Controlling luminescence properties of 2D perovskites by structural design

Cortecchia, Daniele

2018

Cortecchia, D. (2018). Controlling luminescence properties of 2D perovskites by structural design. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/73255>

<https://doi.org/10.32657/10356/73255>

NANYANG
TECHNOLOGICAL
UNIVERSITY

**CONTROLLING LUMINESCENCE PROPERTIES
OF 2D PEROVSKITES BY STRUCTURAL DESIGN**

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2017

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

2017

Statement of Originality

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

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Abstract

Metal halide perovskites are rapidly emerging for their light emitting properties, making perovskite-based light-emitting diodes, transistors, lasers and scintillators the new frontier of solution-processable optoelectronic devices. In this regard, two-dimensional perovskites are extremely appealing due to their increased synthetic versatility, which allows the incorporation of a wider range of organic and metallic cations for the fine-tuning of their optoelectronic properties. Hybrid functional materials can be synthesized by including optoelectronically active cations within the perovskite framework and provide new emissive properties to the resulting hybrid system. On the other hand, the templating properties of organic cations can be exploited to control the structural arrangement of the inorganic motif and the interplay between excitonic and polaronic properties to induce narrow- to ultrabroad-band luminescence. The rational synthetic design to achieve optical properties on demand is conditional to the understanding of the self-assembling behaviour and photophysical processes underlying the emissive properties of these materials, which are still mostly unexplored.

In this thesis project, crystal engineering principles are applied for the design and synthesis of perovskites with desired luminescence properties. Such model materials are studied by a combination of steady state and time resolved spectroscopic measurements and *ab initio* simulations to reveal the interplay between structure and optical properties in both lead-free and lead-based systems. Firstly, we show that active functional cations can be used in combination to copper perovskites to overcome their limitations in terms of emission tunability and stability. Furthermore, we employ the organic cations as templating elements to induce specific structural arrangements and distortions of the inorganic framework in lead-based perovskites and to selectively tailor their luminescence bandwidth and energy by structural design. We argue that the formation of small polaronic species localized at specific sites of the

inorganic lattice are responsible for the photoluminescence broadening in 2D perovskites, ultimately leading to white light emission.

Our results highlight the importance of perovskite's structural engineering to achieve a rational synthetic design of the material, and point to a wider consideration of the role of polarons and charge self-trapping in hybrid perovskites. The ability to selectively control the optoelectronic properties in these low-dimensional systems will provide distinctive advantages for their application in solid-state lighting and scintillators.

Acknowledgements

First and foremost, I want to sincerely thank my PhD supervisor Prof. Cesare Soci for his valuable guidance. I deeply appreciate his contributions of ideas, time and funding which were essential to strengthen my work and allowed me to grow as a research scientist. I am grateful to the members of my Thesis Advisory Committee, Prof. Nripan Mathews and Prof. Lam Yeng Ming, for their continuous support during my PhD candidature and their precious advice and feedback on my research progress.

I also thank Prof. Subodh Mhaisalkar and all the members of the Energy Research Institute (ERI@N) whom I had the opportunity to work with and who contributed to broaden my vision and research perspectives.

A special thank goes to Dr. Annamaria Petrozza and Dr. Javier Marti-Rujas and all the members at the Italian Institute of Technology (IIT-CNST) for their fruitful collaboration.

I sincerely acknowledge Prof. Filippo De Angelis, Prof Jean-Luc Brédas, Dr. Yin Jun, Dr. Edoardo Mosconi and Dr. Daniele Meggiolaro for their precious contribution for the computational methods, as well as Prof. Gagik Gurzadyan and Dr Shu-Zee Alencious Lo for the ultrafast measurements.

I am thankful to the staff of the Interdisciplinary Graduate School (IGS) for their assistance and patience.

I thank all the colleagues and friends who gave me the greatest support in these years, in particular Annalisa Bruno, Ajay S. R. Kandada, Stefanie Neutzner, Chin Xin Yu, Herlina Arianita Dewi, Majid P. Fard, Danang Birowosuto, Teddy Salim, Giorgio Adamo, Lew Kar Cheng, Chaudhary Bhumika, Paola Lova, Zilong Wang, Walter Wong Pei De, and Harish N. S. Krishnamoorthy.

Finally, my deepest recognition goes to my family, especially to my parents, who always gave me indispensable help and support to complete this adventure. The most special and hearted gratitude goes to my wife Lidiane, who shared with me happiness and hurdles of this 4 years journey in Singapore.

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Abbreviations

AEQT	5,5'''-bis(2-aminoethyl)-2,2':5',2'':5'',2'''-quaterthiophene
AFM	Atomic Force Microscopy
API	N-(3-Aminopropyl)imidazole
ATU	2-(aminoethyl)isothiurea
BPOA	4,4'-(1,1'-biphenyl-4,4'-diyldioxy)dianiline
BSE	Bethe-Salpeter Equation
CBM	Conduction Band Minimum
CCD	Charge Coupled Device
CEA	Cyclohexylammonium
CPCM	Conductor-like Polarizable Continuum Model
CRI	Colour Rendering Index
CT	Charge Transfer
DABCO	1,4-diazabicyclo[2.2.2]octane
DFT	Density Functional Theory
DMA	dimethylammonium
DMEN	2-(dimethylamino)ethylamine
DMF	Dimethylformamide
DMSO	Dimethyl Sulfoxide
DSC	Differential Scanning Calorimetry
EBE	Exciton Binding Energy
EDBE	(Ethylenedioxy)bis(ethylammonium)
EDX	Energy Dispersive X-ray Spectroscopy
EPR	Electron Paramagnetic Resonance
FA	Formamidinium
FE-SEM	Field Emission Scanning Electron Microscope
FET	Field Effect Transistor
FWHM	Wull Width at Half Maximum
GGA	General Gradient Approximation

HOMO	Highest Occupied Molecular Orbital
IFA	Iodoformamidinium
IRAV	Infrared Active Vibrations
IRF	Instrument Response Function
ITC	Inverse Temperature Crystallization
LED	Light Emitting Diode
LUMO	Lowest Unoccupied Molecular Orbital
MA	Methylammonium
MOF	Metal-organic Framework
NBT	<i>n</i> -Buthylammonium
N-MEDA	N1-methylethane-1,2-diammonium
N-MPDA	N1-methylpropane-1,3-diammonium
ODA	Octadecylammonium
PAW	Projector-augmented Wave
PBE	Perdew–Burke–Ernzerhof
PDOS	Projected Density of States
PEA	Phenethylammonium
PL	Photoluminescence
PLQY	Photoluminescence Quantum Yield
PMT	Photomultiplier
SAXS	Small-angle X-ray Scattering
SOC	Spin Orbit Coupling
SSC	Second Sphere Coordination
SSL	Solid State Lighting
STEL	Self-trapped Electrons
STH	Self-trapped Holes
TA	Transient Absorption
TCSPC	Time-correlated Single Photon Counting
TMA	Trimethylammonium
TRPL	Time Resolved Photoluminescence

VBM	Valence Band Maximum
WAXS	Wide-angle X-ray Scattering
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
Z	Atomic Number

Chapter 1

Introduction

Two-dimensional hybrid perovskites are rapidly emerging for their exceptional light emitting properties, which makes them very attractive for a wide range of applications. Nevertheless, the achievement of high performing perovskites with properties tunable on demand is conditional to the understanding of the interplay between structural and optoelectronic properties of this class of materials. This chapter highlights the key issues for a fully rational synthetic design of perovskite materials, and provides a rationale for the research contextualizing the goals and scope of this thesis.

1.1 Problem Statement

The establishment of a new technology framework combining high performance and greater energy efficiency, both in terms of energy conversion and consumption, is imperative for the sustainable development of our society.¹⁻

⁴ This need stimulates the research for smarter advanced materials that can be produced at low-cost and implemented in large-area optoelectronic devices.

In this context, organic inorganic hybrid perovskites have received tremendous attention over the latest five years from the scientific community for their unique optoelectronic properties and solution processability. After reshaping the field of photovoltaic reaching power conversion efficiencies above 20%,^{5,6} hybrid perovskites are now emerging for their extraordinary light emitting properties.⁷⁻⁹ Applications such as ultrathin, flexible perovskite light-emitting sources can now be envisioned for the near future, boosted by scalable fabrication processes for the production of large-area devices for lighting, displays and optical diagnostics.

Until now, this field has been dominated by three-dimensional (3D) perovskites, with limited tunability of their structural and optoelectronic properties. On the other hand, the synthetic versatility of this class of semiconductors allows the fabrication of an unlimited variety of self-assembled, low dimensional structures with superior light emitting properties, which just start being explored.^{10,11} Such low-dimensional structures multiply the synthetic possibilities and provide distinctive advantages for light-emitting applications: the increased structural flexibility sustains the incorporation in the perovskite framework of both heavy and light metallic cations in combination with bulkier organic molecules, opening the way for the design of alternative lead-free materials or the incorporation of functional organic cation to improve the emissive properties and the material stability. In certain cases, the unique excitonic characteristics allow modulating the photoluminescence from extremely narrow to ultrabroad and highly Stoke-shifted bandwidth, ultimately

leading to purely white chromaticity from a single emissive material.

Nevertheless, significant advances are required toward the incorporation of functional cations leading to enhanced optical properties of the resulting hybrid material, while avoiding the disruption of the metal-halide perovskite framework. Moreover, the organic cation can be used to template the structural motif of the inorganic scaffold, but the impact of these structural properties on the energetic landscape of the material is only partially understood. For example, the lack of a comprehensive description of the photophysical phenomena underlying photoluminescence broadening in relation to the host perovskite structure has so far hampered a fully rational design of the perovskite emission bandwidth. At this stage, to foster materials design and applications in actual devices, it is urgent to draw a connection between perovskite composition, structural properties and the resulting optoelectronic characteristics. Upon achieving full control over the perovskite unique tunable properties, it is foreseeable that such materials will soon set new benchmarks in solid state lighting, light emitting diodes¹² and transistors,¹³ lasers¹⁴ and scintillators.¹⁵

1.2 Objectives and Scope

The scope of this project is to study the correlation between structural and optical properties of two-dimensional (2D) hybrid perovskites and ultimately establish rational synthetic strategies for the control of the luminescence properties in both lead-based and lead-free perovskites. In these systems, crystal engineering principles allow the incorporation of organic cations within the layered metal-halide framework inducing either a direct or indirect modulation of the luminescence properties. An example of direct modulation consists in the use of optoelectronically active functional cations which confer enhanced optical properties to the final hybrid. On the other hand, the templating properties of the organic cation can be exploited to induced different structural

properties of the metal-halide framework in terms of perovskite orientation and distortions of the octahedral coordination and connectivity, with indirect impact on the optical properties. As it will be discussed in the next chapters, such structural engineering allows to tailor the perovskite bandgap as well as the luminescence from narrow linewidth to ultra-broad, “white” emission throughout the entire visible range.

Figure 1.1 Main topics covered in this thesis.¹⁶⁻¹⁸

In this work, I adopted the aforementioned synthetic strategies to fabricate, *ad hoc*, model perovskite materials with desired compositional, structural and optical properties. Structural characterization techniques were combined with steady state and time-resolved spectroscopy as well as density functional simulations to study the impact of the organic cation on the perovskite’s defectivity, luminescence properties and the trade-off between excitonic and polaronic properties in relation to its structure and composition. Specifically, we intended to develop crystal engineering strategies for the incorporation of active organic cations in lead-free perovskites (Figure 1.1 a), to investigate the origin and mechanism underlying white light emission in 2D perovskites (Figure 1.1 b) and to elucidate the relation between structural distortions and perovskite’s optical properties (Figure 1.1 c). Our findings have advanced synthetic design strategies, modeling and understanding of structure-property relationships of 2D perovskites, which will aid the development of perovskites with

optoelectronic properties tunable on demand, for application in solid-state lighting, lasers and high-energy radiation scintillators.

1.3 Dissertation Overview

The thesis addresses the tuning of luminescence properties of two-dimensional perovskites by structural design and is divided in the following 7 Chapters:

Chapter 1 provides a rationale for the research and outlines the goals and scope.

Chapter 2 reviews the literature concerning the fundamental aspects of synthetic design in hybrid perovskites from 3D to low dimensional structures. The state of the art concepts regarding the excitonic properties of hybrid perovskites are reviewed and the current understanding of photoluminescence broadening (and white light emission) in hybrid perovskites is presented from an historical perspective. The main topics addressed by this thesis are finally contextualized in light of the latest progresses of this research field.

Chapter 3 discusses the rationale behind the choice of methodologies adopted in this research project. The detailed description of experimental and computational procedures as well as details on data analysis are presented.

Chapter 4 presents the study of optoelectronic properties of lead-free, copper based hybrid perovskites. After investigating the characteristic trap induced luminescence in the archetype system $\text{MA}_2\text{CuCl}_x\text{Br}_{4-x}$, we show how crystal engineering strategies can be applied to design a novel perovskite incorporating a functional organic cation and further tune the luminescence properties beyond those of the methylammonium-based system.

Chapter 5 elucidates the mechanism underlying white light emission in two-

dimensional perovskites. The system (EDBE)PbX₄ (where X = Cl, Br) is chosen as model compound and studied by a combination of steady state and time resolved spectroscopy as well as *ab initio* calculations. Our results provide evidence for the ultrafast formation of photoinduced color centers with wide energy distribution. Supported by density functional theory (DFT) simulations, we developed an exciton relaxation model based on the formation of emissive intra-gap polaronic species, localized at specific points of the inorganic lattice, responsible for the observed ultrabroadband, highly Stoke shifted luminescence.

Chapter 6 shows the impact of structural deformation on the perovskite's optical properties. (NBT)₂PbI₄ and (EDBE)PbI₄, characterized by different orientation of the inorganic motif and different degree of octahedral distortion, are used to show that only the latter, with stronger deformations of the inorganic lattice, favours the formation of V_F colour centres leading to broader photoluminescence. On the other hand, we show that the octahedral connectivity (Pb-I-Pb bond angles) strongly affects the perovskite bandgaps and is responsible for the characteristic thermochromism observed in the multidimensional series (NBT)₂(MA)_{n-1}[Pb_nI_{3n+1}].

Chapter 7 concludes the thesis summarizing the main achievements and draws general guidelines for the tailoring of perovskites luminescence properties by structural design. Based on the obtained results, the starting points for future works are discussed, together with preliminary results and future perspectives for the application of two-dimensional perovskites in X-ray scintillators, light emitting field-effect transistors and perovskite-based metamaterials.

1.4 Findings and Outcomes/Originality

This research led to several original outcomes by:

1. Establishing a crystal engineering strategy based on second sphere

coordination interaction to incorporate optoelectronically active organic cations in 2D copper-based perovskites to fabricate functional hybrid materials with improved luminescence and stability.

2. Formulating an exciton relaxation model for broadband emission in hybrid perovskites based on the photoinduced formation of emissive colour centers with wide energy distribution. These involve a zoo of self-localized small polarons such as self-trapped electrons, self-trapped holes and V_F centers.

3. Correlating structural distortions to the optoelectronic properties of the perovskite, stressing the importance of structural engineering to control the exciton self-localization processes and recombination dynamics in layered Pb-based perovskites.

4. Demonstrating the potential of two-dimensional perovskites for applications in low-cost X-ray detectors for medical, security and scientific applications.

References

- [1] International Energy Agency. "World energy outlook 2016". International Energy Agency, Paris, 2016.
- [2] B. Obama. *Science*. **2017**.
- [3] T. F. Stocker *et al.* *Climate Change 2013: The Physical Science Basis: Working Group I Contribution to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*; Cambridge Univ. Press: New York, 2013.
- [4] M. H. Crawford. *IEEE Journal of Selected Topics in Quantum Electronics*. **2009**, 15, 1028.
- [5] X. Li, D. Bi, C. Yi, J.-D. Décoppet, J. Luo, S. M. Zakeeruddin, A. Hagfeldt, M. Grätzel. *Science*. **2016**, 353, 58.

- [6] M. Saliba, T. Matsui, J.-Y. Seo, K. Domanski, J.-P. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt, M. Gratzel. *Energy & Environmental Science*. **2016**, 9, 1989.
- [7] S. A. Veldhuis, P. P. Boix, N. Yantara, M. Li, T. C. Sum, N. Mathews, S. G. Mhaisalkar. *Advanced Materials*. **2016**, 28, 6804.
- [8] S. D. Stranks, H. J. Snaith. *Nat Nanotechnol*. **2015**, 10, 391.
- [9] S. Adjokatse, H.-H. Fang, M. A. Loi. *Materials Today*.
- [10] B. Saparov, D. B. Mitzi. *Chemical Reviews*. **2016**, 116, 4558.
- [11] M. I. Saidaminov, O. F. Mohammed, O. M. Bakr. *ACS Energy Letters*. **2017**, 2, 889.
- [12] H. Cho, S.-H. Jeong, M.-H. Park, Y.-H. Kim, C. Wolf, C.-L. Lee, J. H. Heo, A. Sadhanala, N. Myoung, S. Yoo, S. H. Im, R. H. Friend, T.-W. Lee. *Science*. **2015**, 350, 1222.
- [13] X. Y. Chin, D. Cortecchia, J. Yin, A. Bruno, C. Soci. *Nat Commun*. **2015**, 6, 7383.
- [14] G. Xing, N. Mathews, S. S. Lim, N. Yantara, X. Liu, D. Sabba, M. Grätzel, S. Mhaisalkar, T. C. Sum. *Nat Mater*. **2014**, 13, 476.
- [15] M. D. Birowosuto, D. Cortecchia, W. Drozdowski, K. Brylew, W. Lachmanski, A. Bruno, C. Soci. **2016**, 6, 37254.
- [16] D. Cortecchia, S. Neutzner, A. R. Srimath Kandada, E. Mosconi, D. Meggiolaro, F. De Angelis, C. Soci, A. Petrozza. *Journal of the American Chemical Society*. **2017**, 139, 39.
- [17] D. Cortecchia, C. Soci, M. Cametti, A. Petrozza, J. Martí-Rujas. *ChemPlusChem*. **2017**, 82, 681.
- [18] D. Cortecchia, J. Yin, A. Bruno, S.-Z. A. Lo, G. G. Gurzadyan, S. Mhaisalkar, J.-L. Bredas, C. Soci. *Journal of Materials Chemistry C*. **2017**, 5, 2771.

Chapter 2

Literature Review

This Chapter reviews the crystal engineering principles of hybrid perovskites, presenting the structural evolutions from 3D to low dimensional structures. The tuning of the optoelectronic properties by compositional engineering is discussed, with special emphasis on the role of the organic cation to control the perovskite functional properties. The trade-off between narrowband excitonic emission and white light luminescence in 2D perovskites and their relevance for applications in light emitting devices is finally reviewed on the base of the most recent developments in this field.

2.1 Overview

Driven by their excellent optoelectronic properties and wide synthetic versatility, hybrid metal halide perovskites have been attracting great interest from a broad scientific community. The pioneering works of D. B. Mitzi in '90s (then at IBM Watson Research Centre) established the first milestones for the synthetic design of hybrid perovskites. After a period of stagnation, the field has revived in the last 5 years, pushed by the impressive breakthroughs of perovskites in photovoltaics, reaching power conversion efficiencies beyond 20%,^{1,2} and taking advantage of the unique properties of 3D perovskites,³ which combine solution processability with long charge diffusion length^{4,5} and charge-carrier lifetime,⁶ high absorption coefficient,⁷ low defect density,⁸ high photoluminescence efficiency⁹ and photon recycling.¹⁰ Hybrid perovskites are now rapidly extending to new fields and are making new strides for applications in light emitting devices.^{11,12} For example, from the early electroluminescent diodes operating only at cryogenic temperatures,¹³ perovskite based light emitting devices are now approaching performance of traditional organic semiconductors.¹⁴ Beyond this, interest is rapidly growing for the development of perovskite-based light emitting diodes (LEDs),¹⁵ light emitting transistors (LETs),¹⁶ tunable lasers^{17,18} and scintillators for X-ray detection.^{19,20}

Differently from photovoltaic applications, where the main interest resides in 3D perovskite systems thanks to their better charge transport, photo- and electroluminescent devices allow for a much broader synthetic flexibility, opening immense opportunities for the design and application of low-dimensional perovskites.²¹ Indeed, recent works point to the superior light emitting properties of 2D and low dimensional perovskites.

Having a much broader synthetic tunability, and thanks to their structural properties, low dimensional perovskites offer increased emission tunability, improved photoluminescence quantum yield and stability. Their increased structural tolerance makes possible a wider choice of metal and organic cations,

opening the way to the design of alternative lead-free materials and hybrid structures with functional properties. Moreover, the interplay between excitonic and polaronic effects in relation to the perovskite structure allows, rather uniquely, tuning the luminescence spectra from narrow linewidth to ultra-broad, “white” emission over a wide spectral range.

These properties have renewed the interest for perovskite crystal engineering, making it a key focus of this field. At the same time, the ability of controlling the optoelectronic properties in perovskite systems through rational synthetic design is conditional to the understanding of the photophysical phenomena underlying their emissive properties, which are still partly unknown. The next paragraphs will summarize the main concepts underling hybrid perovskites structural engineering before introducing its close relationship with the materials optoelectronic properties.

2.2 Structural engineering of hybrid perovskites

2.2.1 Crystalline systems of perovskite type

Borrowing the terminology originally used to refer to calcium titanium oxide CaTiO_3 , the basic perovskite structure is indicated with the formula ABX_3 . When $\text{X} = \text{O}_2^-$, the derived materials are known as oxide perovskites, while when $\text{X} = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-$ the family of halide perovskites is originated. In this case, B can be a wide range of divalent cations, typically a group IV element (Ge^{2+} , Sn^{2+} , Pb^{2+}) but also an alkaline earth, transition and rare earth metal (e.g. Ba^{2+} , Sr^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+} , Mn^{2+} , Pd^{2+} , Cd^{2+} , Eu^{2+} , etc.). To maintain the electroneutrality, A must be a monovalent cation, either an alkali metal (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) or an organic cation in the case of hybrid perovskites.

2.2.2 3D perovskites

When the A cation is of suitable size, a 3D perovskite ABX_3 is formed, characterized by a continuous 3D network of corner-sharing octahedra BX_6 (Figure 2.1 a), while the A cations are 12-fold coordinated and occupy the cuboctahedral cavities of the system (Figure 2.1 b).

However, the inorganic scaffold limits the dimension of the A cation that has to enter the cuboctahedral site. If the organic cation is too big, the 3D structure will not be stable. The stability can be predicted combining the so called Goldshmit tolerance factor $t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)}$ and octahedral factor $\mu = \frac{R_B}{R_X}$,^{22,23} where R_A , R_B and R_X indicate the effective ionic radii of the ions A, B and X. Empirically, it is found that the perovskite with cubic symmetry is formed when $0.8 < t < 1$ and $0.442 < \mu < 0.895$, even though slightly distorted structures are also possible.

Figure 2.1 a) Structure of 3D perovskite AMX_3 consisting of a lattice of corner sharing MX_6 octahedra. b) Coordination of A cation in a cuboctahedral cavity.

Taking $APbI_3$ ($\mu = 0.54$) as example, the 3D structure will be stable when $163 \text{ pm} < R_A < 259 \text{ pm}$, and as a consequence, only small organic cations will be allowed; typical examples include methyl ammonium $CH_3NH_3^+$ (MA, 217 pm)

formamidinium $\text{HC}(\text{NH}_2)_2^+$ (FA, 253 pm) and cesium (Cs^+ , 167 pm). These empirical tolerance factors have been used to guide the design of more stable materials and tuning of their optical properties,²⁴⁻²⁶ as well as to predict the stability of novel structures. Using this approach, G. Kieslich et al. combined a set of 13 different ammonium salts, 8 anionic species and 21 divalent metal ions (Fig. 2.2) calculated the hypothetical existence of more than 600 new compounds, including perovskites based on organic anions (e.g. HCOO^- and CN^-).²⁷

Figure 2.2 Calculation approach based on tolerance factors used to predict the stability of new 3D perovskites. Overall, 2352 tolerance factors t were calculated, of which 742 (562 organic anion based, 180 halide based) lie in the range $0.8 < t < 1$.²⁷

2.2.3 From 3D to low dimensional perovskites

When big organic cations are used, steric constraints induce structural rearrangement leading to the formation of crystal lattices where the octahedra

BX_6^{2-} share only partially their corners with their neighbours and the resulting inorganic framework is not continuous along all the 3 dimensions (Figure 2.3).²⁸ The different connectivity of the octahedral network defines the classification of the resulting low-dimensional perovskites: two-dimensional (2D) perovskites are characterized by octahedra connected along two octahedral axes; when the octahedral connectivity is lowered to 1 and 0 the corresponding one-dimensional (1D) and zero-dimensional (0D) perovskites are formed, characterized by infinite metal halide chains or isolated clusters, respectively.

Figure 2.3 Tuning of the perovskite dimensionality through the choice of templating cation: 3D perovskite (e.g. MAPbI_3 , where MA=methylammonium),²⁹ 2D perovskite (e.g. $(\text{PEA})_2\text{PbCl}_4$, where PEA = phenethylammonium),³⁰ 1D perovskite (e.g. $(\text{IFA})_2(\text{FA})\text{SnI}_5$, where IFA = iodoformamidinium and FA = formamidinium),³¹ 0D perovskite (e.g. $(\text{DMA})_2\text{SnCl}_6$, where DMA = dimethylammonium).³²

Low dimensional hybrid perovskites can also be seen as a particular case of metal-organic framework (MOF) built up using a second sphere coordination

approach (SSC), where the organic molecules are linked to the primary coordination sphere of the metal cations.²⁶ The organic cations are usually ammonium salts functionalized with 1 or 2 ammonium moieties which can bind the negatively charged inorganic sheets through coulombic interaction. On the other hand, the organic cations can undergo Van der Waals interactions, π - π staking or hydrogen bonding within nearest neighbours, driving the self-assembly of the hybrid structure.^{33,34}

2.2.4 Structural engineering of 2D perovskites

Figure 2.4 Derivation of differently oriented 2D perovskites from the parental 3D structure: a,b) $\langle 100 \rangle$ -oriented (e.g. $(\text{PEA})_2\text{PbCl}_4$, where PEA = phenethylammonium);³⁰ c,d) $\langle 110 \rangle$ -oriented (e.g. $(\text{API})\text{PbBr}_4$, where API = N-(3-Aminopropyl)imidazole);³⁵ e,f) $\langle 111 \rangle$ -oriented (e.g. $(\text{TMA})_3\text{Sb}_2\text{Cl}_9$, where TMA = trimethylammonium).³⁶

2D perovskites form self-assembled multi-quantum well structures³⁷ where inorganic sheets are stacked in alternation with organic layers and can be conceptually derived by cutting the 3D perovskite ABX_3 along different crystallographic orientations: $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$. This imaginary process is represented in Figure 2.4, where the parental 3D perovskite is shown along

different axis direction (Fig. 2.4 a, c, e) which lead to the corresponding cut of the 2D perovskite. The orientation of the perovskite cut influences deeply the structural properties of the material with strong consequences on the optoelectronic properties.

