cyclic core is expanded.

Herein are proposed two ways to achieve the generation of monomer-based hybrids through systematic tuning of the organic cations:

1.) Expansion of the cyclic core.

As shown in **Figure 11.4**, expanding the cyclic system in the organic cation would exert more steric demand to the inorganic lattices and thus this could lead to breaking of the structure. Aromatic ring, such as quinoline, benzimidazole, and acridine would satisfy the requirement due not only to their versatility, but also rigidity nature.

2.) Incorporation of bulky substituents to the cyclic ring core.

Using similar concept as above, but carried out at different location (**Figure 11.5**), the purpose is to apply more steric strain into the inorganic lattices. This is achieved by introducing bulky substituents such as dihalo, dicyano, tert-butyl, and even di-phenyl groups.

Figure 11.5 Molecular structures of proposed organic cations where the substituents are endowed with bulky functionalities.

11.3.4 Broadband emitters based on Sn-Br lattices

Toxicity of Pb-based compound has been a major problem for its commercialization. This revived interest in Sn-based materials. However, as epitomized by these results, Sn^{+2} is less stable due to weaker inert pair effect. As a consequence, it would compromise the photovoltaic device performances due to high background charge carriers. Fortunately, the tendency of the Sn^{+2} to get oxidized depends on the halide and the lighter counterpart is known to feature better stability. This is a good opportunity to develop Sn-Br-based broadband emitting from the organic cations used in Pb-Br counterpart as the light absorption capability becomes irrelevant.

11.4 Bibliography

1. Stoumpos, C. C.; Malliakas, C. D.; Kanatzidis, M. G. *Inorg. Chem.* **2013**, *52* (15), 9019-9038.
2. Wang, S.; Mitzi, D. B.; Feild, C. A.; Guloy, A. *J. Am. Chem. Soc.* **1995**, *117* (19), 5297-5302.
3. Gilday, L. C.; Robinson, S. W.; Barendt, T. A.; Langton, M. J.; Mullaney, B. R.; Beer, P. D. *Chem. Rev.* **2015**, *115* (15), 7118-7195.
4. Engelhardt, L. M.; Patrick, J. M.; Whitaker, C. R.; White, A. H. *Aust. J. Chem.* **1987**, *40* (12), 2107-2114.
5. Gómez, V.; Fuhr, O.; Ruben, M. *CrystEngComm* **2016**, *18* (42), 8207-8219.
6. Takahashi, Y.; Obara, R.; Nakagawa, K.; Nakano, M.; Tokita, J.-Y.; Inabe, T., *Chem. Mater.* **2007**, *19* (25), 6312-6316.
7. Geselle, M.; Fuess, H. *Z. Kristallogr. - New Cryst. Struct.* **1997**, *212* (JG), 243-243.
8. Smith, M. D.; Pedesseau, L.; Kepenekian, M.; Smith, I. C.; Katan, C.; Even, J.; Karunadasa, H. I. *Chem. Sci.* **2017**, *8* (3), 1960-1968.

Scientific portfolio

This thesis is based on the following publications:

1. Febriansyah, B.; Koh, T. M.; John, R. A.; Ganguly, R.; Li, Y.; Bruno, A.; Mhaisalkar, S. G.; England, J. Inducing panchromatic absorption and photoconductivity in polycrystalline molecular 1D lead-iodide perovskites through π -stacked viologens. *Chem. Mater.* **2018**, *30* (17), 5827-5830 (**Chapter 4**).
2. Febriansyah, B.; Lekina, Y.; Ghosh, B.; Harikesh, P. C.; Koh, T. M.; Li, Y.; Shen, Z. X.; Mathews, N.; England, J.* Pyridinium-templated 2D lead-iodide perovskites: specific formability, reduced band gap, and relaxed dielectric confinement. *chemsuschem*, under review. (**Chapter 5**).
3. Febriansyah, B.; Koh, T. M.; Lekina, Y.; Jamaludin, N. F.; Bruno, A.; Ganguly, R.; Shen, Z. X.; Mhaisalkar, S. G.; England, J. Improved photovoltaic efficiency and amplified photocurrent generation in mesoporous $n = 1$ two-dimensional lead-iodide Perovskite Solar Cells. *Chem. Mater.* **2019**, *31* (3), 890-898 (**Chapter 6**).
4. Febriansyah, B.; Lekina, Y.; Hooper, T. J. N.; Harikesh, P. C.; Lim, M. H.; Koh, T. M.; Li, Y.; Shen, Z. X.; Mathews, N.; England, J.* Structural and optoelectronic properties of a 3×3 corrugated 2D tin-iodide perovskite. *In preparation* (**Chapter 7**).
5. Febriansyah, B.; Giovanni, D.; Sankaran, R.; Koh, T. M.; Li, Y.; Sum, T. C.; Mathews, N.; England, J.* Inducing formation of a corrugated, white-light emitting 2D lead-bromide perovskite via subtle changes in templating cation. *J. Mater. Chem. C*, 2020, Advance Article. DOI: 10.1039/C9TC05357C. (**Chapter 8**).
6. Febriansyah, B.;[†] Borzda, T.;[†] Cortecchia, D.; Neutzner, S.; Folpini, G.; Koh, T. M.; Li, Y.; Mathews, N.; Petrozza, A.;^{*} England, J.* Two-dimensional hybrid lead-bromide perovskite broadband emitters with highly deformed metal coordination spheres. *Angew. Chem. Int. Ed.*, in revision. (**Chapter 9**).

7. Febriansyah, B.; Neo, D. C. S.; Giovanni, D.; Lekina, Y.; Koh, T. M.; Li, Y.; Shen, Z. X.; Sum, T. C.; Mathews, N.; England, J.* Selective generation of trimeric organic-bromoplumbate hybrids that display intrinsic, highly Stokes-shifted, efficient broadband emission. *Chem. Mater.*, in revision. (**Chapter 10**).

Other publications by the author:

8. Febriansyah, B.; Koh, T. M.; Rana, P. J. S.; Hooper, T. J. M.; Ang, Z. Z. Li, Y.; Bruno, A.; Grätzel, M.; England, J.; Mhaisalkar, S. G.; Mathews, N.* Hybrid 2D CH₃NH₂-PbI₂ as CH₃NH₂-gas carrier for scalable perovskite deposition. *In preparation*.
9. Yantara, N.; Jamaludin, N. F.; Febriansyah, B.; Bruno, A.; Tay, Y. B.; Mhaisalkar, S. G.; Mathews, N.* Regulating Vertical Domain Distribution in Ruddlesden–Popper Perovskites for Electroluminescence Devices. *J. Phys. Chem. Lett.* **2019**, *10* (24), 7949-7955.
10. Lekina, Y.; Dintakurti, S. S. H.; Yan, J.; Febriansyah, B.; England, J.; White, T.; Shen, Z. X.* Methylammonium dynamics and its influence on optical properties in 2D hybrid perovskite. *In preparation*.
11. Lekina, Y.; Febriansyah, B.; Yan, J.; England, J.; Shen, Z. X.* Anisotropy of photoluminescence energy in hybrid 2D perovskite. *In preparation*.
12. Yantara, N.;[†] Jamaludin, N. F.;[†] Febriansyah, B.; Giovanni, D.; Bruno, A.; Soci, C.; Sum, T. C.; Mhaisalkar, S. G.; Mathews, N.* Designing the perovskite structural landscape for highly efficient blue emission. *Adv. Mater.*, in revision.
13. Chaudhary, B.; Koh, T. M.; Febriansyah, B.; Bruno, A.; Mathews, N.; Mhaisalkar, S. G.; Soci, C.* Thermally stable and efficient mixed dimensional methylammonium-naphthalene based perovskite. *Sci. Rep.*, accepted.