The $\langle 100 \rangle$ -oriented and $\langle 110 \rangle$ -oriented perovskites share the same general formula C_2BX_4 or $C'BX_4$ (where C and C' are bulky mono- and bi-positive cations). $\langle 100 \rangle$ -oriented perovskites (Figure 2.4 a, b) are characterized by flat inorganic sheets formed by the BX_6 octahedra sharing the 4 corners in equatorial position; in this configuration, the perovskite slabs are always terminated by one corner from each octahedron in apical position. On the other hand, $\langle 110 \rangle$ -oriented perovskites are characterized by a rippled configuration of the inorganic sheets (Figure 2.4 c, d) arranged in such a way that the inorganic slabs are always terminated by two halides from each octahedron, which therefore ends the layer exposing one edge. The $\langle 111 \rangle$ -oriented perovskites are made of octahedra sharing only 3 corners and terminating the inorganic slabs by exposing one face, therefore contributing 3 halides to the terminating surface (Figure 2.4 e, f). Having general formula $C_3B_2X_9$, they differ from the other orientations since they need a trivalent metal to stabilize the structure (e.g. Sb^{3+} , Bi^{3+}).

Figure 2.5 Example of multidimensional perovskite series $(C)_2(A)_{n-1}BX_{3n+1}$ using PEA and MA cations: a) $(PEA)_2PbI_4$,³⁸ $n=1$; b) $(PEA)_2(MA)Pb_2I_7$,³⁸ $n=2$; c) $MAPbI_3$,²⁹ $n=\infty$.

An interesting case is achieved by mixing big and small cations (C and A respectively, as defined above) to create an intergrowth of the 3D and 2D perovskites. The resulting material, sometimes denoted “multidimensional perovskite”, is analogous to the oxide perovskites known as Ruddlesden-Popper phase, and in the most common case of the $\langle 100 \rangle$ -oriented perovskites, bare the general formula $(C)_2(A)_{n-1}B_nX_{3n+1}$. By tuning the stoichiometric ratio between the 2 organic cations and the inorganic precursor, the number of perovskite sheets within the organic layers can be controlled, obtaining perovskites with different n index. For example, in the case of $(PEA)_2(MA)[Pb_2I_7]$, where PEA=phenethylammonium and $n=2$, perovskite bilayers alternate to the phenethylammonium organic layers (Figure 2.5).

2.3 Tuning the optoelectronic properties of hybrid perovskites

The structural flexibility of these materials allows the fine tuning of their optoelectronic properties through different approaches. Compositional design aims at replacing the individual components of the perovskite, either the halide, the metal or the organic cation. In the last case, an optoelectronically active organic cation can be used to add functional properties to the resulting hybrid material. On the other hand, structural design exploits the templating properties of the organic cation to induce specific arrangement or deformations of the inorganic lattice, offering an alternative and powerful way to tune the energetic landscape of the material.

2.3.1 Compositional engineering

Halide substitution is the most straightforward way of tuning the perovskite bandgap to obtain the desired absorption or emissive properties, and has been widely exploited for the optimization of 3D perovskites,^{39,40} such as the case of $FAPbI_yBr_{3-y}$ (FA=formamidinium) shown in Figure 2.6 a.²⁵ In general, the

bandgap will increase with the decrease of halide electronegativity (in the order F, Cl, Br, I)^{41,42} regardless the perovskite dimensionality, so the same trend applies also to 2D perovskites²⁸ such as the series $(C_{12}H_{25}NH_3)_2PbI_{4(1-y)}Br_{4y}$ ($0 < y < 1$) systematically studied by Ahamd et al.⁴³

Figure 2.6 a) Halide substitution for PL and colour tuning in $FAPbI_yBr_{3-y}$;²⁵ b) Bandgap tuning by modification of the Pb/Sn ratio in $MAPb_xSn_{1-x}I_3$;⁴⁴ c) Absorption (black) and photoluminescence (red) spectrum of the Sn-based perovskite $CsSnI_3$;⁴⁵ d) optical properties and crystal structure of the 2D perovskite $NH_3(CH_2)_5NH_3MnCl_4$.⁴⁶

While attention has focused so far on the archetype Pb-based perovskites, the high toxicity of this metal poses serious concerns for the commercialization of these materials and their large-scale production, urging the development of alternative lead-free perovskites.⁴⁷⁻⁴⁹ While replacing lead is sought after for safety and environmental perspectives, metal substitution also strongly affects the nature of the band-to-band electronic transition impacting the overall optoelectronic properties: a typical example is the bandgap redshift in the mixed perovskite $MAPb_xSn_{1-x}I_3$ when increasing the Sn/Pb ratio (Figure 2.6 b)⁴⁴ - $CsSnI_3$ has recently been applied for NIR electroluminescent devices

(absorption and NIR luminescence spectrum in Figure 2.6 c).⁴⁵ Similarly, the 2D perovskite series (NBT)₂MI₄ (NBT = n-butylammonium) shows a strong band-gap redshift when M = Pb→Sn→Ge.⁵⁰ Furthermore, the structural tolerance of 2D perovskites allows the incorporation of a wider number of metals other than those of the IV group, including for example transition metals. This opens the way to an entire series of new compounds whose properties, deeply different from those of the heavy metals-based perovskites, are largely unexplored. An example is given by NH₃(CH₂)₅NH₃MnCl₄, where the ⁴T_{1g}(G) - ⁶A_{1g}(S) transition of Mn²⁺ ions originates its characteristic orange luminescence (Figure 2.6 d).⁴⁶

Figure 2.7 a) Schematic structure of the perovskite combining lead bromide with functionalized polyacetylene;⁵¹ b) Crystal structure of (H₂AEQT)PbBr₄;⁵² c) cross section of the light emitting device using (AEQT)PbCl₄ as emissive layer;⁵³ d) PL (dashed, $\lambda_{\text{exc}}=360\text{nm}$) and electroluminescence (solid) spectra of (AEQT)PbCl₄.⁵³

The incorporation of optoelectronically active organic cations is another way to design new tailor-made smart functional materials, an approach suitable only for low dimensional perovskites that can host bulky organic molecules. 2D perovskites are particularly interesting for this purpose as they can combine in the final hybrid functional material the luminescent properties of the organic molecule with the transport properties of the continuous metal-halide sheets. Even though there is no theoretical limitation to the length of the organic cation, the steric hindrance of the cation often results in the undesired disruption of the metal-halide framework, and only very few attempts have been successful. For example, H. Xu *et al* succeeded in incorporating a functionalized polyacetylene chain within a lead bromide perovskite (Figure 2.7 a), enhancing the polymer photoluminescence quantum yield up to 63%.^{51,54} In a pioneering remarkable work, D. B. Mitzi *et al* designed a lead chloride 2D perovskite incorporating an oligothiophene chromophore (Figure 2.7 b)⁵⁵ and achieved room temperature green electroluminescence (in a light emitting diode) arising from the organic layer (Figure 2.7 c,d).⁵³

2.3.2 Structural distortions vs perovskite band gap

The band structure of the material is significantly affected by the connectivity of the inorganic motif, mainly resulting from the steric hindrance of the templating cation. Considering the simplest case of <100>-oriented 2D perovskites, distortions of the inorganic framework compared to the ideal case can result in in-plane and out-of-plane tilt of the octahedra, defined by the deviation of the B-X-B angle from the ideal geometry (180°) and indicated with θ_{in} and θ_{out} in Figure 2.8 a and b, respectively. Such deviations will generally result in poorer overlap between the metal and halide orbitals and consequent widening of the band gap. For example, Figure 2.8 c shows the trend of the excitonic absorption energy against the Sn-I-Sn bond angle in 2D tin-based

perovskites, and correlate the bandgap increase with the diminution of Sn-I-Sn angles as expected.⁵⁶

Figure 2.8 a) In-plane, θ_{in} and b) out-of-plane, θ_{out} octahedral tilting indicated by the distortion of the B-X-B connecting angle from the ideal geometry (180°); c) calculated band gap versus in-plane (solid) and out-of-plane (dashed) distortions for Sn based 2D perovskites. The filled symbols represent experimental values for real structure with pure in-plane distortion (blue triangles), combined in-plane and out-of-plane (red triangles), alkylammonium-based perovskites (purple circles) and [Me₃NCH₂CH₂NH₃]²⁺-based perovskite (green squares).⁵⁶

Other studies on 2D Pb-based perovskites, namely (C₄H₉NH₃)₂PbBr₄, (C₆H₅CH₂NH₃)₂PbBr₄ and (C₆H₅C₂H₄NH₃)₂PbBr₄, revealed that the luminescence properties are influenced by the distortion of the PbBr₆²⁻ octahedra induced by the specific templating cation. Specifically, it was found that the phenethylammonium containing compound having the lowest value of Br-Pb-Br angle within the octahedral units, also showed the highest photoluminescence quantum efficiency and longest lifetime.⁵⁷ The authors attributed this phenomenon to the reduced mass of the excitons in relation to these structural distortions which led to a decrease in the Bohr radius of the excitons in the perovskite with the highest distortion of the inorganic lattice. Concluding, steric engineering is not exclusive of 2D perovskites, but has been widely exploited to optimize the optical band-gaps of 3D perovskites^{58,59} and,

more broadly, to tune the physical properties of the whole class of oxide perovskites.⁶⁰

2.3.3 Excitonic properties in 2D perovskites

One of the main characteristics of 3D perovskites which determined their success in photovoltaics is the extremely low exciton binding energy (EBE~50 meV)⁶¹ resulting from the high dielectric constant of the perovskite which guarantees a good Coulombic screening: in such conditions, free charges are predominantly generated under photovoltaic operating conditions.⁶² On the other hand, lowering the perovskite dimensionality down to layered systems strongly modifies the energetic landscape of the material. 2D perovskites are formed by a stack of alternating organic and inorganic layers, which behave in a similar way to multi-quantum well inorganic structures, with the advantage of being self-assembled, solution processed materials.

The layered structure induces both electronic and dielectric confinement arising from differences in band-gap and polarizability of inorganic barriers and inorganic quantum wells.⁶³ A typical case is formation of a type I quantum well structure where the bandgap of the organic layer is larger than that of the inorganic wells (Figure 2.9 a).^{34,37} These conditions enormously increase the electron-hole Coulomb interaction (through image charge effect)⁶⁴ largely increasing the exciton binding energy (EBE) up to few hundreds of meV, so that excitonic population becomes predominant compared to free-charges. The confinement can be further tuned by modifying either the dielectric constant of the organic layer,⁶⁵ or by modulating the width of the inorganic layers to form multidimensional perovskites with tunable band-gap and emission.^{66,67}

Figure 2.9 a) Energy level diagram for a type I quantum well structure, where the bandgap of the inorganic layers is narrower than the HOMO-LUMO separation of the organic layers;³⁴ b) absorption (black) and emission (blue) spectrum of $(\text{ODA})_2\text{PbBr}_4$, where ODA=octadecylammonium.⁶⁸

The resulting excitonic properties are particularly evident in lead-based 2D perovskites and drive their characteristic photophysics, typically resulting in sharp excitonic absorption and extremely narrowband photoluminescence characteristic of free-excitonic states (see Figure 2.9 b),^{63,68} concurrently favouring radiative recombination and high photoluminescence quantum yield (PLQY). This is very desirable for light emitting applications. Consequently, 2D perovskites are rapidly emerging for light emitting devices with tunable emission, high brightness and large colour purity.^{13,14,69-71}

2.4 From narrowband to white-light emission

In contrast with the typical free excitonic emission discussed above, an increasing number of low dimensional perovskites with opposite behaviour (ultra-broadband photoluminescence) has recently been shown. This subclass of low dimensional perovskites is characterized by surprisingly highly Stokes-shifted luminescence with full-width at half maximum (FWHM) up to 600 meV, with excellent colour rendering index (CRI) approaching 90 (CRI > 80 are

usually required for a natural colour appearance to the human eye).^{72,73} These characteristics are highly valuable, for example, in solid state lighting (SSL); current techniques to obtain white light are based on phosphore mixtures which, despite the good colour rendering qualities, suffer from low-efficiency due to self-absorption and gradual loss of colour purity due to inhomogeneous degradation of the different components.^{74,75} Therefore, a strategy using a single broadband emissive material would increase stability, colour reproducibility and simplify the fabrication process. At the same time, high Stokes shift and binding energy typical of white light emitting perovskites reduce the probability of self-absorption and exciton thermal quenching, which is useful in applications such as scintillators and lasers.

White light emission in hybrid perovskites was achieved irrespectively of the crystal orientation and with no evident correlation with the chemical composition, and many open questions still remain on the fundamental excitonic physics and multibody interactions in these perovskite low dimensional systems. The development of a unified theory to explain the origin of photoluminescence broadening in perovskites is therefore highly needed to foster a rational synthetic design of new materials with improved properties.

2.4.1 White-light emitting perovskites: a historical perspective

The first examples of broadband emitting perovskites were achieved with the <110>-oriented perovskites (API)PbBr₄³⁵ and (ATU)PbBr₄,⁷⁶ where API = N-(3-aminopropyl)imidazole and ATU = 2-(aminoethyl)isothiourea (Figure 2.10 a, d). Back in 2006, Y. Li *et al* observed for the first time the characteristic emission of (API)PbBr₄, composed of a narrow peak centered at 424 nm and a predominant broadband at 502 nm (Figure 2.10 b). The authors attributed the first to exciton emission, and the latter to luminescence from the organic ligand, proposing a mechanism where photoinduced exciton formation in the perovskite is followed by self-emission and simultaneous energy transfer to the

organic layer, resulting in the broad emission from the lower π^* levels of the organic molecule (Figure 2.10 c).³⁵

Figure 2.10 a) Crystal structure and b) optical properties of (API)PbBr₄,³⁵ c) Energy diagram for the proposed emission mechanism of (API)PbBr₄ involving energy transfer from the exciton level of the inorganic layers to the lowest π^* level of the organic molecule leading to the broadband, Stokes shifted emission;³⁵ d) crystal structure and e) optical properties of (ATU)PbBr₄.⁷⁶

However, this preliminary model teeters to explain broadband emission in perovskites containing optically inert organic cations, like the case of (ATU)PbBr₄ (Figure 2.10 d, e).⁷⁶ In this material, the 2-(aminoethyl)isothioureia ligand forces the inorganic layer in a very contorted geometry, in which one of the bridging angles Pb-Br-Pb (144.23°) highly deviates from the ideal geometry (180°), giving rise to a sharp emission at 402 nm with a broad shoulder extending up to 600 nm. Similar broadband emission was also reported in isostructural layered hybrid materials with formula Cd_{2-x}Zn_xE₂(alkylamine) (E = S, Se, and Te), where it was attributed to distributed trap states at the interface between organic and inorganic layers.⁷⁷⁻⁷⁹

In 2014, Dhoner *et al* used slightly different diammonium organic cations, N-MPDA = N1-methylpropane-1,3-diammonium and N-MEDA = N1-methylethane-1,2-diammonium (the first being one carbon unit longer than the second) to drive the self-assembly of the perovskite into different orientations (Figure 2.11 a): Figure 2.11 b and c show that, while the $\langle 100 \rangle$ -oriented (N-MPDA)PbBr₄ has typical sharp excitonic emission (FWHM = 24 nm), the $\langle 110 \rangle$ -oriented (N-MEDA)PbBr₄ has Stoke-shifted broadband luminescence (FWHM = 165 nm).⁸⁰

Figure 2.11 Crystal structures of the $\langle 100 \rangle$ -oriented perovskite (N-MPDA)[PbBr₄] (left) and $\langle 110 \rangle$ -oriented perovskite (N-MEDA)[PbBr₄] (right).⁸⁰ Absorption and luminescence spectra of b) (N-MPDA)[PbBr₄] and c) (N-MEDA)[PbBr₄].⁸⁰

Even though this experiment seemed to prove that broadband emission is exclusive characteristic of the $\langle 110 \rangle$ -orientation, similar white light luminescence was surprisingly shown also in planar $\langle 100 \rangle$ perovskites in independent works by Dhoner *et al* and Yanguí *et al*, reopening the discussion on the origin of perovskite's broadband emission (Figure 2.12 a, b).^{72,81} In these works, together with proving the broadband luminescence to be an intrinsic

property of the bulk material, the authors related the peculiar emission either to distributed trap states or to the formation of self-trapped excitons.

Figure 2.12 a) Crystal structure and b) luminescence properties of the $\langle 100 \rangle$ -oriented perovskite $(\text{C}_6\text{H}_{11}\text{NH}_3)_2\text{PbBr}_4$,⁸¹ c) Energy diagram for the emission mechanism of $(\text{C}_6\text{H}_{11}\text{NH}_3)_2\text{PbBr}_4$ representing the coexisting free exciton (Ex) and self-trapped exciton (S) originating narrowband and broadband emission, respectively. The formation of S state might follow 3 different pathways: 1-direct relaxation, 2-thermal overcoming of the barrier, and 3-tunneling.⁸¹

The proposed emission mechanism (Figure 2.12 c) involves the conversion of free excitons into self-trapped excitons resulting from either 1) direct relaxation from upper excited states, 2) thermally activated process upon overcoming the elastic deformation of the lattice necessary to allow the charge trapping or 3) tunnelling. While band-to-band recombination gives rise to the sharp excitonic emission, charge-self trapping is responsible for the broadened and Stoke shifted PL.⁸¹ Exciton self-trapping became then the most accredited model after Hu et al further supported it by probing photocarrier dynamics with THz spectroscopy in a $\langle 110 \rangle$ -oriented Pb-Br based 2D perovskite,⁸² and showed

that the ultrafast charge trapping was consistent with the vibrational modes of the Pb-Br lattice.

Nevertheless, comprehensive description of the charge localization sites in relation to the hosting perovskite structure is still lacking, and the reason why self-localization is favoured only in certain perovskites, in competition with sharp free-excitonic emission, remained to be clarified.

2.4.2 Broadband emission beyond 2D perovskites

Recent works have revealed that broadband photoluminescence is not only limited to two-dimensional (2D) perovskites, but more generally is an intrinsic property of hybrid metal halides with common structural characteristics.

Figure 2.13 Crystal structure and broadband luminescence properties of a) α -(DMEN)PbBr₄,⁸³ b) C₄N₂H₁₄PbBr₄,⁸⁴ c) 3D haloplumbate (DABCO)Pb₂Cl₆, where DABCO = 1,4-diazabicyclo[2.2.2]-octane.⁸⁵

For example, similar broadband emission was observed in a 3x3 type of <110>-oriented perovskite α -(DMEN)PbBr₄ (where DMEN=2-(dimethylamino)ethylamine; Figure 2.13 a),⁸³ as well as in perovskites with lower dimensionality like the quasi-1D C₄N₂H₁₄PbBr₄ (Figure 2.13 b)⁸⁴ and the 0D tin-based (C₄N₂H₁₄X)₄SnX₆, X = Br, I.⁸⁶ The same emissive properties with

high colour rendering were also found in 3D haloplumbate frameworks (Figure 2.13 c),⁸⁵ which can be regarded as a highly defective and distorted perovskite framework. Such remarkable synthetic advances reveal a ubiquitous emissive behaviour, irrespective of their crystal orientation and with no apparent correlation to chemical composition. However, in order to develop a fully rational synthetic design strategy, it is crucial to understand the physical processes underpinning photoluminescence broadening in these systems and their relation with the materials structure.

2.5 Challenges and open questions

Differently from photovoltaic devices, where 3D perovskites based on group IV metals largely dominate the field thanks to their ideal band-gap and better charge transport properties, applications based on photoluminescence offer a huge increase in terms of synthetic flexibility, opening the way to the wide family of 2D perovskites which is just starting to be explored. This will open new opportunities as well as challenges for the rational synthetic design towards the development of materials with improved emissive properties, stability and environmental compatibility. In particular, this thesis work has addressed the following:

- How to develop alternative lead-free perovskites and hybrid-functional materials incorporating optoelectronically active organic cations?
- What is the origin of photoluminescence broadening in low-dimensional perovskites? How does the interplay between excitonic and polaronic effects impact the photophysics of hybrid organic-inorganic perovskites?
- What is the correlation between structural deformations and optoelectronic properties of 2D perovskites? Can the materials optical properties be controlled through structural engineering?

References

- [1] M. Saliba, T. Matsui, J.-Y. Seo, K. Domanski, J.-P. Correa-Baena, N. Mohammad K, S. M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt, M. Gratzel. *Energy & Environmental Science*. **2016**.
- [2] N. J. Jeon, J. H. Noh, W. S. Yang, Y. C. Kim, S. Ryu, J. Seo, S. I. Seok. *Nature*. **2015**, 517, 476.
- [3] T. M. Brenner, D. A. Egger, L. Kronik, G. Hodes, D. Cahen. *Nature Reviews Materials*. **2016**, 1, 15007.
- [4] S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza, H. J. Snaith. *Science*. **2013**, 342, 341.
- [5] G. Xing, N. Mathews, S. Sun, S. Lim, Y. Lam, M. Grätzel, S. Mhaisalkar, T. Sum, M. Gratzel. *Science*. **2013**, 342, 344.
- [6] C. Wehrenfennig, G. E. Eperon, M. B. Johnston, H. J. Snaith, L. M. Herz. *Advanced Materials*. **2014**, 26, 1584.
- [7] S. De Wolf, J. Holovsky, S.-J. Moon, P. Löper, B. Niesen, M. Ledinsky, F.-J. Haug, J.-H. Yum, C. Ballif. *The Journal of Physical Chemistry Letters*. **2014**, 5, 1035.
- [8] D. Shi, V. Adinolfi, R. Comin, M. Yuan, E. Alarousu, A. Buin, Y. Chen, S. Hoogland, A. Rothenberger, K. Katsiev, Y. Losovyj, X. Zhang, P. A. Dowben, O. F. Mohammed, E. H. Sargent, O. M. Bakr. *Science*. **2015**, 347, 519.
- [9] F. Deschler, M. Price, S. Pathak, L. E. Klintberg, D.-D. Jarausch, R. Higler, S. Hüttner, T. Leijtens, S. D. Stranks, H. J. Snaith, M. Atatüre, R. T. Phillips, R. H. Friend. *The Journal of Physical Chemistry Letters*. **2014**, 5, 1421.
- [10] L. M. Pazos-Outón, M. Szumilo, R. Lamboll, J. M. Richter, M. Crespo-Quesada, M. Abdi-Jalebi, H. J. Beeson, M. Vrućinić, M. Alsari, H. J. Snaith, B. Ehrler, R. H. Friend, F. Deschler. *Science*. **2016**, 351, 1430.

- [11] S. A. Veldhuis, P. P. Boix, N. Yantara, M. Li, T. C. Sum, N. Mathews, S. G. Mhaisalkar. *Advanced Materials*. **2016**, 28, 6804.
- [12] S. D. Stranks, H. J. Snaith. *Nat Nanotechnol*. **2015**, 10, 391.
- [13] M. Era, S. Morimoto, T. Tsutsui, S. Saito. *Applied Physics Letters*. **1994**, 65, 676.
- [14] M. Yuan, L. N. Quan, R. Comin, G. Walters, R. Sabatini, O. Voznyy, S. Hoogland, Y. Zhao, E. M. Beauregard, P. Kanjanaboos, Z. Lu, D. H. Kim, E. H. Sargent. *Nat Nano*. **2016**, 11, 872.
- [15] H. Cho, S.-H. Jeong, M.-H. Park, Y.-H. Kim, C. Wolf, C.-L. Lee, J. H. Heo, A. Sadhanala, N. Myoung, S. Yoo, S. H. Im, R. H. Friend, T.-W. Lee. *Science*. **2015**, 350, 1222.
- [16] X. Y. Chin, D. Cortecchia, J. Yin, A. Bruno, C. Soci. *Nat Commun*. **2015**, 6, 7383.
- [17] G. Xing, N. Mathews, S. S. Lim, N. Yantara, X. Liu, D. Sabba, M. Grätzel, S. Mhaisalkar, T. C. Sum. *Nat Mater*. **2014**, 13, 476.
- [18] V. D'Innocenzo, A. R. Srimath Kandada, M. De Bastiani, M. Gandini, A. Petrozza. *Journal of the American Chemical Society*. **2014**, 136, 17730.
- [19] H. Wei, Y. Fang, P. Mulligan, W. Chuirazzi, H.-H. Fang, C. Wang, B. R. Ecker, Y. Gao, M. A. Loi, L. Cao, J. Huang. *Nat Photon*. **2016**, advance online publication.
- [20] S. Yakunin, M. Sytnyk, D. Kriegner, S. Shrestha, M. Richter, G. J. Matt, H. Azimi, C. J. Brabec, J. Stangl, M. V. Kovalenko, W. Heiss. *Nat Photon*. **2015**, 9, 444.
- [21] J. Albero, H. Garcia. *Journal of Materials Chemistry C*. **2017**, 5, 4098.
- [22] H.-S. Kim, S. H. Im, N.-G. Park. *The Journal of Physical Chemistry C*. **2014**, 118, 5615.
- [23] C. Li, X. Lu, W. Ding, L. Feng, Y. Gao, Z. Guo. *Acta Crystallographica Section B*. **2008**, 64, 702.
- [24] P. Gao, M. Gratzel, M. K. Nazeeruddin. *Energy & Environmental Science*. **2014**, 7, 2448.