14. Han, G.; Koh, T. M.; Li, J.; Febriansyah, B.; Fang, Y.; Jamaludin, N. F.; Mhaisalkar, S. G.; Mathews, N.* Towards efficient and stable perovskite photovoltaics with fluorinated phosphonate salt surface passivation. *In preparation*.
15. Vishwanath, S. K.; Febriansyah, B.; Ng, S.; John, R. A.; Jagadeeswararo, M.; Tiwari, N.; Periyal, S. S.; Nirmal, A.; Mathews, N.* One-Dimensional Halide Perovskites for Large-Area Flexible Cross-Bar Memristors and Neuromorphic Computing. *Adv. Mater.*, *submitted*.
16. Ghosh, B.; Febriansyah, B.; Harikesh, P. C.; Koh, T. M.; England, J.; Mhaisalkar, S. G.; Mathews, N.* Direct bandgap mixed-valence organic-inorganic gold perovskite as visible light absorber. *In preparation*.
17. Guo, X.; Koh, T. M. Febriansyah, B.; Han, G.; Bhaumik, S.; Li, J.; Jamaludin, N. F.; Ghosh, B.; Chen, X.; Mhaisalkar, S. G.; Mathews, N.* Cesium Oleate Passivation for Stable Perovskite Photovoltaics. *ACS Appl. Mater. Interfaces* **2019**, *11* (31), 27882-27889.
18. Ko, J.; Surendran, A.; Febriansyah, B.; Wei Lin Leong.* Self-healable electrochromic ion gels for low power and robust displays. *Org. Electron.* **2019**, *71*, 199-205.
19. Ghosh, D.; Febriansyah, B.; Gupta, D.; Ng, L. K. S.; Xi, S.; Du, Y.; Baikie, T.; Dong, Z.; Soo, H. S.* Hybrid nanomaterials with single-site catalysts by spatially controllable immobilization of nickel complexes via photoclick chemistry for alkene epoxidation. *ACS Nano*. **2018**, *12* (6), 5903-5912.
20. Salim, K. M. M.; Koh, T. M.; Bahulayan, D.; Harikesh, P. C.; Jamaludin, N. F.; Febriansyah, B.; Bruno, A.; Mhaisalkar, S.; Mathews, N.* Extended Absorption Window and Improved Stability of Cesium-Based Triple-Cation Perovskite Solar Cells Passivated with Perfluorinated Organics. *ACS Energy Lett.* **2018**, *3* (5), 1068-1076.

21. Koh, T. M.; Febriansyah, B.; Mathews, N.* Ruddlesden-Popper Perovskite Solar Cells. *Chem.* **2017**, 2 (3), 326-327.

Conferences, Workshops, and Seminars

1. Febriansyah, B.; Wan, J. J. F. Y.; Koh, T. M.; Bruno, A.; Mhaisalkar, S.; Mathews, N. 10th International Conference on Materials for Advanced Technologies (ICMAT 2019), Singapore, June 2019.
2. Febriansyah, B.; Mathews, N.; England, J. 2nd Chemistry National Meeting Singapore (ChnmSG 2019), Singapore, May 2019.
3. Febriansyah, B.; Koh, T. M.; Lekina, Y.; Jamaludin, N. F.; Bruno, A.; Ganguly, R.; Shen, Z.; Mhaisalkar, S.; England, J. 4th International Conference on Perovskite Solar Cells and Optoelectronics (PSCO 2018), Lausanne, Switzerland, October 2018 (Best Poster Award).
4. Febriansyah, B.; Koh, T. M.; John, R. A.; Ganguly, R.; Li, Y.; Bruno, A.; Mhaisalkar, S.; England, J. E-MRS 2018 Fall Meeting, Warsaw, Poland, September 2018.
5. Febriansyah, B.; England, J. 4th Singapore Inorganic Chemistry Symposium (SICS 2018), Singapore, July 2018.
6. Febriansyah, B.; Mhaisalkar, S.; Mathews, N.; England, J. 7th MRS-S Conference on Advanced Materials & 7th Trilateral Conference on Nanoscience: Energy, Water & Healthcare, Singapore, December 2016.