- [25] G. E. Eperon, S. D. Stranks, C. Menelaou, M. B. Johnston, L. M. Herz, H. J. Snaith. *Energy & Environmental Science*. **2014**, 7, 982.
- [26] L. Li, J. Tong, F. Guo, J. Marti-Rujas. *CrystEngComm*. **2016**, 18, 2284.
- [27] G. Kieslich, S. Sun, A. K. Cheetham. *Chemical Science*. **2015**, 6, 3430.
- [28] Z. Cheng, J. Lin. *CrystEngComm*. **2010**, 12, 2646.
- [29] C. C. Stoumpos, C. D. Malliakas, M. G. Kanatzidis. *Inorganic Chemistry*. **2013**, 52, 9019.
- [30] D. B. Mitzi. *Journal of Solid State Chemistry*. **1999**, 145, 694.
- [31] D. B. Mitzi, K. Liang, S. Wang. *Inorganic Chemistry*. **1998**, 37, 321.
- [32] J. Zaleski, A. Pietraszko. *Acta Crystallographica Section B*. **1996**, 52, 287.
- [33] D. B. Mitzi In *Progress in Inorganic Chemistry*; John Wiley & Sons, Inc.: 2007, p 1.
- [34] B. Saparov, D. B. Mitzi. *Chemical Reviews*. **2016**, 116, 4558.
- [35] Y. Y. Li, C. K. Lin, G. L. Zheng, Z. Y. Cheng, H. You, W. D. Wang, J. Lin. *Chemistry of Materials*. **2006**, 18, 3463.
- [36] A. Kallel, J. W. Bats. *Acta Crystallographica Section C*. **1985**, 41, 1022.
- [37] D. B. Mitzi In *Functional Hybrid Materials*; Wiley-VCH Verlag GmbH & Co. KGaA: 2005, p 347.
- [38] J. Calabrese, N. L. Jones, R. L. Harlow, N. Herron, D. L. Thorn, Y. Wang. *Journal of the American Chemical Society*. **1991**, 113, 2328.
- [39] Q. A. Akkerman, V. D’Innocenzo, S. Accornero, A. Scarpellini, A. Petrozza, M. Prato, L. Manna. *Journal of the American Chemical Society*. **2015**, 137, 10276.
- [40] E. L. Unger, L. Kegelmann, K. Suchan, D. Sorell, L. Korte, S. Albrecht. *Journal of Materials Chemistry A*. **2017**.
- [41] E. Mosconi, P. Umari, F. De Angelis. *Physical Chemistry Chemical Physics*. **2016**, 18, 27158.
- [42] I. E. Castelli, J. M. García-Lastra, K. S. Thygesen, K. W. Jacobsen. *APL Materials*. **2014**, 2, 081514.

- [43] S. Ahmad, J. J. Baumberg, G. V. Prakash. *Journal of Applied Physics*. **2013**, *114*, 233511.
- [44] M. T. Klug, A. Osharov, A. A. Haghighirad, S. D. Stranks, P. R. Brown, S. Bai, J. T. W. Wang, X. Dang, V. Bulovic, H. J. Snaith, A. M. Belcher. *Energy & Environmental Science*. **2017**, *10*, 236.
- [45] W. L. Hong, Y. C. Huang, C. Y. Chang, Z. C. Zhang, H. R. Tsai, N. Y. Chang, Y. C. Chao. *Advanced Materials*. **2016**, *28*, 8029.
- [46] X.-H. Lv, W.-Q. Liao, P.-F. Li, Z.-X. Wang, C.-Y. Mao, Y. Zhang. *Journal of Materials Chemistry C*. **2016**, *4*, 1881.
- [47] A. Babayigit, D. Duy Thanh, A. Ethirajan, J. Manca, M. Muller, H.-G. Boyen, B. Conings. *Scientific Reports*. **2016**, *6*, 18721.
- [48] A. Babayigit, A. Ethirajan, M. Muller, B. Conings. *Nat Mater*. **2016**, *15*, 247.
- [49] R. A. Goyer. *Environmental Health Perspectives*. **1993**, *100*, 177.
- [50] D. B. Mitzi. *Chemistry of Materials*. **1996**, *8*, 791.
- [51] H. Xu, J. Sun, A. Qin, J. Hua, Z. Li, Y. Dong, H. Xu, W. Yuan, Y. Ma, M. Wang, B. Z. Tang. *The Journal of Physical Chemistry B*. **2006**, *110*, 21701.
- [52] D. B. Mitzi. *Journal of the Chemical Society, Dalton Transactions*. **2001**, 1.
- [53] K. Chondroudis, D. B. Mitzi. *Chemistry of Materials*. **1999**, *11*, 3028.
- [54] J. Hua, Z. Li, J. W. Y. Lam, H. Xu, J. Sun, DongDong, DongDong, A. Qin, W. Yuan, H. Chen, M. Wang, B. Z. Tang. *Macromolecules*. **2005**, *38*, 8127.
- [55] D. B. Mitzi, K. Chondroudis, C. R. Kagan. *Inorganic Chemistry*. **1999**, *38*, 6246.
- [56] J. L. Knutson, J. D. Martin, D. B. Mitzi. *Inorganic Chemistry*. **2005**, *44*, 4699.

- [57] N. Kawano, M. Koshimizu, Y. Sun, N. Yahaba, Y. Fujimoto, T. Yanagida, K. Asai. *The Journal of Physical Chemistry C*. **2014**, *118*, 9101.
- [58] A. Amat, E. Mosconi, E. Ronca, C. Quarti, P. Umari, M. K. Nazeeruddin, M. Grätzel, F. De Angelis. *Nano Letters*. **2014**, *14*, 3608.
- [59] M. R. Filip, G. E. Eperon, H. J. Snaith, F. Giustino. *Nature Communications*. **2014**, *5*, 5757.
- [60] A. Herklotz, A. T. Wong, T. Meyer, M. D. Biegalski, H. N. Lee, T. Z. Ward. *Scientific Reports*. **2016**, *6*, 26491.
- [61] K. Galkowski, A. Mitioglu, A. Miyata, P. Plochocka, O. Portugall, G. E. Eperon, J. T.-W. Wang, T. Stergiopoulos, S. D. Stranks, H. J. Snaith, R. J. Nicholas. *Energy & Environmental Science*. **2016**, *9*, 962.
- [62] V. D’Innocenzo, G. Grancini, M. J. P. Alcocer, A. R. S. Kandada, S. D. Stranks, M. M. Lee, G. Lanzani, H. J. Snaith, A. Petrozza. *Nature Communications*. **2014**, *5*, 3586.
- [63] T. Kenichiro, T. Takayuki, K. Takashi, U. Kenichi, E. Kazuhiro, U. Tsutomu, A. Keisuke, U. Kazuhito, M. Noboru. *Japanese Journal of Applied Physics*. **2005**, *44*, 5923.
- [64] T. Ishihara In *Optical Properties of Low-Dimensional Materials*, p 288.
- [65] M. D. Smith, L. Pedesseau, M. Kepenekian, I. C. Smith, C. Katan, J. Even, H. I. Karunadasa. *Chemical Science*. **2017**, *8*, 1960.
- [66] C. C. Stoumpos, D. H. Cao, D. J. Clark, J. Young, J. M. Rondinelli, J. I. Jang, J. T. Hupp, M. G. Kanatzidis. *Chemistry of Materials*. **2016**, *28*, 2852.
- [67] Z. Yuan, Y. Shu, Y. Xin, B. Ma. *Chemical Communications*. **2016**, *52*, 3887.
- [68] S. Gonzalez-Carrero, G. M. Espallargas, R. E. Galian, J. Perez-Prieto. *Journal of Materials Chemistry A*. **2015**, *3*, 14039.
- [69] D. N. Congreve, M. C. Weidman, M. Seitz, W. Paritmongkol, N. S. Dahod, W. A. Tisdale. *ACS Photonics*. **2017**, *4*, 476.

- [70] H. Hu, T. Salim, B. Chen, Y. M. Lam. *Scientific Reports*. **2016**, 6, 33546.
- [71] D. Liang, Y. Peng, Y. Fu, M. J. Shearer, J. Zhang, J. Zhai, Y. Zhang, R. J. Hamers, T. L. Andrew, S. Jin. *ACS Nano*. **2016**, 10, 6897.
- [72] E. R. Dohner, A. Jaffe, L. R. Bradshaw, H. I. Karunadasa. *Journal of the American Chemical Society*. **2014**, 136, 13154.
- [73] M. H. Crawford. *IEEE Journal of Selected Topics in Quantum Electronics*. **2009**, 15, 1028.
- [74] S. Pimputkar, J. S. Speck, S. P. DenBaars, S. Nakamura. *Nat Photon*. **2009**, 3, 180.
- [75] E. F. Schubert, J. K. Kim. *Science*. **2005**, 308, 1274.
- [76] Y. Li, G. Zheng, J. Lin. *European Journal of Inorganic Chemistry*. **2008**, 2008, 1689.
- [77] W. Ki, J. Li, G. Eda, M. Chhowalla. *Journal of Materials Chemistry*. **2010**, 20, 10676.
- [78] W. Ki, J. Li. *Journal of the American Chemical Society*. **2008**, 130, 8114.
- [79] M. Roushan, X. Zhang, J. Li. *Angewandte Chemie International Edition*. **2012**, 51, 436.
- [80] E. R. Dohner, E. T. Hoke, H. I. Karunadasa. *Journal of the American Chemical Society*. **2014**, 136, 1718.
- [81] A. Yangui, D. Garrot, J. S. Lauret, A. Lusson, G. Bouchez, E. Deleporte, S. Pillet, E. E. Bendeif, M. Castro, S. Triki, Y. Abid, K. Boukheddaden. *The Journal of Physical Chemistry C*. **2015**, 119, 23638.
- [82] T. Hu, M. D. Smith, E. R. Dohner, M.-J. Sher, X. Wu, M. T. Trinh, A. Fisher, J. Corbett, X. Y. Zhu, H. I. Karunadasa, A. M. Lindenberg. *The Journal of Physical Chemistry Letters*. **2016**, 7, 2258.
- [83] L. Mao, Y. Wu, C. C. Stoumpos, M. R. Wasielewski, M. G. Kanatzidis. *Journal of the American Chemical Society*. **2017**, 139, 5210.
- [84] Z. Yuan, C. Zhou, Y. Tian, Y. Shu, J. Messier, J. C. Wang, L. J. van de Burgt, K. Kountouriotis, Y. Xin, E. Holt, K. Schanze, R. Clark, T. Siegrist, B. Ma. *Nature Communications*. **2017**, 8, 14051.

- [85] G.-E. Wang, G. Xu, M.-S. Wang, L.-Z. Cai, W.-H. Li, G.-C. Guo. *Chemical Science*. **2015**, 6, 7222.
- [86] C. Zhou, Z. Yuan, Y. Tian, H. Lin, R. Clark, B. Chen, L. J. v. d. Burgt, J. C. Wang, K. Hanson, Q. J. Meisner, J. Neu, T. Besara, T. Siegrist, E. Lambers, P. Djurovich, B. Ma. *arXiv:1702.07200*. **2017**.

Chapter 3*

Experimental Methodology

The nature of this project required a highly multidisciplinary approach combining synthetic chemistry, structural characterization techniques, steady state and ultrafast spectroscopy and ab initio simulations. Here we explain the rationale behind the choice of these methodologies to address our research topics. The description of the experimental and computational procedures is provided, together with details on data analysis.

*This section published substantially as reference:

D. Cortecchia, H. A. Dewi, J. Yin, A. Bruno, S. Chen, T. Baikie, P. P. Boix, M. Grätzel, S. Mhaisalkar, C. Soci, N. Mathews. *Inorganic Chemistry*. **2016**, 55, 1044.

D. Cortecchia, C. Soci, M. Cametti, A. Petrozza, J. Martí-Rujas, *ChemPlusChem* **2016**, 81, 1

D. Cortecchia, J. Yin, A. Bruno, S-Z A. Lo, G. Gurzadyan, S. Mhaisalkar, J-L Brédas, C. Soci, *J. Mater. Chem. C* **2017**, 5, 2771

J. Yin, H. Li, D. Cortecchia, C. Soci, J-L Brédas, *ACS Energy Lett.* **2017**, 2 (2), 417

D. Cortecchia, S. Neutzner, A. R. S. Kandada, E. Mosconi, D. Meggiolaro, F. De Angelis, C. Soci, A. Petrozza, *J. Am. Chem. Soc.* **2017**, 139 (1), 39–42

3.1 Rationale for selection

This thesis project aims at the development of rational synthetic design strategies of 2D perovskites for the control of their luminescence properties. This topic required a highly multidisciplinary approach, combining synthetic chemistry with advanced spectroscopic characterization techniques and ab-initio simulations to correlate structural effects and luminescence properties.

The interrelation between structural and compositional effects on the perovskite properties was considered by acting on each component of the perovskite structure: halide substitution (Cl, Br, I), metal substitution (both lead-based and lead-free perovskites) and replacement of organic cation. Among these, the organic cation played a major role in the tuning of the optical properties and was used both as an active component (e.g. optoelectronically active functional cation) and as a passive component. In the latter case, the templating properties of the organic cation were used to induce specific structural motif and deformation of the inorganic metal-halide framework, resulting in both, bandgap tuning and modulation of the excitonic/polaronic effects.

3.1.1 Materials selection for lead-free perovskites

The study of Pb-free materials is strongly motivated by the need of finding non-toxic, environmentally friendly alternatives to the standard lead perovskites. A wide range of compounds is currently under investigation, including bismuth and antimony perovskites like $\text{Rb}_3\text{Sb}_2\text{I}_9$, $\text{Cs}_3\text{Bi}_2\text{I}_9$ and $\text{MA}_3\text{Bi}_2\text{Br}_9$ quantum dots,¹⁻³ halide double perovskites and “vacancy ordered” double perovskites such as $\text{Cs}_2\text{AgBiBr}_6$ and Cs_2SnI_6 ; however, their performances are usually limited by high defect densities which result in very low emission yields.⁴ Driven by the research of lead-free materials for photovoltaics, Sn^{2+} based 3D (e.g. MASnI_3) and related multidimensional perovskites have been intensively studied, reaching power conversion efficiencies up to 9% in solar cells.⁵ Even

though CsSnX_3 quantum dots have been reported to have very low PLQY ($\sim 0.14\%$),⁶ films of CsSnI_3 have been successfully applied for the realization of electroluminescent devices (see section 2.3.1).⁷ Thanks to these achievements, Sn^{2+} stands out as main candidate for lead replacement,⁸ however its tendency to be easily oxidized add serious stability issues,^{9,10} in addition to the fact that, in the same way as lead, also tin presents serious health and environmental concerns.¹¹

Despite few examples reporting the orange photoluminescence of Mn^{2+} perovskites (see section 2.3.1)¹² and its use as dopant in lead based bulk perovskites and quantum dots,¹³ hybrid perovskites of transition metals have been scarcely investigated concerning their optoelectronic properties. Among them, we selected to work on copper because it's an earth abundant material (mainly found in nature as sulfide, oxide or carbonate), environmentally friendly, and its +2 oxidation state is stable in aerobic environment. It is known to easily form halide perovskites, in which the increased covalency from chlorine to bromine allows to tune the materials bandgap across the visible spectral region. Iodine ions reduce Cu^{2+} to Cu^+ , quickly resulting in the formation of CuI , and therefore cannot be taken into account for the perovskite synthesis. The reach coordination chemistry of Cu^{2+} allows to design a wide range of second sphere coordination adducts for the assembling of complex supramolecular architectures (see section 4.3),¹⁴ making it an ideal platform for the development of novel functional hybrid materials. As a general design rule, the Goldshmit tolerance factor t and the octahedral factor μ can be used to predict the structural effect of the organic cation. The simple case of a copper perovskite based on MA^+ and Cl^- results in $t = 1.004$ and $\mu = 0.403$, which are out of the stability range for a 3D perovskite (see section 2.2.2). This consideration indicates that, even with the smallest alkylammonium cation, the formation of low dimensional structures should be expected with Cu^{2+} , differently from the case of Pb^{2+} .

In the first part of the thesis, the structural and electronic properties of the green-emitting archetype 2D perovskite series $\text{MA}_2\text{CuCl}_x\text{Br}_{4-x}$ were studied. Then, a crystal engineering approach was developed for the synthesis of alternative lead-free, copper-based perovskites incorporating a functional organic cation. To achieve this, methylammonium was replaced with the functional cation BPOA to obtain a hybrid material with blue photoluminescence induced by the organic molecule.

3.1.2 Materials selection for lead-based perovskites

In the second part of the thesis, the nature of white-light emission in Pb-based 2D perovskites was studied in relation to their structural properties. As a general guideline, bulkier organic molecules can be expected to induce distortions in the perovskite lattice due to the increased steric hindrance resulting in the appearance of broadband emission, although the templating properties of each cation should be assessed on an individual basis. At the beginning of this project, only a restricted group of broadband layered perovskites was known, characterized by remarkable distortions of the octahedral coordination (see section 3.5): $(\text{API})\text{PbBr}_4$, $(\text{AETU})\text{PbBr}_4$, $(\text{N-MEDA})\text{PbBr}_4$, $(\text{EDBE})\text{PbX}_4$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) $(\text{CEA})_2\text{PbBr}_4$ and $(\text{PEA})_2\text{PbCl}_4$. The choice of the cation is particularly important to induce the desired structural properties. For example, N-(3-aminopropyl)imidazole (API^{2+}) bears one ammonium moiety typical for 3D perovskite stabilization, and a ternary amine in the imidazole unit, whose steric hindrance would obstacle the formation of the layered structure, while $\text{AETU}^{2+} = (\text{aminoethyl})\text{isothioure}$ a combines a primary amine with a formamidine unit and induces strong structural constraints leading to a very contorted geometry. In the corresponding perovskite $(\text{AETU})\text{PbBr}_4$, S-Br bridges cause also a remarkable octahedral tilting leading to strong deviation from the ideal geometry of one of the Pb-Br-Pb bond angles 144.23° . Both the bromide perovskites resulting from these two

cations show $\langle 110 \rangle$ -oriented corrugated structure and broadband emission.^{15,16} Among this group of broadband emitters, we selected EDBE²⁺ as model cation because it allows to study a wide range of perovskite properties in relation to its luminescence, showing broadband emission in all the series of halides from Cl to I. With its unique ethylenedioxy core, it templates the formation of distorted perovskites with different orientations: $\langle 100 \rangle$ -oriented (EDBE)PbCl₄ (with the highest octahedral distortion among the 2D lead halide perovskites) and $\langle 110 \rangle$ -oriented (EDBE)PbBr₄ and (EDBE)PbI₄. Moreover, up to now, (EDBE)PbI₄ is the only iodide 2D lead perovskite with $\langle 110 \rangle$ -orientation to be structurally characterized. In comparison with these broadband emitters, (NBT)₂PbI₄ (NBT = *n*-butylammonium) was chosen as model narrowband emitting perovskite, since its spacing between adjacent inorganic layers is comparable to that of (EDBE)PbI₄.

Starting from (EDBE)PbX₄ with X = Cl, Br, steady state and time resolved spectroscopic techniques were combined with first principles simulations to show evidence for the photogeneration of polaronic species deriving from self-trapping of charge carriers at specific inorganic lattice sites, which create local distortion in the perovskite inorganic framework.

Finally, the role of structural deformations in relation to the photoluminescence broadening was elucidated. By synthesizing two *ad hoc* hybrid perovskites with different structural and optical properties ((NBT)₂PbI₄ and (EDBE)PbI₄, respectively narrowband and broadband emitter), it was shown how charge self-localization and consequent photoluminescence broadening can be controlled through structural engineering of the material by carefully choosing the templating organic cation.

3.2 Chemical synthesis and film fabrication

3.2.1 Materials

The following chemicals were purchased from Sigma-Aldrich: hydrochloric acid (HCl 37 wt % in water), hydrobromic acid (HBr 48% in water), hydriodic acid (HI 57% wt in water, distilled, stabilized), copper(II) chloride (CuCl_2 , 99%), copper(II) bromide (CuBr_2 , 99%), lead(II) chloride (PbCl_2 , 99.999% trace metal basis), lead(II) bromide (PbBr_2 , 99.999% trace metal basis), lead(II) iodide (PbI_2 , 99.0%), 2,20-(Ethylenedioxy)bis(ethylamine)(98%), butylamine 99.5%, 4,4'-(1,1'-biphenyl-4,4'-diyldioxy)dianiline 97%, dimethyl sulfoxide (DMSO, anhydrous 99.9%), dimethylformamide (DMF, anhydrous 99.8%).

The following chemicals were purchased from Tokyo Chemical Industry, TCI: methylamine solution (CH_3NH_2 , 40% in methanol), lead(II) iodide (PbI_2 , 99.99%)

The following chemicals were purchased from Dyesol: n-butylammonium iodide (NBT)I.

3.2.2 Synthesis of organic precursors MAX (X=Cl, Br, I)

Figure 3.1 Reaction scheme: synthesis of MAX from methylamine.

Methylammonium chloride and bromide (MACl and MABr) were synthesized

by mixing 16.7 and 18.0 mL of methylamine solution (CH_3NH_2 , 40% in methanol) with 11.3 mL of hydrochloric acid HCl (37 wt % in water) and 8.0 mL of hydrobromic acid HBr (48% in water), respectively (Figure 3.1). For the synthesis of methylammonium iodide $\text{CH}_3\text{NH}_3\text{I}$, 14ml of hydroiodic acid (57% wt in water) were added dropwise to 10ml of ice-cooled methylamine solution (Figure 3.1). For all the three compounds, the reaction was left under stirring for 2h at room temperature. The powders obtained were purified by crystallization from ethanol and re-precipitation with diethyleter (the washing procedure was repeated 3 times for the chloride and bromide salts, and 6 times for the iodide) until white powders were achieved, and finally dried in vacuum oven (12 h, 60 °C).

3.2.3 Synthesis of the $[\text{H}_2\text{BPOA}]\text{Cl}_2$ salt

White powders of $[\text{H}_2\text{BPOA}]\text{Cl}_2$, where $\text{BPOA} = 4,4'-(1,1'\text{-biphenyl-4,4'-diyldioxy})\text{dianiline}$, were obtained by dissolving BPOA (1g) of L in DMSO (12 ml). Subsequently, 5ml of HCl (37% wt in water) were slowly added to the DMSO solution under vigorous stirring (Figure 3.2).

Figure 3.2 Reaction scheme: synthesis of $[\text{H}_2\text{BPOA}]\text{Cl}_2$

The solution was cooled with ice during the addition. After 12h of reaction, the product was recovered by precipitation with ethanol and washed several times with ethanol. The white powders of the chlorinated salt $[\text{H}_2\text{BPOA}]\text{Cl}_2$ were dried under vacuum and recovered with a yield of 55%. Single crystals were synthesized following two strategies: co-crystals of $[\text{H}_2\text{BPOA}]\text{Cl}_2$ and DMSO

were obtained by dissolving 100 mg of $[\text{H}_2\text{BPOA}]\text{Cl}_2$ in 1ml of DMSO and the solution was exposed to diethyl ether vapours (Figure 3.3 a). On the other hand, water free and solvent free crystals of the chloride salt $[\text{H}_2\text{BPOA}]\text{Cl}_2$ were obtained by dissolving 10mg of BPOA in DMF and exposing the solution to HCl vapours, causing the formation and precipitation of the chloride salt (Figure 3.3 b). In both the cases, crystals of suitable size for X-ray diffraction were achieved after 1 week.

Figure 3.3 Different synthetic strategies for the synthesis of a) $(\text{H}_2\text{BPOA})\text{Cl}_2$ co-crystallized with DMSO; b) water-free and solvent-free $(\text{H}_2\text{BPOA})\text{Cl}_2$ crystals.

3.2.4 Synthesis of the $(\text{EDBE})\text{X}_2$ salt

Figure 3.4 Reaction scheme: synthesis of $[\text{EDBE}]\text{X}_2$.

$(\text{EDBE})\text{Cl}_2$, $(\text{EDBE})\text{Br}_2$ and $(\text{EDBE})\text{I}_2$ were synthesized by dissolving 1ml of (ethylenedioxy)bis(ethylamine) (EDBE) in 10 ml of ethanol and reacting the amine with the corresponding inorganic acid: HCl (1 equivalent), HBr (3 equivalents and HI (6 equivalents) as shown in Figure 3.4. The addition of the acid was performed dropwise while cooling the solution in an ice bath, then the reaction was run for 4h at room temperature. The excess of acid was necessary in the case of bromide and iodide salt to obtain a crystalline, pure product. The

resulting precipitate was washed several times with ethanol/diethyl ether and dried under vacuum at 60 °C.

3.2.5 Synthesis of bis-methylammonium chlorobromocuprates

Figure 3.5 Reaction scheme: synthesis of $\text{MA}_2\text{CuCl}_x\text{Br}_{4-x}$ powders.

MA_2CuCl_4 , $\text{MA}_2\text{CuCl}_2\text{Br}_2$, $\text{MA}_2\text{CuClBr}_3$, and $\text{MA}_2\text{CuCl}_{0.5}\text{Br}_{3.5}$, powders ($\text{MA}=\text{CH}_3\text{NH}_3^+$, methylammonium) were obtained by mixing the organic salts (MACl , MABr) and the inorganic precursors (CuCl_2 , CuBr_2) with the desired stoichiometric ratio (Figure 3.5). An excess of the organic salt (1.2 equivalents) was used to ensure the complete reaction of the inorganic precursor.

In a typical example for the synthesis of $\text{MA}_2\text{CuCl}_{0.5}\text{Br}_{3.5}$, a mixture of MABr and MACl (2.42 g and 0.48 g, respectively) was added to an ethanol solution (100 ml) of CuBr_2 (2.68g) and stirred for 2h at 60 °C. Complete crystallization of the perovskite flakes was achieved after 12h in an ice bath. The precipitate was then collected by filtration, dried under vacuum, and stored under nitrogen for further characterization. MA_2CuBr_4 could not be crystallized from ethanol, and powders were only achieved after complete removal of the solvent, however the pure fully brominated compound could not be isolated.

For film fabrication, 1M DMSO solutions were prepared by dissolving the pre-synthesized perovskite powders. These were spin-coated on glass slides with the ramp 500 rpm, 30 s; 1000 rpm, 30 s; 4000 rpm, 180 s and the film annealed on hot plate at 70 °C for 1 h.

3.2.6 Synthesis of $[\text{H}_2\text{BPOA}][\text{CuCl}_4]$

Figure 3.6 Reaction scheme: synthesis of copper perovskite with functional organic cation $[\text{H}_2\text{BPOA}][\text{CuCl}_4]$.

A solution of DMSO (10 ml) with 4,4'-(1,1'-biphenyl-4,4'-diyldioxy)dianilinium dichloride $[\text{H}_2\text{BPOA}]\text{Cl}_2$ (100 mg) was prepared, and a second solution of CuCl_2 (30.45 mg) in DMSO (2 ml) was added dropwise under stirring at room temperature (Figure 3.6). HCl (2ml, 12M) was then added to the mixture causing the formation of a yellow precipitate. After running the reaction for 12h at room temperature, the yellow powder was recovered with a yield of 74% by washing with ethanol (2x) and diethyl ether (x2), and finally dried under vacuum.

3.2.7 Synthesis of $(\text{EDBE})\text{PbX}_4$ and $(\text{NBT})_2\text{PbI}_4$

Figure 3.7 Reaction scheme: synthesis of the perovskites $(\text{EDBE})\text{PbX}_4$ and $(\text{NBT})_2\text{PbI}_4$ films and single crystals.

Perovskite films were prepared by mixing stoichiometric amounts of (EDBE) X_2 and PbX_2 ($X = Cl, Br, I$) to obtain (EDBE) $PbCl_4$, (EDBE) $PbBr_4$ or (EDBE) PbI_4 as shown in Figure 3.7 a. Similarly, the perovskite (NBT) $2PbI_4$ was prepared by mixing the precursors (NBT)I and PbI_2 (Figure 3.7 b). The powders of the precursors were dissolved in DMSO at 100 °C for 1h to achieve the desired concentration (e.g. 0.1 M, 0.25 M and 0.5 M). In a typical process for the synthesis of 0.5 M solutions of (EDBE) PbI_4 , (EDBE) I_2 (100 mg) and PbI_2 (115 mg) were dissolved in DMSO (500 μ l). Similarly, NBTI (50.3 mg) and PbI_2 (57.6 mg) were dissolved in DMSO (250 μ l) for the preparation of 0.5M solutions of (NBT) $2PbI_4$. The solutions were spin-coated on the substrates at 4000 rpm, 30 s and the films annealed at 100 °C for 30 min.

(EDBE) PbI_4 crystals were synthesized using a vapour diffusion technique (Figure 3.7 a):¹⁷ (EDBE) I_2 (33.5 mg) and PbI_2 (26.5 mg) were dissolved in 3ml of HI water solution. This was left in a sealed bottle under diethyl ether vapours, which caused the precipitation of small yellow crystals by diffusing slowly in the HI solution.

(NBT) $2PbI_4$ crystals were synthesized with a slow cooling technique (Figure 3.7 b):¹⁸ (NBT)I (100.52 mg) and PbI_2 (115.25 mg) were added to hot HI concentrated water solution (1.2 ml) and heated at 100 °C for 5 mins. Cooling at room temperature was performed at the rate 2 °C/h and afterwards the solution was further cooled in refrigerator at 2 °C. Perovskite orange crystals (sheets) were obtained after 1 week.

3.2.8 Synthesis of bulk crystals for scintillation

Inverse temperature crystallization (ITC) was used for the synthesis of the 3D perovskite methylammonium lead bromide ($MAPbBr_3$), exploiting its characteristic retrograde solubility to obtain bulk crystals in only few hours. This was done by mixing at room temperature stoichiometric amounts of $PbBr_2$ and MABr in DMF (1M solution). The resulting solution was then left

overnight on the hotplate at 110 °C, inducing the precipitation of orange crystals.

Methylammonium lead iodide (MAPbI₃) was achieved by slow solvent evaporation of 1M DMF solution of PbI₂ and MAI mixed in stoichiometric amounts.

(EDBE)PbCl₄ bulk crystals were obtained by preparing a concentrate DMSO solution (1M) mixing (EDBE)Cl₂ and PbCl₂ in 1:1 molar ratio until complete solubilisation at 110 °C. The mixture was then left to cool naturally at room temperature slightly opening the vial to allow the slow evaporation of the solvent. White perovskite crystals (cm-scale) formed after a period of 1 month.

In all cases, the reactions were conducted under N₂ inert atmosphere. The crystals were extracted from the solution, gently dried on filter paper, washed with diethyl ether and dried in vacuum overnight to ensure the complete removal of the solvent.

3.3 Characterization techniques

3.3.1 X-Ray diffraction (XRD)

X-Ray powder and thin film diffraction was performed in a BRUKER D8 ADVANCE using Bragg–Brentano geometry, Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$), step increment of 0.02°, and 1 s of acquisition time. In the case of highly moisture sensitive samples (e.g. Cu-based perovskites) an air tight sample holder was used to protect the sample during the measurement. Temperature-dependent powder X-ray diffraction was performed with the SAXS/WAXS system Nano-inXider from Xenocs (power range 50 kV, 0.6 mA) equipped with Linkam HFSX350 temperature stage. The measurement was performed with beam size of 200 μm , flux 4Mph/s, cooling-heating rate of 3° C/min, 1min stabilization time and 5 min exposure time.

Structural determination of new materials was performed with a single-crystal

diffractometer Bruker X8 Prospector APEX-II/CCD provided with a focusing mirror (Cu K α radiation, $\lambda = 1.54056 \text{ \AA}$) and cooling system (Oxford Cryosystems; 700 Series Cryostream Cooler).

TOPAS 3.0¹⁹ was used to analyse the XRD data and perform Pawley fitting of the diffraction patterns using a fundamental parameters approach.²⁰ TCHZ Pseudo-Voigt function and a fifth order Chebichev polynomial were used to fit the peak profiles and the background, respectively. The initial structural parameters used for the series MA₂CuCl_xBr_{4-x} were those reported in the ICSD No. 110687 and ICSD No. 110677 and by Y. Kimishima *et al.*²¹ For (EDBE)PbX₄ and (NBT)₂PbX₄ the data reported by Dhoner *et al*, D. G. Billing *et al* and C. C. Stoumpos *et al* were used as reference structures.^{17,18,22}

The software Diamond 3.2 and Vesta were used to draw the crystal structures.

3.3.2 Composition and morphological characterization

Raman measurements were performed on both single crystals and perovskite films. In the last case, films were deposited on intrinsic silicon to minimize the background from the substrate which tends to overcome the weak signal from the sample. The spectra were acquired with a confocal micro Raman microscope (in Via Raman microscope) in the spectral range 50-2000 cm⁻¹. The measurements were performed in air with 10x objective and $\lambda_{\text{exc}} = 785 \text{ nm}$. X-Ray photoelectron spectroscopy (XPS) measurements were used to study the composition of the sample, verify the stoichiometry and oxidation state of the perovskite's components. The sample was directly transferred from the glovebox to vacuum to avoid degradation due to air exposure. The X-ray source Al K α ($h\nu = 1486.7 \text{ eV}$) and a hemispherical analyzer (EA125, Omicron) were used for data collection.

Differential scanning calorimetry (DSC) was used to probe the perovskites phase transition at low temperature. The instrument Universal V4.5A (TA Instruments) was used with a cooling/heating rate = 10° C/min.

Morphological characterization of films and crystals was performed with atomic force and scanning electron microscopy. Atomic force microscopy (AFM) images were acquired with a scanning probe microscope Digital Instrument Dimension V using tapping mode, to avoid surface damages due to the contact with the scanning tip. The data were edited and plotted with the software WSxM. A Jeol JSM-6700F field emission scanning electron microscope (FE-SEM) with integrated energy dispersive X-ray spectroscopy (EDX) was used for sample imaging.

3.3.3 Steady state optical measurements and data analysis

Samples were generally spin-coated on glass or quartz substrates for optical characterization. Highly moisture sensitive materials were protected with a layer of poly(methyl methacrylate) (PMMA).

Steady state absorption and reflection measurements were done on perovskite films or powders with a UV–vis–NIR spectrophotometer (UV3600, Shimadzu) with scanning resolution of 0.1 nm and equipped with integrating sphere. In case of powder reflectance, the material was encapsulated within two quartz windows to avoid direct contact with the barium sulfate (BaSO_4) of the integrating sphere, which might react with the material and induce degradation. To obtain the molar absorption coefficient of the material, the film thickness was estimated with the surface profiler Alpha-Step IQ.

Steady state photoluminescence spectra were measured with the spectrofluorimeter Fluorolog-3 (Horiba, Jobin Yvon) with 0.5 nm resolution wavelength. Excitation spectra and photoluminescence quantum yield (PLQY) were measured with a NanoLog (Horiba Jobin Yvon) coupled to an integrating sphere.

Power dependent photoluminescence was measured in vacuum using a mode-locked Ti:sapphire oscillator (Coherent Micra) combined with a regenerative amplifier Coherent RegA 900 (50 fs pulses at 800 nm, repetition rate = 250

kHz). A BBO crystal was used for frequency doubling of the pump pulses, which were focused on the sample (500 mm lens) and hitting the sample surface at 45° to allow the frontal collection of the photoluminescence with an Ocean Optics Maya pro 2000 fiber coupled spectrometer. Scattered pump light was filtered out using a long pass filter (450 nm) placed in front of the spectrometer. Relative photoluminescence quantum yield (PLQY) was calculated dividing the integrated PL signal by the pump power.

For the analysis of photoluminescence and absorption spectra, principal component fitting was performed using Voigt functions to take into account multiple broadening mechanisms. In the case of (EDBE)PbX₄ (X=Cl, Br), a Frank-Condon progression was used to fit the vibronic features of the low temperature (78 K) excitonic absorption.^{23,24} In a Frank-Condon progression, the intensities of the vibronic features are coupled to phonons following the relation:

$$[1] \quad I_{0 \rightarrow n} = I_0 \frac{S^n e^{-S}}{n!}$$

Where I_0 = intensity of the transitions, while $I_{0 \rightarrow n}$ is the transition from the 0 vibronic level of the S_0 electronic state to the n^{th} vibronic level in the state S_1 and follows the relation:

$$[2] \quad I_0 = \sum_{n=0}^{\infty} I_{0 \rightarrow n}$$

The S parameter, known as Huang-Rhys factor, is defined as:

$$[3] \quad S = \frac{k(\Delta Q)^2}{2\hbar\omega_p}$$

Here k = spring constant, ω_p = angular frequency of the phonon mode with energy E_p , while ΔQ is the change in coordination coordinate after the transition $S_0 \rightarrow S_1$.

Frank-Condon series of 2 and 10 coupled Voigt profiles (having associated Gaussian and Lorentian curves with width WG and WL) were used for the fitting of the excitonic absorption of (EDBE)PbCl₄ and (EDBE)PbBr₄, respectively. Additional fitting parameters were the energy of 0-0 transition (E_0), the Huang-Rhys factor (S_n) and the phonon energy (E_{pn}). Coupling with 4

phonon modes and 1 phonon mode were used for (EDBE)PbCl₄ and (EDBE)PbBr₄ and the energy of the phonons was set according to the experimental values obtained from Raman spectroscopy: $E_{p1} = 16 \text{ meV}$ (131 cm^{-1}), $E_{p2} = 24 \text{ meV}$ (190 cm^{-1}), $E_{p3} = 49 \text{ meV}$ (400 cm^{-1}), $E_{p4} = 68 \text{ meV}$ (549 cm^{-1}) for (EDBE)PbCl₄; $E_{p1} = 19 \text{ meV}$ (150 cm^{-1}) for (EDBE)PbBr₄. The set of fitting parameters are summarized in Table 3.1.

Table 3.1 Fitting parameters for the Frank-Condon progression used for the excitonic absorption of (EDBE)PbCl₄ and (EDBE)PbBr₄.

	E_0 eV	E_{p1} meV	E_{p2} meV	E_{p3} meV	E_{p4} meV	S1	S2	S3	S4	WL	WG
(EDBE)PbCl ₄	3.678	16	24	49	68	0.018	0.444	1.098	0.165	0.013	0.027
(EDBE)PbBr ₄	3.286	-	-	-	-	2.387	-	-	-	0.016	0.024

3.3.4 Time resolved photoluminescence (TRPL)

Time-correlated single photon counting (TCSPC) technique was used to measure photoluminescence kinetics. The system consisted in a PicoQuant PicoHarp 300 with 10 ps time resolution; the sample was excited with the second harmonic of a Ti:sapphire laser (Chameleon, Coherent Inc.) at 400 nm (100 fs, 80MHz). The components of the photoluminescence decays were obtained by fitting with a deconvolution procedure.

3.3.5 Transient absorption (TA) measurements

A home built pump-probe setup is used for our transient absorption measurement as schematically shown in Figure 3.8.

Figure 3.8 Scheme of transient absorption (TA) home-built setup.

The laser Quantronix Integra-C (repetition rate = 1 KHz; pulse width = 100 fs) was used in the home-built setup. White light continuum generation with a CaF₂ crystal (3 mm thick, moved during the measurement to avoid degradation) was used to obtain broadband white light with highest cut-off at 3.54 eV. Transient absorption spectra were recorded with the spectrometer Jobin Yvon CP140-104 with a silicon photodiode array (Entwicklungsbüro Stresing). A shortwave pass filter (SWP, 1.77 eV) was used to cut the low energy tail of the white light and remove the higher diffraction order artefacts. High energy excitation wavelength (266 nm) was obtained by generation of 400 nm beam with a type I BBO crystal, followed by third harmonic generation (THG) with a second BBO crystal suitable for sum frequency generation combining the 400 nm wavelength with the residue 800 nm. To match the excitation energy with the excitonic absorption of the perovskites, pump beams at wavelength 330 and 370 nm were generated. For this purpose, the output of a Quantronix Palitra working at 660 nm and 740 nm was doubled with a BBO crystal (1 mm thick, cut at 29.21). To overcome artefacts arising from white light stability,

selected spectra at different time delays were obtained for 3000 measurement cycles. Photoluminescence dynamics were obtained for 900 measurement cycles to optimize the measurement time.

3.3.6 X-ray scintillation measurements

A setup combining the X-ray source Inel XRG3500 (Cu-anode tube, 45 kV/10 mA), the monochromator SpectraPro-500i (Acton Research Corporation), photomultiplier Hamamatsu R928 PMT, and liquid helium cooling system APD Cryogenics Inc. was used to measure X-ray luminescence and thermoluminescence of perovskite crystals in the temperature range 350 K-10 K (heating rate 0.14 K/s). Corrections for monochromator transmittance and PMT efficiency were applied to the final spectra.

3.4 Computational methods

3.4.1 $\text{MA}_2\text{CuCl}_x\text{Br}_{4-x}$ band structure and anisotropic effective masses calculation

Experimental crystal structures were used as starting guess, then the structures were relaxed until residual atomic forces were below 0.002 eV/Å (Cu atoms position was fixed during the relaxation). Quantum-Espresso code²⁵ and density functional theory (DFT) were used for band structure calculation, applying the general gradient approximation functional of Perdew–Burke–Ernzerhof²⁶ and describing electron-ion interaction by ultrasoft pseudopotentials.²⁷ Single-particle wave functions (charges) were expanded on a plane-wave basis set up to a kinetic energy cutoff of 50 Ry (300 Ry). K-point mesh 4×4×4 for monoclinic MA_2CuCl_4 and 4×4×2 for the orthorhombic $\text{MA}_2\text{CuCl}_2\text{Br}_2$, $\text{MA}_2\text{CuClBr}_3$ $\text{MA}_2\text{CuCl}_{0.5}\text{Br}_{3.5}$ were used. To take into account the strongly correlated effects on the Cu d states, the DFT+U was adopted (where U = 7.5 eV is the on-site Coulombic parameter).²⁸ Hole/electron effective mass along

the Γ -Z and Γ -Y directions was calculated from the dispersion relation $m^* = \frac{\hbar^2}{\partial^2 E(k)/\partial^2 k}$.

3.4.2 Polaron self-localization and defectivity in (EDBE)PbX₄ (X = Cl, Br, I) and (NBT)₂PbI₄

To simulate the polaron-self localization in (EDBE)PbX₄ (X = Cl, Br) two different approaches were used, the first based on periodic structure calculations and the second on cluster simulation. In the first method, selective perturbations were applied to the crystal structure selectively shortening atomic distances (e.g. X-X, Pb-X and Pb-Pb bond lengths) to mimic the formation of a self-trapped species (molecular polaron) within the periodic crystal. The charge density was then calculated to verify if the applied distortion cause charged localization matching the local distortion, in comparison with the unperturbed, fully delocalised system. In the second method based on cluster structure calculations, a charge is removed or added to the initially neutral perovskite cluster and the calculation is run to check whether the added charges self-localize in the molecular cluster inducing local lattice distortion. This highly computationally demanding method further allowed to estimate the polaron effective radius and binding energy.

Periodic Structure Calculations. Density functional theory (DFT) calculations were performed starting from experimental crystal structures as initial guess,^{17,18} which were relaxed to reach a total force on each atom <0.01 eV/Å and optimized with the PAW method (projector-augmented wave) integrated in VASP code.^{29,30} PBE functional was used to calculate the band structure of the perovskite supercells and the corresponding charge densities,^{31,32} using $6 \times 6 \times 6$ and $6 \times 6 \times 2$ Γ -centred K-meshes in the Brillouin zone for (EDBE)PbCl₄ and (EDBE)PbBr₄ (cut-off energy of plane-wave 500.0 eV). Calculations were performed with and without consideration of spin orbit coupling (SOC).

Cluster Structure Calculations. Gaussian 09 code (v. D.01) was adopted to optimize the perovskite clusters geometries at the hybrid range-corrected functional level CAM-B3LYP. Pb atoms were described with LANL2DZ basis set, while for H, C, N, O, Cl, and Br 6-31G* basis set was used. Dielectric medium ($\epsilon = 78.35$) via the conductor-like polarizable continuum model (CPCM) was applied to take into account the strongly polarizable dielectric nature of the layered perovskite.

Optical Response Calculations. Quantum-Espresso, PBE functional and PWSCF code were used for calculation of the ground-state Kohn–Sham energies,²⁵ describing the electron-ion interaction with Norm-conserving Troullier–Martins pseudopotentials and including SOC and spinor wave functions.³³ Brillouin zone of chloride and bromide perovskite was described with $4 \times 4 \times 4$ and $4 \times 4 \times 2$ Monkhorst–Pack grids (planewave cut-off and electronic density expansion was set at 80 Ry and 480 Ry for (EDBE)PbX₄ (X=Cl, Br) and 25 Ry and 200 Ry in the case of (EDBE)PbI₄ and (NBT)₂PbI₄). YAMBO code³⁴ and BSE were used to calculate the optical transitions:

$$(E_{ck} - E_{vk})A_{vck}^S + \sum_{k'v'c'} \langle vck | K_{eh} | v'c'k' \rangle A_{v'c'k'}^S = \Omega^S A_{vck}^S$$

E_{ck} , E_{vk} represent the quasiparticle energies of the conduction and valence states while A_{vck}^S and Ω^S are the exciton's expansion coefficients and eigenenergies. The optical response imaginary part ϵ_1 was calculated according to the formula:

$$\epsilon_1(\omega) \propto \sum_S \left| \sum_{cvk} A_{vck}^S \frac{\langle ck | p_i | vk \rangle}{\epsilon_{ck} - \epsilon_{vk}} \right| \delta(\Omega^S - \hbar\omega - \Gamma)$$

considering the dipole matrix elements $\langle ck | p_i | vk \rangle$ for valence to conduction band electronic transitions. The absorption coefficients α are:

$$\alpha = 2\omega \left[\frac{(\epsilon_1^2(\omega) + \epsilon_2^2(\omega))^{1/2} - \epsilon_1(\omega)}{2} \right]^{1/2}$$

3.5 Analysis of structural distortions in two-dimensional perovskites

Different parameters were considered to evaluate the structural distortions of the perovskite structure in relation to the PbX_6 octahedra, building block of the inorganic framework. The software VESTA was used to calculate structural and distortion parameters of a series of broadband and narrowband perovskites reported in literature (Figure 3.9, Table 3.2 and 3.3): $(\text{API})\text{PbBr}_4$,¹⁶ $(\text{AETU})\text{PbBr}_4$,¹⁵ $(\text{N-MEDA})\text{PbBr}_4$,³⁵ $(\text{EDBE})\text{PbBr}_4$,¹⁷ $(\text{EDBE})\text{PbI}_4$,¹⁷ $(\text{EDBE})\text{PbCl}_4$,¹⁷ $(\text{CEA})_2\text{PbBr}_4$,³⁶ $(\text{NBT})_2\text{PbI}_4$,¹⁸ $(\text{NMPDA})\text{PbBr}_4$,³⁵ $(\text{PEA})_2\text{PbCl}_4$,³⁷ $(\text{PEA})_2\text{PbBr}_4$,³⁷ $(\text{MA})\text{PbBr}_3$,³⁸ $(\text{MA})\text{PbI}_3$.³⁹

Quantitative measurement octahedral distortion of the PbX_6 units was evaluated based on the following parameters:

- Bond-length distortion⁴⁰: $\Delta_{oct} = \frac{1}{6} \sum_{i=1}^6 [(d_i - d_m)/d_m]^2$
- Octahedral elongation^{41,42}: $\lambda_{oct} = \frac{1}{6} \sum_{i=1}^6 (d_i/d_0)^2$

where d_i = Pb-X bond length, d_m = average bond length and d_0 = center-to-vertex distance of a regular polyhedron of the same volume.

- Halide Distance Deviation⁴⁰:

$$DI(X-X) = \left[\sum_{i=1}^{12} |(X-X)_i - (X-X)_m| \right] / 12 * (X-X)_m$$

where $(X-X)_i$ represents the distance between neighbour halides (matching with the edge length of the PbX_6 octahedra), and $(X-X)_m$ is the average halide distance.

- Octahedral angle variance⁴⁰⁻⁴³: $\sigma_{oct}^2 = \frac{1}{11} \sum_{i=1}^{12} (\alpha_i - 90)^2$

where α_i = X-Pb-X angle.

- Volume discrepancy⁴⁴: $v(\%) = (V_m - V_r) * 100/V_m$

This parameter indicates how regularly the halides are distributed regardless the position of the central Pb atom. In this equation, the volume of the real (distorted) PbX_6 octahedra is represented by V_r , while V_m indicates the volume of the corresponding regular octahedron with edges length $(X-X)_m$.

The results of the structural analysis are reported in Figure 3.9 and Table 3.2 and 3.3. In particular, it was observed that increased octahedral distortion (measured according to the parameters λ_{oct} and σ_{oct}^2 , introduced by K. Robinson et al for the analysis of polyhedral distortion in various mineral groups)⁴¹ well correlates with the observation of broadband emission in 2D perovskites.

Figure 3.9 Octahedral distortion analysis (λ_{oct} vs σ_{oct}^2) in hybrid perovskites. The different colours indicate respectively: red = iodide-based, green = bromide-based and blue = chloride-based perovskites. The marker filling represents the emissive properties of the perovskite: solid interior = narrowband, open interior = broadband emitters.⁴⁵

Table 3.2 Distortion parameters calculated for broadband emitting hybrid perovskites.⁴⁵

Organic Cation	Name and Abbreviation	Perovskite Formula	Perovskite Type and Orientation	DI(X-X)	$\Delta_{\text{oct}} \times 10^3$	v(%)	λ_{oct}	σ_{oct}^2	Ref
	N-(3-aminopropyl)-imidazole [API]	(API)PbBr ₄	2D - <110>	0.029	2.60	0.67	1.0088	20.8	16
	2-(aminoethyl)-isothiourea [AETU]	(AETU)PbBr ₄	2D - <110>	0.047	0.97	1.59	1.0123	38.9	15
	N1-methylethane-1,2-diammonium [N-MEDA]	(N-MEDA)-PbBr ₄	2D - <110>	0.040	0.82	0.79	1.0080	24.5	35
	2,2'-(ethylene-dioxy)bis(ethylammonium) [EDBE]	(EDBE)PbBr ₄	2D - <110>	0.044	2.40	0.96	1.0090	23.9	17
		(EDBE)PbI ₄	2D - <110>	0.030	1.90	0.50	1.0058	14.2	17
		(EDBE)PbCl ₄	2D - <100>	0.088	0.056	13.02	1.0824	264.2	17
	Cyclohexylammonium [CEA]	(CEA) ₂ PbBr ₄	2D - <100>	0.051	0.6	0.47	1.0103	33.5	36
	Phenethylammonium [PEA]	(PEA) ₂ PbCl ₄	2D - <100>	0.026	0.781	0.20	1.0060	18.7	37

Table 3.3 Distortion parameters calculated for narrowband emitting hybrid perovskites.⁴⁵

Organic Cation	Name and Abbreviation	Perovskite Formula	Perovskite Type and Orientation	DI(X-X)	$\Delta_{\text{oct}} \times 10^3$	v(%)	λ_{oct}	σ_{oct}^2	Ref
	n-butylammonium [BA]	(NBT) ₂ PbI ₄	2D - <100>	0.017	0.011	0.18	1.0016	5.6	18
	N1-methylpropane-1,3-diammonium [N-MPDA]	(NMPDA)-PbBr ₄	2D - <100>	0.014	0.050	0.13	1.0009	3.0	35
	Phenethylammonium [PEA]	(PEA) ₂ PbBr ₄	2D - <100>	0.020	0.989	0.19	1.0056	16.5	37
	methylammonium [MA]	(MA)PbBr ₃	3D - <100>	0.000	0.000	0.00	1.0000	0.00	38
		(MA)PbI ₃	3D - <100>	0.005	0.0005	0.04	1.0001	0.03	39

References

- [1] P. C. Harikesh, H. K. Mulmudi, B. Ghosh, T. W. Goh, Y. T. Teng, K. Thirumal, M. Lockrey, K. Weber, T. M. Koh, S. Li, S. Mhaisalkar, N. Mathews. *Chemistry of Materials*. **2016**, 28, 7496.

- [2] M. Leng, Z. Chen, Y. Yang, Z. Li, K. Zeng, K. Li, G. Niu, Y. He, Q. Zhou, J. Tang. *Angewandte Chemie International Edition*. **2016**, 55, 15012.
- [3] B. Yang, J. Chen, F. Hong, X. Mao, K. Zheng, S. Yang, Y. Li, T. Pullerits, W. Deng, K. Han. *Angewandte Chemie*. **2017**, 129, 12645.
- [4] F. Giustino, H. J. Snaith. *ACS Energy Letters*. **2016**, 1, 1233.
- [5] S. Shao, J. Liu, G. Portale, H.-H. Fang, G. R. Blake, G. H. ten Brink, L. J. A. Koster, M. A. Loi. *Advanced Energy Materials*. 1702019.
- [6] T. C. Jellicoe, J. M. Richter, H. F. J. Glass, M. Tabachnyk, R. Brady, S. E. Dutton, A. Rao, R. H. Friend, D. Credgington, N. C. Greenham, M. L. Böhm. *Journal of the American Chemical Society*. **2016**, 138, 2941.
- [7] W. L. Hong, Y. C. Huang, C. Y. Chang, Z. C. Zhang, H. R. Tsai, N. Y. Chang, Y. C. Chao. *Advanced Materials*. **2016**, 28, 8029.
- [8] W.-L. Hong, Y.-C. Huang, C.-Y. Chang, Z.-C. Zhang, H.-R. Tsai, N.-Y. Chang, Y.-C. Chao. *Advanced Materials*. **2016**, 28, 8029.
- [9] N. K. Noel, S. D. Stranks, A. Abate, C. Wehrenfennig, S. Guarnera, A.-A. Haghighirad, A. Sadhanala, G. E. Eperon, S. K. Pathak, M. B. Johnston, A. Petrozza, L. M. Herz, H. J. Snaith. *Energy & Environmental Science*. **2014**.
- [10] M. H. Kumar, S. Dharani, W. L. Leong, P. P. Boix, R. R. Prabhakar, T. Baikie, C. Shi, H. Ding, R. Ramesh, M. Asta, M. Graetzel, S. G. Mhaisalkar, N. Mathews. *Advanced Materials*. **2014**, 1.
- [11] A. Babayigit, A. Ethirajan, M. Muller, B. Conings. *Nat Mater*. **2016**, 15, 247.
- [12] X.-H. Lv, W.-Q. Liao, P.-F. Li, Z.-X. Wang, C.-Y. Mao, Y. Zhang. *Journal of Materials Chemistry C*. **2016**, 4, 1881.
- [13] K. Xu, C. C. Lin, X. Xie, A. Meijerink. *Chemistry of Materials*. **2017**, 29, 4265.
- [14] In *Chemistry of the Elements (Second Edition)*; Butterworth-Heinemann: Oxford, 1997, p 1173.

- [15] Y. Li, G. Zheng, J. Lin. *European Journal of Inorganic Chemistry*. **2008**, 2008, 1689.
- [16] Y. Y. Li, C. K. Lin, G. L. Zheng, Z. Y. Cheng, H. You, W. D. Wang, J. Lin. *Chemistry of Materials*. **2006**, 18, 3463.
- [17] E. R. Dohner, A. Jaffe, L. R. Bradshaw, H. I. Karunadasa. *Journal of the American Chemical Society*. **2014**, 136, 13154.
- [18] D. G. Billing, A. Lemmerer. *Acta Crystallographica Section B*. **2007**, 63, 735.
- [19] Bruker; Bruker AXS Inc.: Madison, Wisconsin, USA, 2008.
- [20] R. W. Cheary, A. Coelho. *Journal of Applied Crystallography*. **1992**, 25, 109.
- [21] Y. Kimishima. *Journal of the Physical Society of Japan*. **1980**, 49, 62.
- [22] C. C. Stoumpos, D. H. Cao, D. J. Clark, J. Young, J. M. Rondinelli, J. I. Jang, J. T. Hupp, M. G. Kanatzidis. *Chemistry of Materials*. **2016**, 28, 2852.
- [23] P. J. Brown, D. S. Thomas, A. Köhler, J. S. Wilson, J.-S. Kim, C. M. Ramsdale, H. Sirringhaus, R. H. Friend. *Physical Review B*. **2003**, 67, 064203.
- [24] M. Pope, C. E. Swenberg *et al.* *Electronic Processes in Organic Crystals*; Clarendon Press, 1982.
- [25] G. Paolo, B. Stefano, B. Nicola, C. Matteo, C. Roberto, C. Carlo, C. Davide, L. C. Guido, C. Matteo, D. Ismaila, C. Andrea Dal, G. Stefano de, F. Stefano, F. Guido, G. Ralph, G. Uwe, G. Christos, K. Anton, L. Michele, M.-S. Layla, M. Nicola, M. Francesco, M. Riccardo, P. Stefano, P. Alfredo, P. Lorenzo, S. Carlo, S. Sandro, S. Gabriele, P. S. Ari, S. Alexander, U. Paolo, M. W. Renata. *Journal of Physics: Condensed Matter*. **2009**, 21, 395502.
- [26] J. P. Perdew, K. Burke, M. Ernzerhof. *Physical Review Letters*. **1996**, 77, 3865.

- [27] K. F. Garrity, J. W. Bennett, K. M. Rabe, D. Vanderbilt. *Computational Materials Science*. **2014**, 81, 446.
- [28] S. L. Dudarev, G. A. Botton, A. P. Sutton. *ELECTRON MICROSCOPY*. **1998**, 3, 613.
- [29] G. Kresse, J. Furthmüller. *Computational Materials Science*. **1996**, 6, 15.
- [30] G. Kresse, D. Joubert. *Physical Review B*. **1999**, 59, 1758.
- [31] J. Heyd, G. E. Scuseria, M. Ernzerhof. *The Journal of Chemical Physics*. **2003**, 118, 8207.
- [32] J. Paier, R. Hirschl, M. Marsman, G. Kresse. *The Journal of Chemical Physics*. **2005**, 122, 234102.
- [33] B. F. Minaev, Z. M. Muldakhmetov. *Opt. Spektrosk.* **1984**, 56, 48–52.
- [34] A. Marini, C. Hogan, M. Grüning, D. Varsano. *Computer Physics Communications*. **2009**, 180, 1392.
- [35] E. R. Dohner, E. T. Hoke, H. I. Karunadasa. *Journal of the American Chemical Society*. **2014**, 136, 1718.
- [36] A. Yangui, D. Garrot, J. S. Lauret, A. Lusson, G. Bouchez, E. Deleporte, S. Pillet, E. E. Bendeif, M. Castro, S. Triki, Y. Abid, K. Boukheddaden. *The Journal of Physical Chemistry C*. **2015**, 119, 23638.
- [37] D. B. Mitzi. *Journal of Solid State Chemistry*. **1999**, 145, 694.
- [38] A. Jaffe, Y. Lin, C. M. Beavers, J. Voss, W. L. Mao, H. I. Karunadasa. *ACS Central Science*. **2016**, 2, 201.
- [39] C. C. Stoumpos, C. D. Malliakas, M. G. Kanatzidis. *Inorganic Chemistry*. **2013**, 52, 9019.
- [40] A. Ertl, J. M. Hughes, F. Pertlik, F. F. F. Jr., S. E. Wright, F. Brandstatter, B. Marler. *Can Mineral*. **2002**, 40, 153.
- [41] K. Robinson, G. V. Gibbs, P. H. Ribbe. *Science*. **1971**, 172, 567.
- [42] N. Thomas. *Acta Crystallographica Section B*. **1989**, 45, 337.
- [43] M. E. Fleet. *Mineralogical Magazine*. **1976**, 40, 531.
- [44] E. Makovicky, T. Balic-Zunic. *Acta Crystallographica Section B*. **1998**, 54, 766.

- [45] D. Cortecchia, S. Neutzner, A. R. Srimath Kandada, E. Mosconi, D. Meggiolaro, F. De Angelis, C. Soci, A. Petrozza. *Journal of the American Chemical Society*. **2017**, 139, 39.

Chapter 4*

Controlling luminescence properties in hybrid copper perovskites: crystal engineering with a functional organic cation

Crystal engineering principles based on second sphere coordination approach are applied to design a novel hybrid copper perovskite incorporating a functional organic cation and to tune the luminescence properties beyond the trap-induced green luminescence characteristic of the archetype system $MA_2CuCl_xBr_{4-x}$. The chosen organic cation confers UV-blue photoluminescence and improves moisture stability to the final hybrid, making this system an ideal platform to achieve optical properties on demand by synthetic design.

*This section published substantially as reference:

D. Cortecchia, H. A. Dewi, J. Yin, A. Bruno, S. Chen, T. Baikie, P. P. Boix, M. Grätzel, S. Mhaisalkar, C. Soci, N. Mathews. *Inorganic Chemistry*. **2016**, 55, 1044.

D. Cortecchia, C. Soci, M. Cametti, A. Petrozza, J. Martí-Rujas, *ChemPlusChem* **2016**, 81, 1

4.1 Introduction

In the last years, lead based perovskites have emerged for their light emitting properties,¹ leading to impressive breakthroughs in different applications such as light emitting diodes,² field-effect light emitting transistors³ and lasers.⁴ Despite these advances, the toxicity and bioaccumulation issues of lead raise serious concerns for the practical application of this materials, possibly hindering their future commercialization.^{5,6} For these considerations, the study and development of alternative lead-free perovskites is strongly sought after.⁷ Tin has attracted attention as main candidate for lead replacement,⁸ but the easy tendency to oxidation makes difficult to obtain stable devices.^{9,10} Moreover, recent studies showed similar detrimental effects on environment and health.⁵ On the other hand, transition metals might offer great environmentally friendly opportunities for tuning the optoelectronic properties of the material. In particular, copper perovskites have been studied for their ferromagnetic properties¹¹ and lithium cycling materials in electrodes.¹² However, their optoelectronic and luminescence properties are largely unexplored.

In this work, the fundamental optoelectronic properties of the layered series $\text{MA}_2\text{CuCl}_x\text{Br}_{4-x}$ and its characteristic trap-induced green luminescence were firstly investigated. Then, crystal engineering principles based on second sphere coordination approach were applied to design a novel hybrid copper perovskite incorporating a functional organic cation and to further tune the luminescence properties. The chosen organic cation, namely 4,4'-(1,1'-biphenyl-4,4'-diyl)di-aniline, confers UV-blue photoluminescence and improved moisture stability to the final hybrid and makes this system an ideal platform to achieve optical properties on demand by synthetic design.

4.2 Optoelectronic properties of $\text{MA}_2\text{CuCl}_x\text{Br}_{4-x}$

4.2.1 Powder synthesis

Powders of the copper perovskite series $\text{MA}_2\text{CuCl}_x\text{Br}_{4-x}$ were synthesized from ethanol solutions by changing the Br/Cl ratio, and corresponding powder X-ray diffractograms are shown in Figure 4.1a.

Figure 4.1 a) Powder XRD of $\text{MA}_2\text{CuCl}_x\text{Br}_{4-x}$; b) layered perovskite structure of $\text{MA}_2\text{CuCl}_2\text{Br}_2$ (structural data from ICSD #110677);¹³ c) preferential orientation of perovskite thin films: $\text{MA}_2\text{CuCl}_2\text{Br}_2$ (upper panel) and $\text{MA}_2\text{CuCl}_{0.5}\text{Br}_{3.5}$ (lower panel).

Table 4.1 Crystal structure and lattice parameters of Cu-based perovskites. $R_B = \sum_{hkl} |I_{hkl}(\text{obs}) - I_{hkl}(\text{calc})| / \sum_{hkl} |I_{hkl}(\text{obs})|$ where $I_{hkl} = mF_{hkl}^2$, (m = multiplicity).

Formula	Crystal System	Space Group	a [Å]	b [Å]	c [Å]	β [°]	R_B
MA_2CuCl_4	monoclinic	P121/a1	7.2574(8)	7.3504(1)	9.9688(5)	111.20	0.025
$\text{MA}_2\text{CuCl}_2\text{Br}_2$	orthorhombic	Acam	7.3194(4)	7.3281(4)	19.1344(1)	90	0.021
$\text{MA}_2\text{CuClBr}_3$	orthorhombic	Acam	7.3965(1)	7.3686(2)	19.3217(1)	90	0.013
$\text{MA}_2\text{CuCl}_{0.5}\text{Br}_{3.5}$	orthorhombic	Acam	7.4276(2)	7.4686(8)	19.3075(9)	90	0.016

We found that the addition of chlorine was essential to improve the crystallization as well as the material's stability against moisture absorption; while the fully brominated compound was highly deliquescent and it was not possible to crystallize it in a pure form from solution (see Appendix A, Figure A.1); therefore, we focused the analysis on the Cl-containing compounds of the series. Indeed, the addition of chlorine (even in small amounts) provided easier crystallization of the mixed halide product. Pawley fitting was performed on the X-ray powder diffraction patterns of MA_2CuCl_4 , $\text{MA}_2\text{CuCl}_2\text{Br}_2$, $\text{MA}_2\text{CuClBr}_3$ and $\text{MA}_2\text{CuCl}_{0.5}\text{Br}_{3.5}$ using the previously reported structural data for MA_2CuCl_4 and $\text{MA}_2\text{CuCl}_2\text{Br}_2$,^{13,14} and confirmed the high quality of the product. The long-range symmetry along the c-axis (in agreement with the extracted lattice parameters, Table 4.1) are consistent with the formation of a layered perovskite in good match with the reported structures for MA_2CuCl_4 and $\text{MA}_2\text{CuCl}_2\text{Br}_2$.^{13,14} While the fully chlorinated material crystallizes with monoclinic crystal system, the mixed halide perovskites adopted an orthorhombic structure, in which the gradual replacement of Cl with Br is responsible for the observed shift of the diffraction peaks at lower angles (Appendix A, Figure A.2), following the unit cell increase due to the bigger size of Br^- (196 pm) compared to Cl^- (181 pm). For example, $\text{MA}_2\text{CuCl}_2\text{Br}_2$ shows a layered structure in which inorganic layers are separated by 10 Å of methylammonium bilayers (Figure 4.1 b) and is characterized by a strong Jahn-

Teller distortion of the Cu^{2+} octahedral coordination (inset in Figure 4.1 b), where the bond length is 2.272(1) Å for two of the equatorial bonds (green), 2.921(3) Å for the elongated equatorial bonds (pink), and 2.436(2) Å for the terminal bonds (blue). The synthesized powders were dissolved in dimethylsulfoxide (DMSO) and spin coated on glass to perform optical characterization. Compared to the powders diffraction patterns, the corresponding thin films show enhanced 002 reflection, indicating an overall strong preferential orientation toward the 00*l* direction, with the perovskite layers aligned parallel to the substrate (Figure 4.1 c).

4.2.2 Band-gap tuning of $\text{MA}_2\text{CuCl}_x\text{Br}_{4-x}$

Figure 4.2 a) Absorption spectra and b) colour tuning of the series $\text{MA}_2\text{CuCl}_x\text{Br}_{4-x}$.

The absorption spectra show the typical features of CuX_4^{2-} square planar complexes (Figure 4.2 a), in agreement with the strong Jahn-Teller distortion observed in XRD.¹⁵⁻¹⁷ Strong bands with absorption coefficient up to 35000 cm^{-1} are present below 650 nm, with band-edge strongly dependent on the Br/Cl ratio: increasing the bromine content, the bandgap redshifts in the order 2.48 eV (500 nm) for MA_2CuCl_4 , 2.12 eV (584 nm) for $\text{MA}_2\text{CuCl}_2\text{Br}_2$, 1.90 eV (625 nm)

for $\text{MA}_2\text{CuClBr}_3$, and 1.80 eV (689 nm) for $\text{MA}_2\text{CuCl}_{0.5}\text{Br}_{3.5}$; correspondingly, the perovskite colour gradually changed from yellow to dark-brown (Figure 4.2 b). The same trend is also predicted by density functional theory calculations including Coulomb interactions (DFT + U), with calculated bandgap energies of 3.09 eV (MA_2CuCl_4), 3.00 eV ($\text{MA}_2\text{CuCl}_2\text{Br}_2$), 2.88 eV ($\text{MA}_2\text{CuClBr}_3$), and 2.86 eV ($\text{MA}_2\text{CuCl}_{0.5}\text{Br}_{3.5}$).

Figure 4.3 a) Schematic representation of electronic transitions in $\text{MA}_2\text{CuClBr}_3$: 1, 2 = charge-transfer (CT) transitions; 3 = $d-d$ transition. b, c) DFT simulation of band structure, density of states (DOS), of MA_2CuCl_4 and $\text{MA}_2\text{CuClBr}_3$.

From the analysis of the calculated band structure, we could assign the higher energy absorption bands (indicated with 1 and 2 in Figure 4.3 a, whose energies are affected by the halide content) to ligand-to-metal charge transfer transitions, matching previous studies on related CuCl_4^{2-} complexes. In particular, the projected density of states of each atom (PDOS, Appendix A, Figure A.3) allowed the correlation of the 1 and 2 absorption bands to the transitions $\text{Cl, Br } p\sigma \rightarrow \text{Cu } d_{x^2-y^2}$ and $\text{Cl, Br } p\pi \rightarrow \text{Cu } d_{x^2-y^2}$ respectively, suggesting charge transfer (CT) states from ligand-related orbitals toward the highest antibonding of the d orbitals, (the half-filled $d_{x^2-y^2}$).¹⁵ In addition, a low energy

absorption band is observed in the range 700-900 nm (indicated with “3” in Figure 4.3 a) with position nearly independent of the Cl/Br ratio. This band can be ascribed to $d-d$ transitions between the d levels of the copper: this is expected for the electronic configuration of Cu^{2+} ions ($3d^9 (t_{2g}^6 e_g^3)$) as well as from the calculated PDOS (Appendix A, Figure A.3) which predicts the three electronic transitions $\text{Cu}_{d_{xz,yz}} \rightarrow \text{Cu}_{d_{x^2-y^2}}$, $\text{Cu}_{d_{xy}} \rightarrow \text{Cu}_{d_{x^2-y^2}}$, and $\text{Cu}_{d_{z^2}} \rightarrow \text{Cu}_{d_{x^2-y^2}}$.¹⁸ The contribution of each transition, with energies 12111 cm^{-1} , 12918 cm^{-1} and 13606 cm^{-1} , was deconvoluted by in principle component fitting of the featureless near infrared (NIR) absorption band (Appendix A, Figure A.4).

Table 4.2 Calculated effective mass for hole and electron of copper perovskite compounds from band structure using DFT+U method.

Crystal Structure	Hole		Electron	
	Γ -Z	Γ -Y	Γ -Z	Γ -Y
$(\text{CH}_3\text{NH}_3)_2\text{CuCl}_4$	∞	1.71	0.58	0.31
$(\text{CH}_3\text{NH}_3)_2\text{CuCl}_2\text{Br}_2$	∞	2.67	1.86	0.51
$(\text{CH}_3\text{NH}_3)_2\text{CuCl}_{0.5}\text{Br}_{3.5}$	∞	1.55	4.04	0.52
$(\text{CH}_3\text{NH}_3)_2\text{CuClBr}_3$	∞	1.51	2.39	0.57

Calculation of the hole and electron effective masses revealed a strong anisotropy in the transport properties of this system (Table 4.2). The whole series shows a very flat band structure, which causes the charge effective masses along the Γ -Z direction (out-of-plane transport) to be much higher than in the Γ -Y direction (in-plane transport). In particular, the hole effective mass in the Γ -Z direction is ∞ , while electron effective mass in the Γ -Y direction is as low as 0.31–0.57 and comparable to the case of MAPbI_3 .³ This indicates that the charges are strongly confined within the inorganic layers, acting as quantum wells, while they can easily move within the inorganic planes.

4.2.3 Trap-induced green luminescence

Transient absorption measurements revealed the formation of a very broad, photoinduced absorption band peaked around 620 nm. A typical example is given in Figure 4.4 a for the case of $\text{MA}_2\text{CuClBr}_3$. The time resolved signal shows that this photoinduced absorption band has a very fast decay, with about 80% of the charges which recombine in less than 1 ps, with a slower recombination time for the bromine-containing perovskites. Furthermore, the increase in Br/Cl ratio enhances an additional long lived component (>1 ns, See Figure 4.4 b and Table 4.3). While the fast decay is consistent with the strong charge confinement in the layered structure favouring charge recombination, the presence of a much longer-lived component might indicate the presence of trap states, which become more dominant at higher bromine contents.

Figure 4.4 a) Transient absorption (TA) spectrum of $\text{MA}_2\text{CuClBr}_3$ and b) TA decays dynamics.

Table 4.3 Fitting parameters of the transient absorption decay dynamics of $\text{MA}_2\text{CuCl}_x\text{Br}_{4-x}$ (τ = characteristic lifetime; A = amplitude).

	t_1 [ps]	A1	t_2 [ps]	A2	t_3 [ps]	A3
MA_2CuCl_4	0.06	0.91	9.91	0.07	430	0.02
$\text{MA}_2\text{CuCl}_2\text{Br}_2$	0.54	0.87	10	0.10	1400	0.03
$\text{MA}_2\text{CuClBr}_3$	0.54	0.75	2.05	0.15	1414	0.11

Under excitation at 310 nm, the perovskites showed green photoluminescence peaked at 515 nm (Figure 4.5 a). Surprisingly, the emission does not shift with the bandgap, but gradually increases in intensity with the increase in Br/Cl ratio. Moreover, the similar photoluminescence decay across the series (1-4 ns, Table 4.4 and Figure 4.5 b) suggests that the observed emission originates from the same emissive species, a trap state whose concentration increases with the bromine content. Green photoluminescence is indeed characteristic of the Cu^+ ion,¹⁹ which can derive from the partial reduction of Cu^{2+} during the annealing process of the film.²⁰⁻²³ The photoluminescence trend suggests that the Cu^{2+} reduction is fostered at higher bromine content, while chlorine helps to stabilize the Cu^{2+} oxidation state. This hypothesis is further corroborated by X-ray photoelectron spectroscopy (XPS), which revealed the presence of Cu^+ ions increasing with the bromine content of the perovskite (Appendix A, Figure A.5).

Figure 4.5 a) Steady state and b) time-resolved photoluminescence of $\text{MA}_2\text{CuCl}_x\text{Br}_{4-x}$ under 310 nm excitation wavelength.

Table 4.4 Fitting parameters of the double-exponential photoluminescence decays (τ = characteristic lifetime; A = amplitude).

	t_1 [ns]	A1	t_2 [ns]	A2
MA_2CuCl_4	1.0	0.67	3.9	0.33
$\text{MA}_2\text{CuCl}_2\text{Br}_2$	0.86	0.62	3.7	0.38
$\text{MA}_2\text{CuClBr}_3$	0.77	0.62	3.6	0.38
$\text{MA}_2\text{Cu}_{0.5}\text{ClBr}_{3.5}$	0.75	0.71	4.2	0.29

4.3 Crystal engineering with functional organic cation

Since the photoluminescence of $\text{MA}_2\text{CuCl}_x\text{Br}_{4-x}$ is independent on the perovskite bandgap, but is rather determined by Cu^+ trap states, we developed an alternative approach to tune the perovskite luminescence. In this regard, we sought a strategy to minimize the formation of the Cu^+ traps in the copper perovskite while incorporating a luminescent organic molecule which would determine the emissive characteristics of the final hybrid material. While Cu^+ formation can be overcome by avoiding the use of bromine and reducing the processing temperature, the incorporation of a fluorescent cation requires a careful structural design to fit a bulky organic molecule in the layered structure of the perovskite without compromising its stability. This complex problem of crystal engineering can be addressed by driving the self-assembly of metal halide and organic subunits into a stable supramolecular architecture through the use of second sphere coordination.

Crystal engineering is based on the combination of different building blocks to drive the self-assembly of novel materials with properties different from those of the starting components. To control the perovskite's structure at the molecular level, both the primary and secondary valence of the metallic cation can be exploited. While the primary valence refers to the chemical bonds between the metal and ionizable ligands (corresponding to Cu-X bonds in the case of copper perovskites), the secondary valence refers to the non-ionizable ligands associated to the metal.²⁴ The ability of the metal cation to induce a structural ordering beyond its first shell of directly bound ligands is indicated as "second-sphere coordination", a concept introduced by Alfred Werner in 1912.^{25,26} Transition metals such as Cu, Fe, Ir, Pt have a particularly rich second-sphere coordination chemistry which influence biological recognition as well as self-assembly of supramolecular structures.²⁷ Second-sphere adducts are connected through noncovalent bonding with the first coordination sphere of the metal and can involve any kind of intermolecular interaction,²⁸⁻³⁰ for

example hydrogen bonding, coordination and electrostatic interactions, halogen bonding and Van der Waals interactions.³¹ This approach allows the coordination with a wide range of molecular species and is typically used for the synthesis of metal-organic frameworks (MOFs) for applications such as gas adsorption,^{32,33} separation^{34,35} and in non-linear optics.³⁶

Here, second sphere coordination approach through charge assisted hydrogen bonding was used to design a new perovskite combining a copper chloride framework with the organic ligand 4,4'-(1,1'-biphenyl-4,4'-diyl)dioxy)dianiline (BPOA), as shown schematically in Figure 4.6. This molecule is based on a conjugated oligoaromatic biphenyl core acting as a fluorophore, where the conjugation is increased in case of planar geometry. The two aniline terminal units make the ligand ditopic and provide extra stabilization against moisture uptake since the hydrophobic aromatic unit compensate for the hydrophilicity of the amino groups. Additionally, the ether groups linking the biphenyl and aniline moieties allow for torsional flexibility, which is important to relieve steric hindrance and allow the molecular packing in a 2D perovskite framework.

Figure 4.6 Reaction scheme for the synthesis of $(\text{H}_2\text{BPOA})\text{CuCl}_4$.

4.3.1 Self-assembling properties of BPOA

As determined from single-crystal X-ray diffraction, BPOA shows rich self-assembling properties driven by both $\text{C-H}\cdots\pi$ and $\pi\cdots\pi$ stacking interactions of the aromatic units and hydrogen bonding of the amino groups. When crystallized alone, the hydrophilicity of the amino groups causes the formation

of hydrated salts $\text{BPOA} \cdot \text{H}_2\text{O}$ (triclinic, P-1; see Figure 4.7 a). Upon formation of the chloride salt, the structure could also be templated by means of the solvent used for the crystal growth: DMSO gave the tendency to intercalate in the crystal structure giving co-crystals $(\text{H}_2\text{BPOA})\text{Cl}_2 \cdot 2\text{DMSO}$ (triclinic, P-1; see Figure 4.7 b), while synthesis from DMF solutions yielded completely water and solvent-free crystals of $(\text{H}_2\text{BPOA})\text{Cl}_2$ (monoclinic, $\text{P}2_1/\text{c}$; see Figure 4.7 c) where chloride and organic layers are stacked in alternation. In the chloride salts, the self-assembling of the organic crystals is dominated by $\pi \cdots \pi$ stacking interactions, with distances between the aromatic units of adjacent molecules in the range 3.2-3.6 Å. The detailed list of refined crystallographic parameters of the three crystal structures is shown in Appendix A, Table A.1.

Figure 4.7 Crystal structures determined by single crystal X-ray diffraction of a) $\text{BPOA} \cdot \text{H}_2\text{O}$, b) $(\text{H}_2\text{BPOA})\text{Cl}_2 \cdot 2\text{DMSO}$, c) $(\text{H}_2\text{BPOA})\text{Cl}_2$.

The reaction of $(\text{H}_2\text{BPOA})\text{Cl}_2$ with CuCl_2 in acidic DMSO immediately caused precipitation of a yellow powder (Figure 4.8 a). Scanning electron microscope (SEM) characterization revealed the formation of crystals with platelike shape (Figure 4.8 b), typical of layered perovskites. Indeed, SC-XRD performed on a micrometric size crystal confirmed the formation of the 2D perovskite with formula $(\text{H}_2\text{BPOA})\text{CuCl}_4$ with monoclinic crystal system and space group $\text{P}2_1/\text{c}$

(Figure 4.8 c and Appendix A, Table A.1). The structure was further confirmed by powder X-ray diffraction (Appendix A, Figure A.6). In the asymmetric unit, half $[\text{CuCl}_4]^{2-}$ and half cation are present.

Figure 4.8 Layered perovskite $(\text{H}_2\text{BPOA})\text{CuCl}_4$ structural characterization: a) yellow powders and b) SEM pictures of flakes (scale bar = $5\mu\text{m}$). c) Single crystal XRD structure; d) enlarged figure of the copper chloride inorganic framework; e) detail of the second-sphere charge-assisted hydrogen-bonding interactions.

The protonated amino groups allow for second sphere coordination interacting with the copper via three charge-assisted hydrogen bonds $\text{N-H}^+\cdots\text{Cl}^-$ (length = $3.174 - 3.282 \text{ \AA}$, bond angle = $145^\circ - 149^\circ$). Here, the packing of the organic molecules is mediated mainly by $\text{C-H}\cdots\pi$ interactions (bond lengths in the

range 3.0-3.2 Å) and allows the retention of a nearly planar geometry of the biphenyl core (torsion angle=2.718°), ensuring the maximum delocalization between the adjacent aromatic units.³⁷ The copper chloride framework, comprising of Cu···Cl-Cu bridges, extends to form an infinite 2D layer along the *bc* plane (Figure 4.8 d). Similarly, to MA₂CuCl_xBr_{4-x}, Cu²⁺ adopts a strongly Jahn-Teller distorted octahedral coordination with bond lengths Cu-Cl1 = 2.284 Å, 2.283 Å, 2.293 Å and Cu-Cl2 = 2.884 Å, with the two longest distances corresponding to the chloride-bridged Cl-μ-Cl bond (Figure 4.8 e). Charge-assisted hydrogen bonding was so strong to overcome the interaction with water and DMSO, so that a completely water and solvent-free perovskite was obtained. Moreover, the close packing of the organic layers combined with their hydrophobicity, constitutes a barrier to water diffusion in the perovskite structure,³⁸ which is detrimental for the material's stability.³⁹ This was indeed confirmed by exposing perovskite powders for 1 month in air without noticing significant structural changes in the XRD pattern (Appendix A, Figure A.6). This is a considerable improvement compared to MA₂CuCl_xBr_{4-x}, where inert atmosphere is necessary to avoid rapid moisture uptake of the material.

4.3.2 (H₂BPOA)CuCl₄ optical properties

The Jahn-Teller distortion of the octahedral coordination observed from XRD characterization is expected for the Cu²⁺ having electronic configuration 3d⁹ (t_{2g}⁶g³), and gives rise to 3 possible electronic transitions between the d-levels of copper (Figure 4.9 a) resulting in a broadband absorption in the NIR region (8000–1600 cm⁻¹; 625–1250 nm) similar to MA₂CuCl_xBr_{4-x} (Figure 4.9 b). Principal component fitting of this band identified 3 components peaking at 10893 cm⁻¹, 12281 cm⁻¹ and 13286 cm⁻¹ and ascribed to the expected transitions $Cu_{d_{xz,yz}} \rightarrow Cu_{d_{x^2-y^2}}$, $Cu_{d_{xy}} \rightarrow Cu_{d_{x^2-y^2}}$, and $Cu_{d_{z^2}} \rightarrow Cu_{d_{x^2-y^2}}$, respectively.¹⁸ These agree with the energy diagram of a d⁹ configuration in octahedral crystal field (Oh) and *z-out* distortion (*D*_{4h}) having splitting of the e_g

levels $\Delta_e=10893 \text{ cm}^{-1}$, $10Dq=12281 \text{ cm}^{-1}$ and crystal field stabilization energy $CFSE=0.6 \times 10Dq= 88.1 \text{ kJmol}^{-1}$, in close agreement with the typical values of similar copper chloride complexes, as well as with those found in the series $MA_2CuCl_xBr_{4-x}$.^{17,18}

Figure 4.9 a) Energy diagram and allowed electronic transitions for a distorted octahedral coordination (D_{4h} symmetry); b) Near infrared absorption (NIR) of $(BPOA)CuCl_4$ and principle-component fitting showing the presence of three electronic transitions.

Powders of the perovskite and chloride salt of the organic cations were used to study their absorption and photoluminescence properties. Figure 4.10 shows the transformed Kubelka–Munk function calculated as $F(R) = (R-1)^2 / 2R$, where R is the powder reflectance. This gives a spectrum proportional to the absorption coefficient of the material, and in the case of the 2D perovskite it shows two main absorption bands (Figure 4.10 a): one at higher energy (350 nm), and a second peaked at 380 nm with a shoulder at 440 nm. The lower energy band (with direct band-gap at 464 nm, 2.67 eV; Appendix A, Figure A.7), can be assigned to the ligand-to-metal charge transfer transitions $Cl-p_\sigma \rightarrow Cu-d_{x^2-y^2}$ and $Cl-p_\pi \rightarrow Cu-d_{x^2-y^2}$ accordingly to the DFT analysis we performed on the $MA_2CuCl_xBr_{4-x}$ system and in agreement with similar copper perovskites.^{15,40} On the other hand, the higher energy band (bandgap at 326 nm, 3.80 eV; Appendix A, Figure A.7) matches the absorption of $(H_2BPOA)Cl_2$, and can

therefore be associated to electronic transitions of the organic ligand. The chloride salt $(\text{H}_2\text{BPOA})\text{Cl}_2$ also shows bright blue luminescence at 343 nm, with FWHM = 45 nm and Stoke shift = 17 nm, similarly to other biphenyl derivatives, Figure 4.10 b).⁴¹⁻⁴³ Such fluorescence is retained after co-crystallization with CuCl_2 in the perovskite structure: upon 280 nm excitation, $(\text{BPOA})\text{CuCl}_4$ shows indeed a photoluminescence peak at 336 nm: being largely blue-shifted compared to the CT transitions, this emission cannot be related to band-edge (464 nm) emission of the perovskite (Figure 4.10 c). Conversely, the excitation spectrum of the perovskite at the probing wavelength 360 nm overlaps with that of $(\text{H}_2\text{BPOA})\text{Cl}_2$ and with its absorption spectrum, proving the effective functionalization of the perovskite with the active organic cation. The small differences of the perovskite luminescence in terms of blue shift and width might derive from the different packing of the $\text{H}_2\text{BPOA}^{2+}$ cations in the perovskite framework, which induces small differences in the biphenyl torsion angle and modification in the intermolecular interactions ($\text{C-H}\cdots\pi$ and $\pi\cdots\pi$ stacking) affecting both the electronic delocalization and the collective excited state of the resulting solid. The emission spectra of these two materials provide a nearly pure blue colour, with CIE coordinates (0.148; 0.099) for $(\text{H}_2\text{BPOA})\text{Cl}_2$ and (0.125; 0.155) for $(\text{BPOA})\text{CuCl}_4$ (Figure 4.10 d). In addition, a considerable part of the perovskite emission falls in the UV-A range ($\lambda_{\text{em}}=320\text{--}400$ nm) which is a difficult range to cover with standard semiconductors. Currently, typical UV emitters consist of AlGaIn quantum wells⁴⁴ ($\lambda_{\text{em}}<365$ nm) or ZnO nanostructures for the near-UV/blue region⁴⁵ and are used in LEDs for application in high-density information storage, chemical biological analysis, or in combination with phosphor mixtures to obtain white light emission with high colour rendering index (CRI).⁴⁶⁻⁴⁸ While $(\text{BPOA})\text{CuCl}_4$ might be suitable for a similar down-conversion approach, the possibility of synthetically modifying the organic cation makes it an interesting platform to further tune the emission colour in the visible range and increase its relevance for applications in solid-state lighting. For example, the biphenyl

could be functionalized with nitro and sulfonate groups to modulate its luminescence, or the conjugation could be increased including carbazole and anthracene derivatives, placing (BPOA)CuCl₄ as the first member of a big family of functional hybrid, lead-free perovskites.

Figure 4.10 a) Transformed powder reflectance spectrum of the salt (BPOA)Cl₂ (red) and the perovskite (BPOA)CuCl₄ (black). Photoluminescence properties of b) (BPOA)Cl₂ and c) (BPOA)CuCl₄: PL spectrum at $\lambda_{\text{exc}} = 280$ nm (green) and photoluminescence excitation spectrum (PLE) at $\lambda_{\text{probe}} = 360$ nm (blue). d) Chromaticity coordinates (CIE 1931) of (BPOA)Cl₂, (BPOA)CuCl₄, MA₂CuCl_xBr_{4-x}.

Although the colour rendering of (BPOA)CuCl₄ is slightly lower than the pure organic salt (H₂BPOA)Cl₂, the formation of the hybrid material combines the optical properties of the organic cation with the transport properties of the metal halide framework beneficial in view of applications in optoelectronic devices. Notably, the blue luminescence of the BPOA-based perovskite is substantially different from the Cu⁺ traps-induced green emission of the MA₂CuCl_xBr_{4-x} films (Figure 4.10 d). In order to avoid trap states formation, we specifically synthesised and processed the BPOA-based compound at room temperature, and chose to work with the more stable chlorine-based perovskite so to minimize Cu⁺ formation (deriving from Cu²⁺ reduction) and thermally induced traps in the material.

4.4 Conclusions

The optoelectronic properties of layered copper-based perovskites have been extensively studied and characteristic electronic transitions and charge confinement effect have been elucidated by means of DFT calculations. Even though the modification in Br/Cl ratio allows the bandgap tuning in the series $\text{MA}_2\text{CuCl}_x\text{Br}_{4-x}$, only green photoluminescence could be achieved in this system mediated by the formation of Cu^+ trap states induced by the processing conditions.

To further tune the perovskite emission, the rational synthetic design of a new hybrid copper perovskite through a second-sphere coordination approach was adopted to include an optoelectronically active organic cation. The new 2D copper perovskite is based on 4,4'-(1,1'-biphenyl-4,4'-diylldioxy)dianiline as an organic building block, and combines the transport properties of a two-dimensional copper chloride framework with an optoelectronically active bulky cation for the first time; this yielded near-UV/blue photoluminescence and moisture resistance in the resulting hybrid. This study paves the way for the development of a new class of lead-free hybrid perovskites incorporating functional cations and allows tuning the optical properties through synthetic design by exploitation of second-sphere coordination interactions. These characteristics make hybrid functional copper perovskites a valuable alternative to Pb-based materials, with great potential for applications in solid-state lighting.

References

- [1] S. D. Stranks, H. J. Snaith. *Nat Nanotechnol.* **2015**, *10*, 391.
- [2] H. Cho, S.-H. Jeong, M.-H. Park, Y.-H. Kim, C. Wolf, C.-L. Lee, J. H. Heo, A. Sadhanala, N. Myoung, S. Yoo, S. H. Im, R. H. Friend, T.-W. Lee. *Science.* **2015**, *350*, 1222.

- [3] X. Y. Chin, D. Cortecchia, J. Yin, A. Bruno, C. Soci. *Nat Commun.* **2015**, 6, 7383.
- [4] F. Deschler, M. Price, S. Pathak, L. E. Klintberg, D.-D. Jarausch, R. Higler, S. Hüttner, T. Leijtens, S. D. Stranks, H. J. Snaith, M. Atatüre, R. T. Phillips, R. H. Friend. *The Journal of Physical Chemistry Letters.* **2014**, 5, 1421.
- [5] A. Babayigit, A. Ethirajan, M. Muller, B. Conings. *Nat Mater.* **2016**, 15, 247.
- [6] Y. Li, K.-s. Moon, C. P. Wong. *Science.* **2005**, 308, 1419.
- [7] F. Hao, C. C. Stoumpos, D. H. Cao, R. P. H. Chang, M. G. Kanatzidis. *Nat Photon.* **2014**, 8, 489.
- [8] W.-L. Hong, Y.-C. Huang, C.-Y. Chang, Z.-C. Zhang, H.-R. Tsai, N.-Y. Chang, Y.-C. Chao. *Advanced Materials.* **2016**, 28, 8029.
- [9] N. K. Noel, S. D. Stranks, A. Abate, C. Wehrenfennig, S. Guarnera, A.-A. Haghighirad, A. Sadhanala, G. E. Eperon, S. K. Pathak, M. B. Johnston, A. Petrozza, L. M. Herz, H. J. Snaith. *Energy & Environmental Science.* **2014**.
- [10] M. H. Kumar, S. Dharani, W. L. Leong, P. P. Boix, R. R. Prabhakar, T. Baikie, C. Shi, H. Ding, R. Ramesh, M. Asta, M. Graetzel, S. G. Mhaisalkar, N. Mathews. *Advanced Materials.* **2014**, 1.
- [11] R. Willett, H. Place, M. Middleton. *Journal of the American Chemical Society.* **1988**, 110, 8639.
- [12] A. Jaffe, H. I. Karunadasa. *Inorganic Chemistry.* **2014**, 53, 6494.
- [13] R. Willett. *Acta Crystallographica Section C.* **1991**, 47, 1081.
- [14] I. Pabst, H. Fuess, J. W. Bats. *Acta Crystallographica Section C.* **1987**, 43, 413.
- [15] S. R. Desjardins, K. W. Penfield, S. L. Cohen, R. L. Musselman, E. I. Solomon. *Journal of the American Chemical Society.* **1983**, 105, 4590.
- [16] R. Valiente, F. Rodríguez. *Physical Review B.* **1999**, 60, 9423.

- [17] A. Jaffe, Y. Lin, W. L. Mao, H. I. Karunadasa. *Journal of the American Chemical Society*. **2015**, 137, 1673.
- [18] R. D. Willett, O. L. Liles, C. Michelson. *Inorganic Chemistry*. **1967**, 6, 1885.
- [19] G. Susana, U. Iñigo, V. Rafael, R. Fernando. *Journal of Physics: Condensed Matter*. **2010**, 22, 295505.
- [20] T. Nobuyuki, K. Masahiro. *Bulletin of the Chemical Society of Japan*. **1970**, 43, 3468.
- [21] R. R. Hammer, N. W. Gregory. *The Journal of Physical Chemistry*. **1964**, 68, 314.
- [22] M. C. Ball, R. F. M. Coultard. *Journal of the Chemical Society A: Inorganic, Physical, Theoretical*. **1968**, 1417.
- [23] H. D. Hardt. *Zeitschrift für anorganische und allgemeine Chemie*. **1959**, 301, 87.
- [24] D. J. Mercer, S. J. Loeb. *Chemical Society Reviews*. **2010**, 39, 3612.
- [25] H. M. Colquhoun, J. F. Stoddart, D. J. Williams. *Angewandte Chemie International Edition in English*. **1986**, 25, 487.
- [26] E. C. Constable, C. E. Housecroft. *Chemical Society Reviews*. **2013**, 42, 1429.
- [27] M. C. T. Fyfe, P. T. Glink, S. Menzer, J. F. Stoddart, A. J. P. White, D. J. Williams. *Angewandte Chemie International Edition in English*. **1997**, 36, 2068.
- [28] F. Guo, H.-d. Shao, Q. Yang, A. Famulari, J. Martí-Rujas. *CrystEngComm*. **2014**, 16, 969.
- [29] H.-y. Guan, Z. Wang, A. Famulari, X. Wang, F. Guo, J. Martí-Rujas. *Inorganic Chemistry*. **2014**, 53, 7438.
- [30] F. Guo, J. Martí-Rujas. *Dalton Transactions*. **2016**, 45, 13648.
- [31] Z. Liu, S. T. Schneebeli, J. F. Stoddart. *CHIMIA International Journal for Chemistry*. **2014**, 68, 315.

- [32] S. A. Dalrymple, G. K. H. Shimizu. *Journal of the American Chemical Society*. **2007**, *129*, 12114.
- [33] N. Roques, G. Mouchaham, C. Duhayon, S. Brandès, A. Tachon, G. Weber, J. P. Bellat, J.-P. Sutter. *Chemistry – A European Journal*. **2014**, *20*, 11690.
- [34] Z. Liu, M. Frasconi, J. Lei, Z. J. Brown, Z. Zhu, D. Cao, J. Iehl, G. Liu, A. C. Fahrenbach, Y. Y. Botros, O. K. Farha, J. T. Hupp, C. A. Mirkin, J. Fraser Stoddart. *Nature Communications*. **2013**, *4*, 1855.
- [35] Z. Liu, A. Samanta, J. Lei, J. Sun, Y. Wang, J. F. Stoddart. *Journal of the American Chemical Society*. **2016**, *138*, 11643.
- [36] H.-B. Yu, H.-T. Li, P. Zhang, A. Famulari, F. Guo, I. Bargigia, J. Marti-Rujas. *CrystEngComm*. **2016**, *18*, 2408.
- [37] T. A. Su, M. Neupane, M. L. Steigerwald, L. Venkataraman, C. Nuckolls. *Nature Reviews Materials*. **2016**, *1*, 16002.
- [38] I. C. Smith, E. T. Hoke, D. Solis-Ibarra, M. D. McGehee, H. I. Karunadasa. *Angewandte Chemie*. **2014**, *126*, 11414.
- [39] A. M. A. Leguy, Y. Hu, M. Campoy-Quiles, M. I. Alonso, O. J. Weber, P. Azarhoosh, M. van Schilfgaarde, M. T. Weller, T. Bein, J. Nelson, P. Docampo, P. R. F. Barnes. *Chemistry of Materials*. **2015**, *27*, 3397.
- [40] S. Gupta, T. Pandey, A. K. Singh. *Inorganic Chemistry*. **2016**, *55*, 6817.
- [41] E. Abuin, E. Lissi, L. Gargallo, D. Radic. *European Polymer Journal*. **1982**, *18*, 319.
- [42] S. Chen, N. E. Fahmi, C. Bhattacharya, L. Wang, Y. Jin, S. J. Benkovic, S. M. Hecht. *Biochemistry*. **2013**, *52*, 8580.
- [43] H. Du, R.-C. A. Fuh, J. Li, L. A. Corkan, J. S. Lindsey. *Photochemistry and Photobiology*. **1998**, *68*, 141.
- [44] A. Khan, K. Balakrishnan, T. Katona. *Nat Photon*. **2008**, *2*, 77.
- [45] J. H. Lim, C. K. Kang, K. K. Kim, I. K. Park, D. K. Hwang, S. J. Park. *Advanced Materials*. **2006**, *18*, 2720.
- [46] E. F. Schubert, J. K. Kim. *Science*. **2005**, *308*, 1274.

- [47] M. H. Crawford. *IEEE Journal of Selected Topics in Quantum Electronics*. **2009**, 15, 1028.
- [48] S. Pimputkar, J. S. Speck, S. P. DenBaars, S. Nakamura. *Nat Photon*. **2009**, 3, 180.

Chapter 5*

Polaron self-localization in white-light emitting hybrid perovskites

Ultra-broadband photoluminescence in 2D perovskites (EDBE)PbX₄ (EDBE = 2,2-(ethylenedioxy)bis(ethylammonium)) is shown to originate from self-trapped polaronic excitons localised at specific inorganic lattice sites. Experimental measurements of the exciton dynamics and first principle calculations performed on perturbed crystal structures and molecular clusters point to the ultrafast formation of self-trapped electrons (STEL) and holes (STH) acting as intra-band colour centres with wide energy distribution. In view of these findings, localised polarons may also play an important role for charge transport in hybrid perovskite devices.

*This section published substantially as reference:

D. Cortecchia, J. Yin, A. Bruno, S-Z A. Lo, G. Gurzadyan, S. Mhaisalkar, J-L Brédas, C. Soci, *J. Mater. Chem. C* **2017**, 5, 2771

J. Yin, H. Li, D. Cortecchia, C. Soci, J-L Brédas, *ACS Energy Lett.* **2017**, 2 (2), 417

5.1 Introduction

Contrary to copper-based perovskites, the inorganic framework of lead-based perovskites plays a major role in determining their luminescence properties. Here, the combination of spin orbit coupling, quantum confinement in the low dimensional structure and excitonic properties of the Pb-X lattice have strong influence on transport and optical properties. In the case of 2D perovskites, the energetic landscape of the material can be tuned structurally offering the rather unique possibility to modulate the emission from narrow- to ultrabroad-band, and even to achieve white light luminescence. These characteristics, jointly with the solution processability and improved moisture resistance offered by these layered materials, are extremely appealing for application in light emission for solid-state lighting, displays (light emitting diodes, transistors and lasers) and large area X-ray scintillators for medical and security applications.

As explained in Chapter 2, recent works have identified charge self-trapping as the main process underlying white light emission, however a comprehensive description of the charge-trapping sites in relation with the host perovskite structure is still missing. Understanding the trapping mechanism is essential to rationally control the optical properties through synthetic design towards the development of better performing emitting materials.

In this work, the white light emitting 2D perovskite (EDBE)PbX₄ (where EDBE=2,2-(ethylenedioxy)bis(ethylammonium)), characterized by different orientation of the perovskite sheets depending on the halide used (X=Cl, Br), is adopted as a model compound.¹ Ultra-broadband photoluminescence is shown to originate in this system from self-trapped polaronic excitons localised at specific inorganic lattice sites. Steady state and time resolved experimental measurements of the exciton dynamics and *first principles* calculations performed on perturbed crystal structures and molecular clusters point to the ultrafast formation of self-trapped electrons (STEL) and holes (STH) acting as intra-band colour centres with wide energy distribution. In view of these

findings, localised polarons are expected to play a general role in the charge transport properties of hybrid perovskite devices.

5.2 Quantum confinement in (EDBE)PbX₄

Thin films of 2D perovskites (EDBE)PbCl₄ and (EDBE)PbBr₄ were fabricated as described in the experimental section, Paragraph 3.2.7. High-quality, smooth films were obtained on quartz substrates and used for optical characterization (Appendix B, Figure B.1). The synthesis of the correct material was confirmed by XRD characterization (Appendix B, Figure B.1): (EDBE)PbCl₄ and (EDBE)PbBr₄ crystallize as <100> and <110>-oriented perovskite sheets (Paragraph 2.1.4 and insets of Figure 5.1 a, b), respectively, alternating to EDBE²⁺ organic layers.^{1,2}

Figure 5.1 Temperature dependent absorption of a) (EDBE)PbCl₄ and b) (EDBE)PbBr₄ and c,d) corresponding Frank-Condon fitting of the excitonic absorption at 78 K. The blue bars represent the Huang-Rhys factors S_n for the coupling with phonons with energy c) 16, 24, 49 and 68 meV and d) 19 meV.

The characteristic layered structure is responsible for quantum confinement

within the inorganic potential wells and enhanced excitonic absorption,^{3,4} and has strong consequences on the absorption spectrum, which can be divided in two main regions: one high-energy absorption continuum (above 4.1 eV and 3.6 eV for the Cl- and Br-based compound) and a sharp low energy excitonic absorption peak, named E-band, at 3.72 eV and 3.32 eV (Figure 5.1 a, b).

The enhanced Coulomb interaction in the layered structure increases the exciton binding energy up to 412 and 365 meV for (EDBE)PbCl₄ and (EDBE)PbBr₄, as derived from low temperature absorption measurements (Appendix B, Figure B.2). At 78 K, the excitonic absorption of the <100>-oriented (EDBE)PbCl₄ splits into a vibronic series; this is consistent with Frank-Condon replicas of phonons with energies of 16, 24, 49 and 68 meV, that match the vibrational Raman modes at 131, 190, 400 and 549 cm⁻¹ (Figure 5.2 a, c).⁵ The coupling strength with each phonon mode was estimated by quantitative fitting and indicated by the amplitude of the Huang-Rhys factors, S_n (blue bars in Figure 5.1 c, d; see Paragraph 3.3.4 for the detailed fitting procedure). The vibrational modes at 16 and 24 meV (S_1 and S_2 , Figure 5.1 c) are characteristic of the lead-chloride lattice,⁶ and are therefore in agreement with the exciton confinement in the inorganic layers. However, strong coupling was also surprisingly found with the phonons at 49 and 64 meV (S_3 and S_4 in Figure 5.1 c): these high energy vibrations are characteristic of the organic modes, and their strong coupling might derive from the interaction between the inorganic lattice and the organic layers, tightly connected via charge-assisted hydrogen bonds. In the case of the rippled <110>-oriented (EDBE)PbBr₄, vibronic splitting could not be resolved even at 78K: a single phonon at 19 meV was sufficient to account for the charge-phonon coupling in the Frank-Condon fitting. This energy matches the highest vibrational mode of the lead bromide lattice (150 cm⁻¹ Raman mode, Figure 5.2 b) and suggests exclusive coupling with the inorganic framework of the perovskite (Figure 5.1 d).

Figure 5.2 Raman spectra of a,c) (EDBE)PbCl₄ and b) (EDBE)PbBr₄; (*) indicates the signal from silicon substrate.

5.3 Band structure calculation

Starting from the relaxed experimental structures shown in Figure 5.3 a,b, density functional theory (DFT) calculations adopting general gradient approximation (GGA)/Perdew-Burke-Ernzerhof (PBE) were performed to derive the band structure and characteristic electronic transitions (Figure 5.3 c,d). When calculations were performed including spin orbit coupling (PBE/wSOC, blue lines in Figure 5.3 c, d) the bandgaps were strongly underestimated, with values 2.49 eV and 2.00 eV for (EDBE)PbCl₄ and (EDBE)PbBr₄; this discrepancy derives from the retention of band curvatures jointly with the change in conduction band degeneracies caused by the SOC. Even though the exclusion of SOC was shown to give accurate bandgaps due to error cancellation, slightly under-estimated values were still obtained in this case with PBE/woSOC (gray dashed lines in Figure 5.3 c, d), corresponding to 3.32 eV (Γ point) and 2.55 eV (A point) for the chloride and bromide compounds, respectively. Better agreement with the experimental band-gaps could be obtained combining the PBE functional with G_0W_0 implemented in Quantum Espresso/YAMBO for bandgap correction due to inclusion of SOC effect. In this case, calculated bandgaps were $PBE+G_0W_0 = 3.88$ eV for (EDBE)PbCl₄ and $PBE+G_0W_0: 3.45$ eV for (EDBE)PbBr₄. Analysis of the projected density of states shows that band edges of the conduction and valence bands mainly derive from contribution of the inorganic part (Pb-6s, 6p, Cl-3p,

or Br-4p) and account for the transitions $\text{Pb}^{2+}(6s)\text{Cl}^-(3p) \rightarrow \text{Pb}^{2+}(6p)$ and $\text{Pb}^{2+}(6s)\text{Br}^-(4p) \rightarrow \text{Pb}^{2+}(6p)$, which are the same involved in the corresponding inorganic precursors PbX_2 .⁷ On the other hand, similar to the 3D perovskites, the organic part has negligible contribution to these electronic transitions.⁸

Figure 5.3 Density functional theory (DFT) calculations at the GGA/PBE level. Optimized crystal structure and corresponding calculated band structure and projected density of states for a,c) (EDBE)PbCl₄ and b,d) (EDBE)PbBr₄.

Starting from the PBE/SOC level and combining random phase approximation (RA) and Bethe–Salpeter equation (BSE), the electronic transitions could be calculated reproducing the experimental absorption with excellent agreement (Figure 5.4 a, b); a slight shift of the scissors-operator (0.15 eV and 0.12 eV for (EDBE)PbCl₄ and (EDBE)PbBr₄) was applied to account for the small mismatch between experimental and theoretical bandgap. This was possible thanks to the inclusion of BSE which takes into account electron-hole interactions well reproducing the excitonic absorption. Even though EDBE^{2+}

does not contribute to the main inter-band transitions, it indirectly affects the energetic landscape of the inorganic part by inducing specific structural motifs of the lead halide framework as well as the layered structure and the consequent quantum confinement effect, from which the sharp E-band originates. The strong localization of the exciton wavefunction (Figure 5.4 c, d) is indeed in agreement with the exciton confinement in the inorganic layers and the increased experimental exciton binding energy in this low dimensional system.

Figure 5.4 a,b) Experimental PL and absorption spectra for a) (EDBE)PbCl₄ and b) (EDBE)PbBr₄ compared to the calculated absorption spectra with and without consideration of the electron-hole interaction. c,d) Representation of excitonic wavefunction localized in the inorganic layers of the perovskite.

5.4 Photoexcitation properties

Both EDBE perovskites are characterized by ultra-broadband, largely Stokes-shifted white-light emission as shown in Figure 5.4 a, b and in the photoexcitation maps of Figure 5.5.

Figure 5.5 Photoluminescence intensity maps as a function of excitation and emission energy for a,b) (EDBE)PbCl₄ and c,d) (EDBE)PbBr₄. Measurements in the upper panels are recorded at 298 K, while those in lower panels at 78 K.

The Stokes shift is as large as 1.38 eV for the chloride perovskite and is in net contrast with the sharp excitonic emission typical of other 2D perovskites (for example, alkylammonium-based perovskites, as commented in Chapter 6). It was found that efficient emission occurs under excitation resonant to the excitonic absorption: in the case of (EDBE)PbCl₄, the excitation map shows a double peak at 3.84 eV and 3.74 eV, tracing the low temperature vibronic

splitting of the E-band. The wider separation in photexcitation might be due to differences in the vibronic features of the ground and excited state. Likewise, the excitation spectrum of (EDBE)PbBr₄ shows only a single peak at 3.32 eV which matches the excitonic absorption. Surprisingly, excitation at higher energies yields a progressively weaker emission with an extremely fast decay $\ll 40$ ps (at $E_{\text{exc}}=4.66$ eV) probably due to the activation of non-radiative relaxation pathways, compared to the characteristic slower photoluminescence time decay ($\tau \sim 3$) under resonant excitation (Appendix B, Figure B.3 and Table B.1). Note that conventional trap states are expected to be populated even with high-energy excitation and consequent relaxation, while our observation suggests that the generation of the emissive species is closely correlated to the formation of excitons.

5.5 Multicomponent analysis of broadband photoluminescence

Despite the different composition, the emission profiles of the two materials are extremely similar, with emission maximum at 2.34 eV and FWHM = 650 meV, indicating that similar states are probably involved in the emissive process. Principal component fittings of the emission profiles at different temperatures revealed the presence of 3 main emitters contributing to the broadband luminescence which are indicated as W1, W2 and W3 in Figure 5.6 for the case of (EDBE)PbBr₄ (see also Appendix B, Figure B.4 for the chloride perovskite). These are characterized by large and irregular spacing (~ 160 -190 meV) which exclude their possible vibronic nature. Moreover, their position is nearly independent on temperature, as it would be expected for very deep-trap states (Appendix B, Figure B.5,6), while their relative intensity changes leading to an apparent redshift of the overall emission at low temperature (Figure 5.6 a). The total emission intensity enhances significantly at lower the temperatures, which is likely due to a combination of reduced line broadening and suppression of non-radiative recombination channels at low temperature. Thermal activation

energies of $E_a=147$ meV and $E_a=105$ meV, much greater than thermal vibrations, were estimated by means of Arrhenius plots⁹ of the total photoluminescence intensity for the chloride and bromide compound, respectively (Appendix B, Figure B.4). Such large values are indeed characteristic of deep intra-band radiative states, in agreement with the previous observations.

Figure 5.6 Analysis of broadband PL and transient absorption of (EDBE)PbBr₄. a) Temperature dependent PL: W1, W2 and W3 indicate the central wavelength of the three components (peaked respectively at 1.98 eV, 2.14 eV and 2.32 eV) determined from principle component fittings of the emission profiles. b) Spectral dependence of TRPL decays ($E_{exc} = 3.26$ eV). c) Transient absorption (TA) spectrum ($E_{exc} = 3.26$ eV) and d) corresponding decay dynamics at different wavelengths.

Time resolved luminescence measurements (TRPL), performed under resonant excitation of the E-band and probed at various emission wavelength across the luminescence profile, also confirmed the presence of multiple emitters, as shown in Figure 5.6 for (EDBE)PbBr₄. The PL dynamics were fitted as triexponential decays and the characteristics time decays ($\tau_1=40$ ps, $\tau_2=0.74$ ns,

and $\tau_3=3.24$ ns for the bromide perovskite) were obtained by global fitting the entire dataset at different probing wavelengths. By analysing the spectral dependence of the amplitude A1, A2, A3 of each component, we ascribed the ultrafast time decay $\tau_1=40$ ps, which prevails at higher energies (2.82 eV and 2.64 eV), to hot exciton emission having low impact on the steady state photoluminescence spectrum. Conversely, we assigned the intermediate time decay $\tau_2=0.74$ ns to the partially overlapped W1-W2 emitters (which could not be individually resolved) and the slowest $\tau_3=3.24$ ns to the lower energy emitter W3, due to its correspondence with the spectral dependence of the amplitude A3.

Transient absorption measurements (TA) with resonant excitation revealed the presence of a broad photoinduced absorption band across the visible spectral region (Figure 5.6 c and Appendix B, Figure B.7), which is consistent with the photoinduced formation of colour centres with wide energy distribution. The rise of the photoinduced absorption is extremely fast, comparable to the time resolution of the setup (~ 100 fs), supporting the ultrafast formation of these trap states as previously suggested by Hu *et al.*,¹⁰ who correlated this fast rising time with the vibrations of the inorganic lattice of the perovskite. The TA dynamics were fitted with double exponential decays: the fastest characteristic time $\tau_1 \sim 10$ ps is comparable to the fast TRPL component ($\tau \ll 40$ ps) and might be related to the population of S_1 (first excited singlet state) undergoing transition to S_n states (higher energies excited singlet states). On the other hand, the slower TA decay $\tau_2 = 0.74$ ns (Appendix B, Table B.2) corresponds to the τ_2 TRPL decay time (Table 5.1), and is therefore possible to correlate it to the excited-state absorption from the photoinduced colour centres with energy levels within the perovskite band gap.

Table 5.1 TRPL decay dynamics ($E_{\text{exc}} = 3.26$ eV) fitting parameters: characteristic time decays (τ) and amplitudes (A) were extracted by global fitting the entire dataset. τ_1 is actually $\ll 40$ ps, since the measured value is comparable to the instrument response function (IRF = 20–30 ps).

Emission Energy (eV)	τ_1 (ns)	A_1	τ_2 (ns)	A_2	τ_3 (ns)	A_3
2.82	0.04	0.81	0.74	0.10	3.24	0.10
2.64	0.04	0.49	0.74	0.28	3.24	0.23
2.34	0.04	0.00	0.74	0.09	3.24	0.91
2.25	0.04	0.20	0.74	0.18	3.24	0.63
2.14	0.04	0.00	0.74	0.41	3.24	0.59

5.6 Polaron self-localization

Density functional theory (DFT) calculations were performed to investigate the intrinsic nature of the white-light emission process. In the recent years, polaron formation has emerged as the most plausible mechanism to explain transport and luminescence properties of hybrid perovskites,¹⁰⁻¹⁹ in a certain way following the evolution of the photophysics of traditional organic semiconductors.^{20,21} In particular, A. J. Neukirch et al proposed that in the 3D perovskite MAPbI₃ charges might couple to the crystal lattice and be screened by collective rotations of MA⁺ cations in form of small polarons.¹⁷ A similar mechanism was also suggested to be at the root of the photodegradation observed in the same hybrid semiconductor.¹⁶ Indeed, crystals with soft lattices like the metal halide framework of hybrid perovskites can easily undergo structural deformation and induce charge localization at specific lattice points, where it remains confined in its own distortion field: this will give rise to self-trapped holes (STH) or self-trapped electrons (STEL) depending on the type of charge which gets trapped.^{22,23} A typical consequence is the formation of a “molecular polaron”, which is a sort of dimer embedded in the crystal lattice where the trapped charge establishes a temporary, short range chemical bond

between nearest ionic neighbours.²⁴ When the specific energetic landscape of the material induces high exciton binding energy, then the trapped species will be in the form of bound electron-hole pairs, known as polaron-excitons (PE). Self-trapping phenomena are common in alkali, alkaline-earth and halide perovskites such as KCl, CaF₂, KMgF₃ where they have been thoroughly studied with electron paramagnetic resonance (EPR).^{23,25} These studies identified characteristic species which include Pb₂³⁺ (STEL) as well as the STH Pb³⁺ and X₂⁻, where X=Cl, Br.^{23,26-32} In particular, the X₂⁻ species, also named V_k centres,^{33,34} are very common in alkali halides and involve the coupling of a hole to the crystal lattice by formation of a temporary chemical bond between nearest neighbour halides.^{23,25} In all the cases, a self-trapped charge goes along with a local lattice distortion, and their formation at low temperature has been shown responsible for appearance of Stoke shifted, broad photoluminescence in lead halides PbX₂ (X = Cl, Br).^{26,27,35,36}

5.6.1 Polaron simulation by perturbative method

In the previous paragraphs, it was shown how the (EDBE)PbX₄ electronic transitions are mainly based on characteristic transitions of the inorganic framework. Moreover, its photoexcitation properties strongly resembles those of the corresponding inorganic precursors PbX₂,³⁷ which suggests that self-trapped charges might play a role also in the Pb-based layered perovskites. This hypothesis was verified by calculating the charge density maps for electrons and holes in the perovskites (Figure 5.7), visualized as a plot of the valence band maximum (VBM) and conduction band minimum (CBM) on the base of PBE/wSOC results: to mimic the formation of the expected polaronic species, perturbations of the experimental crystal structure were applied by shortening selectively the interatomic distances Pb-Pb, Pb-X and X-X to induce dimerization at specific lattice points.

Figure 5.7 Calculated charge density maps for a-c) (EDBE)PbCl₄ and d-f) (EDBE)PbBr₄ by means of perturbative method. a,d) electron localization induced by Pb-Pb shortening characteristic of self-trapped electrons STEL Pb₂³⁺; b,e) and c,f) hole localization induced by shortening of X-X and Pb-X distances, inducing the formation of self-trapped holes STH X₂⁻ and Pb³⁺ (X = Cl, Br).

While the pristine crystal structure shows a complete delocalization of the charge density distribution (Appendix B, Figure B.8,9), the perturbed systems show strong charge localization. Pb-Pb dimers resulted in strong electron localization matching the lattice deformation, indicative of the formation of Pb₂³⁺ STEL species (Figure 5.7 a, d).²⁸⁻³⁰ In a similar way, shortening Cl-Cl and Br-Br distances resulted in strong hole localization, consistent with the formation of the V_k centres Cl₂⁻ and Br₂⁻ (Figure 5.7 b, e). Hole localization was also observed on Pb²⁺ sites, which can be partially oxidized to Pb³⁺ causing the

shortening of the related Pb-X distances around the localization point due to the increased positive charge (Figure 5.7 c, f); a similar case is typical of AgCl where tetragonal distortion is induced by hole localization at Ag^+ sites.³⁸ Therefore, two independent STH species were identified from the calculations: X_2^- and Pb^{3+} . Moreover, the same set of self-trapped species was observed both in (EDBE)PbCl₄ and (EDBE)PbBr₄, regardless the different orientation of the perovskite ($\langle 100 \rangle$ vs $\langle 110 \rangle$).

5.6.2 Polaron simulation from perovskite molecular clusters

To strengthen the model and obtain the actual polaron size upon charge addition (or removal) to the material, calculations were repeated by using a different approach based on a perovskite molecular cluster. This was modelled starting from the experimental crystal structures of (EDBE)PbX₄ and taking a single inorganic slab surrounded by EDBE²⁺ cations. The outer ammonium head of EDBE²⁺ was then modified to an amine moiety, and the cluster was generated according to the scheme $6n_{\text{Pb}} = n_{\text{X1}} + 2n_{\text{X2}}$ and $2n_{\text{Pb}} + n_{\text{EDBE}} = n_{\text{X1}} + n_{\text{X2}}$ to ensure electroneutrality. Here, n indicates the number of corresponding unit, while X1 and X2 are halogen atoms bonded to one or two Pb atoms, respectively. To simplify the cluster and make it less computationally demanding, the organic molecule was then shortened to CH_3NH_3^+ units, so that structures with formula up to $(\text{CH}_3\text{NH}_3)_{52}\text{Pb}_{21}\text{Cl}_{94}$ and $(\text{CH}_3\text{NH}_3)_{31}\text{Pb}_{12}\text{Br}_{55}$ were finally obtained. The calculated charge densities of the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and the polaron charge (spin) density are shown in Figure 5.8. Compared to the fully delocalized neutral cluster, the removal of one electron induces charge localization at one Pb^{2+} site and in the halides of the first coordinating sphere (consistent with the Pb^{3+} species predicted by the perturbative method): the increased Coulomb attraction also causes a shortening of the Pb-X bond lengths, which for the case of the chloride perovskite corresponds to a shrinkage from

2.95 to 2.69 Å. On the other hand, addition of one electron results in localization of the charge density over two neighbours lead atoms, indicative of the Pb_2^{3+} STEL; electron localization also causes a relaxation of the lattice with the expansion of the Pb-X bonds (from 2.96 to 4.23 Å for Pb-Cl) around the localization site. In any case, charge delocalization spanned between one lead atom and the nearest neighbour halides, with a typical radius $r \sim 6$ Å which allows to identify these as “small polarons”.

Figure 5.8 HOMO-LUMO and polaron charge (spin) densities for a) the $(\text{CH}_3\text{NH}_3)_{52}\text{Pb}_{21}\text{Cl}_{94}$ and b) $(\text{CH}_3\text{NH}_3)_{31}\text{Pb}_{12}\text{Br}_{55}$ clusters.

Furthermore, the estimate of the effective polaron size also allowed determining the polaron binding energy (E_{polaron}) from the energy difference between the neutral and charged clusters. The positive polaron energies were 884 and 392 meV for the chloride and bromide perovskite respectively, while negative polarons resulted in 1240 and 1041 meV for $(\text{CH}_3\text{NH}_3)_{52}\text{Pb}_{21}\text{Cl}_{94}$ and $(\text{CH}_3\text{NH}_3)_{31}\text{Pb}_{12}\text{Br}_{55}$. Despite overestimating the experimental values, such high polaron relaxation energies are in agreement with the large Stokes shift characteristic of the white-light emission of these materials, and further confirm that the inorganic framework undergoes significant structural deformations upon generation of positive or negative polarons.

5.7 Exciton relaxation model

Based on the experimental results and *ab initio* simulations, it is possible to draw the exciton relaxation model sketched in Figure 5.9 a, b to explain the origin of white-light luminescence in (EDBE)PbX₄.

Figure 5.9 Schematic exciton relaxation diagram for a) (EDBE)PbCl₄ and b) (EDBE)PbBr₄.

Free Wannier-Mott excitons are formed by photoexcitation of the material, where they are confined in the inorganic wells and undergo fast localization converting into polaronic excitons: the partial charge screening caused by the trapping reduces of the exciton binding energy of the polaronic species down to 100-150 meV (according to the activation energy derived in Appendix B, Figure B.4). These polaronic excitons consist of a set of three species divided in self-trapped electrons (STEL, Pb₂³⁺), and self-trapped holes (STH, Pb³⁺ and X₂⁻) identifying intra-gap emissive states with relative energies $E_{X_2^-}^{STH} < E_{Pb^{3+}}^{STH} < E_{Pb_2^{3+}}^{STEL}$ (Appendix B, Figure B.10) associated to the emissive components W1, W2 and W3 (Figure 5.9 a, b). The characteristic photoexcitation properties of these compounds also suggest that excitation of high-energy inter-band

transitions might open alternative non-radiative relaxation pathways and disfavour the formation of polaronic species. It is possible to note that hole trapping is favoured at lower temperature in comparison to electron trapping, leading to the apparent red-shift of the photoluminescence; this observation is in agreement with previous results predicting smaller localization energy for holes compared to electrons in alkali halides.³⁹ The strong electron phonon coupling characteristic of polaronic species is responsible for the large Stokes shift as well as for the photoluminescence line broadening. In this scheme, the organic cation is not actively involved in the self-trapping mechanism, but indirectly affects the polaron formation by inducing quantum confinement in the layered structure and enhancing charge-phonon coupling in the layered system.

We think the proposed model may not be limited to layered perovskites, but could apply to other perovskites with reduced dimensionality (e.g. 1D and 0D) or structures where lattice distortions are induced by physical (hydrostatic pressure) or chemical means (compositional and structural engineering).

5.8 Conclusions

The origin of white-light emission in 2D perovskites (EDBE)PbX₄ (X = Cl, Br) was systematically studied by combining temperature dependent and time resolved spectroscopic measurements with *ab initio* simulations. The study allowed to formulate an exciton relaxation model where a set of polaronic excitons (Pb₂³⁺, Pb³⁺, and X₂⁻, where X = Cl, Br) define the emissive intra-gap trap states responsible for the emission of ultrabroadband, white-light and highly Stoke shifted luminescence. Computationally intensive simulations performed on perovskite molecular clusters allowed a quantitative study of these species, identifying them as small polarons (effective radius $r \sim 6 \text{ \AA}$) localized over a distance of 1-2 lattice sites.

These findings point to the importance of charge-phonon interactions in the deformable lattice of hybrid perovskites, where structural distortions play a fundamental role in determining the characteristic optoelectronic response. The proposed model may apply not only to layered perovskites, but also to other low dimensional perovskites (e.g. 1D and 0D), assisting the synthetic design of novel materials with improved emissive properties for applications in light emitting devices.

References

- [1] E. R. Dohner, A. Jaffe, L. R. Bradshaw, H. I. Karunadasa. *Journal of the American Chemical Society*. **2014**, *136*, 13154.
- [2] D. B. Mitzi. *Journal of the Chemical Society, Dalton Transactions*. **2001**, 1.
- [3] T. Kenichiro, T. Takayuki, K. Takashi, U. Kenichi, E. Kazuhiro, U. Tsutomu, A. Keisuke, U. Kazuhito, M. Noboru. *Japanese Journal of Applied Physics*. **2005**, *44*, 5923.
- [4] T. Ishihara In *Optical Properties of Low-Dimensional Materials*, p 288.
- [5] D. B. Straus, S. Hurtado Parra, N. Iotov, J. Gebhardt, A. M. Rappe, J. E. Subotnik, J. M. Kikkawa, C. R. Kagan. *Journal of the American Chemical Society*. **2016**, *138*, 13798.
- [6] R. G. Niemann, A. G. Kontos, D. Palles, E. I. Kamitsos, A. Kaltzoglou, F. Brivio, P. Falaras, P. J. Cameron. *The Journal of Physical Chemistry C*. **2016**, *120*, 2509.
- [7] R. A. Abreu. *Physics Letters A*. **1984**, *100*, 375.
- [8] A. M. A. Leguy, P. Azarhoosh, M. I. Alonso, M. Campoy-Quiles, O. J. Weber, J. Yao, D. Bryant, M. T. Weller, J. Nelson, A. Walsh, M. van Schilfgaarde, P. R. F. Barnes. *Nanoscale*. **2016**.
- [9] Y. Fang, L. Wang, Q. Sun, T. Lu, Z. Deng, Z. Ma, Y. Jiang, H. Jia, W. Wang, J. Zhou, H. Chen. *Scientific Reports*. **2015**, *5*, 12718.

- [10] T. Hu, M. D. Smith, E. R. Dohner, M.-J. Sher, X. Wu, M. T. Trinh, A. Fisher, J. Corbett, X. Y. Zhu, H. I. Karunadasa, A. M. Lindenberg. *The Journal of Physical Chemistry Letters*. **2016**, 7, 2258.
- [11] X. Y. Zhu, V. Podzorov. *The Journal of Physical Chemistry Letters*. **2015**, 6, 4758.
- [12] K. Gauthron, J. S. Lauret, L. Doyennette, G. Lanty, A. Al Choueiry, S. J. Zhang, A. Brehier, L. Largeau, O. Mauguin, J. Bloch, E. Deleporte. *Opt. Express*. **2010**, 18, 5912.
- [13] A. M. Soufiani, F. Huang, P. Reece, R. Sheng, A. Ho-Baillie, M. A. Green. *Applied Physics Letters*. **2015**, 107, 231902.
- [14] F. Maddalena, P. P. Boix, C. Xin Yu, N. Mathews, C. Soci, S. Mhaisalkar In *Organic-Inorganic Halide Perovskite Photovoltaics: From Fundamentals to Device Architectures*; Park, N.-G., Grätzel, M., Miyasaka, T., Eds.; Springer International Publishing: Cham, 2016, p 201.
- [15] C. Wehrenfennig, M. Liu, H. J. Snaith, M. B. Johnston, L. M. Herz. *The Journal of Physical Chemistry Letters*. **2014**, 5, 1300.
- [16] W. Nie, J.-C. Blancon, A. J. Neukirch, K. Appavoo, H. Tsai, M. Chhowalla, M. A. Alam, M. Y. Sfeir, C. Katan, J. Even, S. Tretiak, J. J. Crochet, G. Gupta, A. D. Mohite. *Nat Commun*. **2016**, 7.
- [17] A. J. Neukirch, W. Nie, J.-C. Blancon, K. Appavoo, H. Tsai, M. Y. Sfeir, C. Katan, L. Pedesseau, J. Even, J. J. Crochet, G. Gupta, A. D. Mohite, S. Tretiak. *Nano Letters*. **2016**, 16, 3809.
- [18] G. Borstel, R. I. Eglitis, E. A. Kotomin, E. Heifets. *physica status solidi (b)*. **2003**, 236, 253.
- [19] V. S. Vikhnin, R. I. Eglitis, S. E. Kapphan, G. Borstel, E. A. Kotomin. *Physical Review B*. **2002**, 65, 104304.
- [20] J. L. Bredas, G. B. Street. *Accounts of Chemical Research*. **1985**, 18, 309.
- [21] A. J. Heeger. *The Journal of Physical Chemistry B*. **2001**, 105, 8475.

- [22] In *Collected Papers of L.D. Landau*; Haar, D. T., Ed.; Pergamon: 1965, p 67.
- [23] R. T. Williams, K. S. Song. *Journal of Physics and Chemistry of Solids*. **1990**, *51*, 679.
- [24] N. F. Mott, A. M. Stoneham. *Journal of Physics C: Solid State Physics*. **1977**, *10*, 3391.
- [25] A. N. Jette, T. L. Gilbert, T. P. Das. *Physical Review*. **1969**, *184*, 884.
- [26] M. Iwanaga, T. Hayashi. *Journal of Luminescence*. **2003**, *102–103*, 663.
- [27] M. Kitaura, H. Nakagawa. *Journal of Luminescence*. **1997**, *72–74*, 883.
- [28] S. V. Nistor, D. Schoemaker. *physica status solidi (b)*. **1995**, *190*, 339.
- [29] M. Iwanaga, J. Azuma, M. Shirai, K. Tanaka, T. Hayashi. *Physical Review B*. **2002**, *65*, 214306.
- [30] S. V. Nistor, E. Goovaerts, D. Schoemaker. *Physical Review B*. **1993**, *48*, 9575.
- [31] H. Toyoharu, F. Toshiaki, K. Yukio. *Japanese Journal of Applied Physics*. **1993**, *32*, 4674.
- [32] M. Iwanaga, M. Shirai, K. Tanaka, T. Hayashi. *Physical Review B*. **2002**, *66*, 064304.
- [33] W. Känzig. *Physical Review*. **1955**, *99*, 1890.
- [34] T. G. Castner, W. Känzig. *Journal of Physics and Chemistry of Solids*. **1957**, *3*, 178.
- [35] V. Babin, A. Krasnikov, M. Nikl, A. Stolovits, S. Zazubovich. *physica status solidi (b)*. **2002**, *229*, 1295.
- [36] R. Kink, T. Avarmaa, V. Kisand, A. Lõhmus, I. Kink, I. Martinson. *Journal of Physics: Condensed Matter*. **1998**, *10*, 693.
- [37] G. Liidja, V. Plekhanov. *Journal of Luminescence*. **1973**, *6*, 71.
- [38] I. Pelant, J. Valenta *et al.* *Luminescence Spectroscopy of Semiconductors*; OUP Oxford, 2012.
- [39] J. H. Crawford, L. M. Slifkin *et al.* *Point Defects in Solids: General and Ionic Crystals*; Springer US, 2013.

Chapter 6*

Role of structural deformations on bandgap tuning and photoluminescence broadening of 2D perovskites

This Chapter shows how structural deformations of the inorganic framework, induced by the templating action of the organic cation, affect the energetic landscape and defectivity of the material. By selecting iodide perovskites with different structural properties, $(\text{NBT})_2\text{PbI}_4$ and $(\text{EDBE})\text{PbI}_4$, we show that the combination of orientation of perovskite's sheet and octahedral distortion lowers the formation energy of emissive colour centres, leading to photoluminescence broadening in highly distorted systems. On the other hand, octahedral tilting and connectivity directly affect the perovskite bandgap and allow tuning the narrowband excitonic emission, originating the characteristic thermochromism of the multidimensional series $(\text{NBT})_2(\text{MA})_{n-1}[\text{Pb}_n\text{I}_{3n+1}]$.

*This section published substantially as reference:

D. Cortecchia, S. Neutzner, A. R. S. Kandada, E. Mosconi, D. Meggiolaro, F. De Angelis, C. Soci, A. Petrozza, *J. Am. Chem. Soc.* **2017**, 139 (1), 39–42

6.1 Introduction

In Chapter 4 it was shown how optical properties of perovskites can be tuned using active organic functional cations, while Chapter 5 has highlighted the role of local lattice distortion of the inorganic framework in the formation of intra-gap polaronic emissive states. In this Chapter, the importance of the templating cation to control the structural motif of the inorganic lattice and its effects on the optoelectronic properties of the material are further discussed.

The role of structural distortions in traditional inorganic perovskites (e.g. oxide perovskites) is known to influence the energetic landscape of the material as well as properties such as piezo- and ferro-electricity and superconductivity. These strongly depend on octahedral tilting, elongation or compression correlated to the characteristic X-B-X and B-X-B bond angles. In the case of hybrid perovskites, these effects have been studied theoretically in 3D and tin-based layered perovskites, however their influence on the luminescence properties of 2D lead perovskites has barely been investigated.

The following discussion shows that distortions of the octahedral coordination lowers the formation energy for self-trapped species and control the interplay between narrowband (free excitonic) emission versus broadband (polaronic) luminescence in 2D perovskites. On the other hand, octahedral tilting and connectivity affect the perovskite band structure and play a key role in the fine tailoring of the perovskite bandgap which can be exploited to synthesize thermochromic materials with phase transition close to room temperature.

6.2 Tailoring structural properties of 2D perovskites

Two iodide-based perovskites with different structural properties were synthesized by carefully selecting the organic templating cations: *n*-butylammonium (NBT) and 2,2-(ethylenedioxy)bis(ethylammonium) (EDBE), having one and two ammonium binding moieties, respectively (see structures in

Figure 6.1). These cations direct the crystal growth along different orientations, originating the $\langle 100 \rangle$ -oriented $(\text{NBT})_2\text{PbI}_4$ and the $\langle 110 \rangle$ -oriented $(\text{EDBE})\text{PbI}_4$, with characteristic planar and zig-zag motif of the inorganic layers (Figure 6.1). Moreover, the two cations were chosen with similar linear chains and with adequate length to guarantee a comparable interplanar distance between the perovskite sheets ($8.6 \text{ \AA}$ and $9.4 \text{ \AA}$ for NBT and EDBE perovskite, respectively). XRD measurements performed on perovskite films confirmed their monoclinic and orthorhombic room temperature phases (Appendix C, Figure C.1), in agreement with previous structural reports.^{1,2}

Figure 6.1 Crystal structures of the a) $\langle 100 \rangle$ -oriented $(\text{NBT})_2\text{PbI}_4$ ¹ and b) $\langle 110 \rangle$ -oriented $(\text{EDBE})\text{PbI}_4$ perovskite,² and structure of the cations NBT=*n*-butylammonium and EDBE=2,2-(ethylenedioxy)-bis(ethylammonium).

The structural properties of these two archetype structures were studied by Raman spectroscopy on perovskite single crystals as well as on crystals of the iodide salts of their corresponding organic precursors, $(\text{NBT})\text{I}$ and $(\text{EDBE})\text{I}_2$. In the low-frequency region ($80\text{--}300 \text{ cm}^{-1}$, Figure 6.2 a, b) four bands are identified similar to the case of MAPbI_3 ,³ and the same features were confirmed also in perovskite thin films (Appendix C, Figure C.2). The comparison with the 3D iodide perovskite allowed us to assign specific vibrational modes to each

component: the modes at 99 cm^{-1} is related to the Pb-I bond stretching,^{3,6} while the three higher energy modes are related to vibrations of the -NH_3^+ groups interacting with the inorganic scaffold. These are distinguished in librations ($116\text{-}118\text{ cm}^{-1}$ and 136 cm^{-1}) and torsions of the ammonium heads (183 cm^{-1}).^{3,5} The Raman spectrum of $(\text{NBT})_2\text{PbI}_4$ resembles very closely the one of MAPbI_3 : here the peak at 99 cm^{-1} is dominant, while it is much weaker in $(\text{EDBE})\text{PbI}_4$. We therefore attribute the partial quenching of the Pb-I vibrations with the increased I-Pb-I angular distortion in the $\langle 110 \rangle$ -oriented perovskite (see Paragraph 3.5 and Figure 3.9). In a similar way, the mode around 136 cm^{-1} is partially weakened, while the one at 183 cm^{-1} is totally quenched: this observation can be explained with a higher degree of conformational constraint in $(\text{EDBE})\text{PbI}_4$, where the ammonium heads are enclosed within the inorganic framework mutually affecting its structural properties due to their strong interaction through second-sphere coordination hydrogen bonding.⁷

The high frequency Raman signal ($300\text{-}1500\text{ cm}^{-1}$, Figure 6.2 c, d) provides useful information on the vibrational modes characteristic of the organic part,⁴ involving CCN and CCC deformations, $\text{CH}_2\text{-CH}_2$ stretching and CH_2 rocking, wagging and twisting.⁸ Figure 6.2 c, d show the characteristic vibrational spectrum of the two perovskites (black lines) compared to that of their corresponding organic precursors $(\text{NBT})\text{I}$ and $(\text{EDBE})\text{I}_2$. While NBT^+ retains the same vibrational modes in the iodide salt and in the perovskite lattice (except for changes in their relative intensity, see Figure 6.2 c). On the other hand, the vibrational spectrum of EDBE^{2+} shows significant differences between $(\text{EDBE})\text{I}_2$ and $(\text{EDBE})\text{PbI}_4$, with new modes arising when embedded in the perovskite lattice (indicated by black arrows in Figure 6.2 d). We suggest that such differences derive from the constraint of the organic molecule forced in a different conformation in the $\langle 110 \rangle$ -perovskite framework, and strongly interacting with the Pb-I network.

Figure 6.2 a,b) Low-energy and c,d) high-energy Raman vibrational modes of a,c) (NBT)₂PbI₄ and b,d) (EDBE)PbI₄. The new active modes of EDBE²⁺ appearing upon perovskite formation are indicated by black arrows.

6.3 Structure-induced broadband photoluminescence

Such structural differences have deep implications on the optical properties as shown in Figure 6.3. Firstly, the absorption onset is strongly blue shifted (44 nm) in the case of (EDBE)PbI₄ having excitonic absorption peaked at 469 nm, compared to that of (NBT)PbI₄ peaking at 513 nm: this absorption shift can be

considered a fingerprint of the structural properties specific of the $\langle 100 \rangle$ and $\langle 110 \rangle$ -oriented perovskites. Upon photoexcitation, (NBT)PbI₄ results in a single peak (517 nm) narrowband emission with only 4 nm Stokes shift and full width at half maximum (FWHM) of 25 nm, which contrasts with the larger bandwidth (FWHM=70 nm) of the (EDBE)PbI₄ photoluminescence characterized by a double peak at 483 nm and 507 nm (indicated as P1 and P2 band in Figure 6.3 b, respectively). Such bands could be individually resolved only in very thin films, because luminescence reabsorption causes the partial quenching of P1 originating a unique broad, featureless band (Appendix C, Figure C.2). Since the absolute photoluminescence quantum yield was rather low (<1%, with (EDBE)PbI₄ being less emissive than (NBT)₂PbI₄) it was possible to measure a reliable luminescence power dependence (Figure 6.3 c-f) only in thick films, where the emissive component P1 of the EDBE perovskites could not be individually resolved; therefore, Figure 6.3 d shows only the trend of the P2 band. The relative PLQY of the two materials shows opposite dependence on excitation density, both in thin films and single crystals (Appendix C, Figure C.3): the luminescence intensity of the NBT perovskite, characteristic of band-to-band recombination, increases with excitation density until reaching a maximum and then decreases due to the onset of Auger recombination at high excitation densities (Figure 6.3 e). On the other hand, the P2 band of (EDBE)PbI₄ is characterized by a monotonic decrease (Figure 6.3 f), consistent with the presence of electronic states whose occupation probability reduces at higher excitation densities. This behaviour suggests that the luminescence is mediated by formation of intra-gap trap states, as previously observed also in 3D perovskites,⁹⁻¹² and indicates that (EDBE)PbI₄ is more prone to the photoinduced formation of a higher concentration of emissive colour centres.

Figure 6.3 a,b) Steady state PL and absorption spectra, c,d) power dependent PL maps and relative photoluminescence quantum yield (PLQY) as function of the excitation density for (NBT)₂PbI₄ (left panels) and (EDBE)PbI₄ (right panels).

Temperature dependent photoluminescence further confirms this behaviour. (NBT)₂PbI₄ undergoes a complex evolution which involves a sharp blue-shift of the excitonic emission around 280 K due to a phase transition (see Paragraph 6.2.1), after which it maintains a preferentially narrowband emission with

appearance of an additional band at 555 nm and a broader emission peaked at 600 nm becoming significant only below 125 K. On the other hand, the (EDBE)PbI₄ photoluminescence is characterized by a much more severe band broadening at low temperature, leading to an exceptionally broad PL emission throughout the whole visible range which, at 78K, approaches the white light emission of the chloride and bromide compounds of the series (see Chapter 5): this is in agreement with the higher concentration of emissive colour centres induced by the specific structural distortions of (EDBE)PbI₄. Moreover, the emission intensity increases at low temperature: this behaviour may result from the reduction of phonon assisted quenching at low T and consequent enhancement of the radiative recombination channels.

Figure 6.4 Temperature dependent photoluminescence maps of a) (EDBE)PbI₄ and b) (NBT)₂PbI₄.

6.4 Formation of colour centres in distorted structures

To determine the interplay between perovskite structure and photoluminescence broadening, we quantified the structural distortion in the two structures in terms of octahedral distortion of the PbI₆ units of the inorganic lattice, which can involve deviations from the ideal octahedral geometry of Pb-X bond lengths (d), X-X distances between neighbour halides, X-Pb-X bond angles and octahedral volume (V).¹³ Following a method proposed by Robinson et al.,¹⁴ we calculated

the octahedral elongation λ_{oct} and octahedral angle variance σ_{oct}^2 according to the equations:

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

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

where d_i are the Pb-X bond lengths, d_0 is the center-to-vertex distance of a regular polyhedron of the same volume and α_i are the X-Pb-X angles. Calculation details are described in the experimental section (Paragraph 3.5). It appears that the increased deviation from the ideal octahedral coordination of (EDBE)PbI₄ ($\lambda_{\text{oct}} = 1.0058$; $\sigma_{\text{oct}}^2 = 14.2$) compared to (NBT)₂PbI₄ ($\lambda_{\text{oct}} = 1.0016$; $\sigma_{\text{oct}}^2 = 5.6$) follows well the broadening of its photoluminescence. This observation was further supported by comparing the octahedral distortion factors for different reported perovskite structures, which empirically showed that perovskites with highly distorted octahedral coordination (such as (EDBE)PbCl₄ and (EDBE)PbBr₄) are characterized by white light emission, while more ideal structures tends to show narrowband luminescence (see Figure 3.9, Chapter 3).

Based on this consideration, we performed ab-initio calculations to elucidate the impact of the structural distortions on the defect formation energy of the material. The simulations were performed on both perfect ideal structures, as well as defective structures considering the presence of iodide interstitials (I_i), iodide vacancies (V_i) and lead vacancies (V_{Pb}) (Appendix C, Figure C.4 and Table C.1).¹⁵ In the case of neutral lead vacancies two scenarios were found, one involving the formation of an I_3^- trimer close to a lead vacancy upon movement of an iodide toward a V_{Pb} vacancy (Figure 6.5 a), and a second where the lead vacancy remains in the site of Pb removal (Figure 6.5 b), in analogy with the stable configuration obtained for 2- and 1- charged states.^{16,17} The energetics of the two configurations strongly depend on the perovskite structure, and are iso-energetic in (NBT)₂PbI₄, while (EDBE)PbI₄ strongly favours the formation of I_3^- trimers by as much as 1 eV. This structure can be

seen as a particular case of self-trapped holes, in which two holes left from the formation of the lead vacancy V_{Pb} upon Pb removal cause the oxidation of two neighbours iodides and consequently localize in the trimer species I_3^- ; this generates a type of defect, previously studied in alkali halides such as lithium fluoride, which couples a V-centre with a vicinal cation vacancy. These are generally treated as “the antimorph of an F centre” which involves electron trapping stabilized by an anion vacancy, and are indicated as V_F centres.^{18,19}

Figure 6.5 Structure of a) (EDBE)PbI₄ and b) (NBT)₂PbI₄ with neutral vacancy and c) isodensity diagram of the I_3^- defect centre in the corresponding density of states of (EDBE)PbI₄.

The particular $\langle 110 \rangle$ -orientation of (EDBE)PbI₄ is characterized by the presence of two undercoordinated iodide atoms at the interface with the organic layers, where their negative charge is only in part counterbalanced by the EDBE²⁺ cations: this specific structural arrangement provides extra flexibility for atomic displacement necessary for the formation of iodide trimers. On the other hand, the $\langle 100 \rangle$ structure of (NBT)₂PbI₄ is characterized by PbI₆ octahedra which expose only one terminal iodide anion for each organic molecule: this creates an electrostatic barrier which prevents the atomic displacement necessary for the formation of the iodide trimers, making their formation energetically unfavourable. The perovskite band structure was then evaluated by means of hybrid density functional theory calculations (DFT) including the spin-orbit coupling (PBE-SOC),¹⁷ which resulted in a simulated bandgap of 2.83 eV for the ideal (EDBE)PbI₄, in good agreement with the experimental energy of its excitonic absorption considering the high exciton binding energy characteristic of layered perovskites.

Figure 6.6 Simulated absorption spectrum of (EDBE)PbI₄, with neutral structure and including lead vacancies.

When lead vacancies are introduced in the material (V_{Pb}), two additional states are found within the band gap, having energies of 0.16 eV above the valence band, and 0.05 eV below the conduction band, with one of them being occupied and the other unoccupied (Figure 6.5 c). Calculations of the corresponding absorption spectrum reveals the presence of an electronic transition at 2.92 eV. This is just 0.21 eV below the main band-edge absorption and can be assigned to the HOMO-LUMO transitions of the I_3^- species, with an absorption cross section of about 0.25% of the main band-to-band transition (Figure 6.6). Therefore, it is possible to correlate the formation of such intra-gap states with the appearance of Stokes-shifted, broadband luminescence assuming a typical relaxation scheme of self-trapped charges (see also discussion in Chapter 5).^{20,21} Their formation is allowed by the structural motif induced by the templating cation, also resulting in stronger distortion of the octahedral coordination in the $\langle 110 \rangle$ -oriented perovskite which lowers the formation energy of V_F colour centres in (EDBE)PbI₄.

6.5 Band-gap engineering through Pb-I-Pb bond angle distortion

6.5.1 Octahedra tilting in (NBT)₂(MA)_{n-1}[Pb_nI_{3n+1}] series

The Ruddlesden-Popper series (NBT)₂(MA)_{n-1}[Pb_nI_{3n+1}] was used to further study the effect of Pb-I-Pb angle on the perovskite's optical properties. Here, the 2D perovskite (NBT)₂PbI₄ corresponds to the n=1 member of the series, while the multidimensional n=2 perovskite corresponds to (NBT)₂(MA)[Pb₂I₇]. Temperature dependent X-ray powder diffraction (XRPD) performed by heating the material from 93K to 298K revealed the presence of a phase transition in (NBT)₂PbI₄ starting around 270 K, while two phase transitions were found for (NBT)₂(MA)[Pb₂I₇] occurring at T₁~280K and T₂~190K. Such transitions appear evident in the wide-angle X-ray scattering (WAXS) measurements shown in Figure 6.7a, b, as well as in the small-angle X-ray scattering (SAXS) where the shift of the 001 diffraction peak around 4.7° can

be probed (Appendix C, Figure C.5). The phase transitions at T_1 were also confirmed by measuring differential scanning calorimetry in the range 170-300K (Appendix C, Figure C.6).

Figure 6.7 Temperature dependent wide angle X-ray scattering (WAXS) of a) $(\text{NBT})_2\text{PbI}_4$ and b) $(\text{NBT})_2(\text{MA})[\text{Pb}_2\text{I}_7]$.

Pawley fits of powder diffraction patterns by using the reference structures reported by D. G. Billing *et al*¹ confirm that, upon transition, $(\text{NBT})_2\text{PbI}_4$ retains the same orthorhombic crystal structure and space group (P_{bca}) but

undergoes a slight modification of the unit cell parameters with a shrinkage along the *a*, *c* axis and elongation of the *b* axis (Appendix C, Figure C.7). This is caused by the tilting of PbI_6 octahedra respect to the *ab* plane (Figure 6.8 a, b), with a change in Pb-I-Pb average angle from 155° to 149° for the high and low temperature phase, respectively. Despite the strong tilting, the low temperature phase maintains a close-to-ideal geometry of the octahedral coordination with values $\lambda_{\text{oct}}=1.0018$; $\sigma_{\text{oct}}^2=6.2$ which well compares to those of the room temperature phase ($\lambda_{\text{oct}}=1.0016$; $\sigma_{\text{oct}}^2=5.6$).

Figure 6.8 Crystal structures of $(\text{NBT})_2\text{PbI}_4$ at a) 293K and b) 223K.¹ Crystal structures of $(\text{NBT})_2(\text{MA})[\text{Pb}_2\text{I}_7]$ at c) 293K²⁰ and d) 100K (determined in this work).

To verify the changes involved in the phase transition of $(\text{NBT})_2(\text{MA})[\text{Pb}_2\text{I}_7]$, the structure of the lowest temperature phase was determined by single crystal X-ray diffraction at 100K and compared to the room temperature phase determined by C.C Stoumpos *et al.*²⁰ Differently from $(\text{NBT})_2\text{PbI}_4$, the $n=2$ compound of the series undergoes an important structural reorganization, with a lowering of the symmetry from orthorhombic structure (Cc2m) of the room temperature phase to the triclinic structure (P-1) of the low temperature phase (100K) (Figure 6.8 c, d and Appendix C, Figure C.7). Also in this case, the perovskite is subject to a tilting of the octahedra (in the ac and bc plane for the high and low temperature phase, respectively) leading to the distortion of the Pb-I-Pb average angle from 168° to 163° . Here, the octahedra are interconnected by sharing the corners in equatorial position and one corner in apical position having a bridging Pb-I-Pb bond angle of 158° . The structural details of the $(\text{NBT})_2(\text{MA})[\text{Pb}_2\text{I}_7]$ phase at 100K obtained from the single crystal structure refinement are listed in Appendix C, Table C.2.

6.5.2 Thermochromism of $(\text{NBT})_2(\text{MA})_{n-1}[\text{Pb}_n\text{I}_{3n+1}]$ series

The band structures of the room temperature and low temperature phases were calculated through *ab-initio* simulations from the experimental crystal structures and optimized atomic coordinates. For the $n=1$ compound, the simulations predict the increases of the band-gap from 2.29 to 2.36 eV (Figure 6.9 a, b). The same trend is found in the multidimensional $n=2$, with calculated band-gaps of 1.49 eV and 2.00 eV for the phase at 298 K and 100 K, respectively (Figure 6.9 c, d). The overall band-gap narrowing in $(\text{NBT})_2(\text{MA})[\text{Pb}_2\text{I}_7]$ compared to NBT_2PbI_4 is related to the increased exciton delocalization in the inorganic wells of the multidimensional perovskite and reduced quantum confinement. Nevertheless, the increased octahedral tilting always causes a widening of the bandgap in both the perovskites, in line with previous studies on Sn-based two-dimensional perovskites.²¹

Figure 6.9 Calculated Electronic bands at GGA-PBE level of a,b) $(\text{NBT})_2\text{PbI}_4$ and $(\text{NBT})_2(\text{MA})[\text{Pb}_2\text{I}_7]$ at room and low temperature.

According to the DFT simulations, the structural distortions induced by the phase transitions are expected to originate strong thermochromic effects in the series $(\text{NBT})_2(\text{MA})[\text{Pb}_2\text{I}_7]$. Indeed, this was confirmed by temperature dependent absorption measurements, which reveal a sharp orange to yellow transition for $(\text{NBT})_2\text{PbI}_4$ involving a remarkable blue-shift of the bandgap as well as of the excitonic absorption from 513 nm to 490 nm (see Figure 6.10 a, b). At 275 K, the coexistence of the two phases can be inferred from the low-energy sideband of the excitonic peak, well matching the phase transition expected from XRD and DSC measurements. On the other hand, the red perovskite $(\text{NBT})_2(\text{MA})[\text{Pb}_2\text{I}_7]$ shows a less marked transition (Figure 6.10 c, d), which is probably a consequence of the increased connectivity of the lead halide framework. Here, the excitonic absorption blue-shifts of only 4 nm, from 571 nm at 298 K to 567 nm of the lowest temperature phase (100 K). Notably,

the first transition at $T_1 \sim 280\text{K}$ results in an evident shift of the excitonic band, while no clear discontinuity in the evolution of the absorption peak is found in correspondence of the second transition at $T_2 \sim 190\text{K}$, suggesting similar structural properties between the lowest and intermediate temperature phases. Structure determination of the intermediate $(\text{NBT})_2(\text{MA})[\text{Pb}_2\text{I}_7]$ phase is currently ongoing to confirm this hypothesis.

Figure 6.10 Temperature dependent absorption of a,b) $(\text{NBT})_2\text{PbI}_4$ and c,d) $(\text{EDBE})\text{PbI}_4$.

Ultimately, the octahedra connectivity in terms of Pb-I-Pb bond angle can be a useful engineering tool to tailor the perovskite optoelectronic properties. Figure 6.11a shows the temperature dependent photocurrent map measured on an NBT_2PbI_4 film under applied bias of 10V. Despite the high exciton binding energy typical of 2D perovskites, it is possible to extract photocarriers from the layered perovskite and modulate its photo-response at different temperatures by

controlling the Pb-I-Pb bond angle distortion. The photoresponsivity of the material traces well the perovskite absorption, reproducing both the excitonic feature and absorption continuum and the overall blue-shift upon phase transition. In a similar way, the temperature dependence of the excitonic photoluminescence follows the evolution of the excitonic absorption, with the emission peak shifting from 517 nm to 492 nm (Figure 6.11b). Interestingly, upon phase transition the photoluminescence spectrum does not broaden (FWHM are 25 and 15 nm at 298 K and 278 K, respectively). Considering the negligible difference in the octahedra distortion factors in the two phases, this indicates that the increased distortion of the Pb-I-Pb angle mainly affects the band-gap width, but does not lower the defect formation energy in this iodide-based perovskite (e.g. I_3^- colour centres).

Figure 6.11 Temperature dependent a) photocurrent and b) photoluminescence measured on $(\text{NBT})_2\text{PbI}_4$ films.

6.6 Conclusions

In this chapter, the relationships between structure and optoelectronic properties

in 2D perovskites have been presented. Different factors contribute to shape the energetic landscape of the perovskite, including its specific orientation, octahedral distortion and octahedral connectivity (Pb-I-Pb bond angles). Strong deformation of the octahedral coordination, easily induced in $\langle 110 \rangle$ -oriented perovskites, lowers the defect formation energy and eases the charge self-trapping process, leading to photoluminescence broadening. This is exemplified by the formation of I_3^- colour centres in (EDBE)PbI₄. On the other hand, Pb-I-Pb bond angle distortions have a major effect on the band-gap width and are responsible for the characteristic thermochromism in the perovskite series (NBT)₂(MA)_{n-1}[Pb_nI_{3n+1}]. The phase transition of this system, occurring near room temperature, makes it very attractive for the design of optical switches for applications in optoelectronic and perovskite-based metamaterials. Overall, these studies highlight the importance of structural engineering to achieve full control on the perovskite optoelectronic properties, and may be generalized to the case of other perovskites with different dimensionalities.

References

- [1] D. G. Billing, A. Lemmerer. *Acta Crystallographica Section B*. **2007**, 63, 735.
- [2] E. R. Dohner, A. Jaffe, L. R. Bradshaw, H. I. Karunadasa. *Journal of the American Chemical Society*. **2014**, 136, 13154.
- [3] C. Quarti, G. Grancini, E. Mosconi, P. Bruno, J. M. Ball, M. M. Lee, H. J. Snaith, A. Petrozza, F. D. Angelis. *The Journal of Physical Chemistry Letters*. **2014**, 5, 279.
- [4] F. Brivio, J. M. Frost, J. M. Skelton, A. J. Jackson, O. J. Weber, M. T. Weller, A. R. Goñi, A. M. A. Leguy, P. R. F. Barnes, A. Walsh. *Physical Review B*. **2015**, 92, 144308.

- [5] R. Gottesman, L. Gouda, B. S. Kalanoor, E. Haltzi, S. Tirosh, E. Rosh-Hodesh, Y. Tischler, A. Zaban, C. Quarti, E. Mosconi, F. De Angelis. *The Journal of Physical Chemistry Letters*. **2015**, 6, 2332.
- [6] M. A. Pérez-Osorio, R. L. Milot, M. R. Filip, J. B. Patel, L. M. Herz, M. B. Johnston, F. Giustino. *The Journal of Physical Chemistry C*. **2015**, 119, 25703.
- [7] T. Ivanovska, C. Quarti, G. Grancini, A. Petrozza, F. De Angelis, A. Milani, G. Ruani. *ChemSusChem*. **2016**, 9, 2994.
- [8] J. J. C. Teixeira-Dias, L. A. E. B. de Carvalho, A. M. A. da Costa, I. M. S. Lampreia, E. F. G. Barbosa. *Spectrochimica Acta Part A: Molecular Spectroscopy*. **1986**, 42, 589.
- [9] S. G. Motti, M. Gandini, A. J. Barker, J. M. Ball, A. R. Srimath Kandada, A. Petrozza. *ACS Energy Letters*. **2016**, 726.
- [10] W. Kong, Z. Ye, Z. Qi, B. Zhang, M. Wang, A. Rahimi-Iman, H. Wu. *Physical Chemistry Chemical Physics*. **2015**, 17, 16405.
- [11] S. Neutzner, A. R. Srimath Kandada, G. Lanzani, A. Petrozza. *Journal of Materials Chemistry C*. **2016**, 4, 4630.
- [12] C. Wehrenfennig, M. Liu, H. J. Snaith, M. B. Johnston, L. M. Herz. *APL Mater*. **2014**, 2, 081513.
- [13] N. Thomas. *Acta Crystallographica Section B*. **1989**, 45, 337.
- [14] K. Robinson, G. V. Gibbs, P. H. Ribbe. *Science*. **1971**, 172, 567.
- [15] E. Mosconi, D. Meggiolaro, H. J. Snaith, S. D. Stranks, F. De Angelis. *Energy & Environmental Science*. **2016**, 9, 3180.
- [16] J. M. Azpiroz, E. Mosconi, J. Bisquert, F. De Angelis. *Energy & Environmental Science*. **2015**, 8, 2118.
- [17] M.-H. Du. *The Journal of Physical Chemistry Letters*. **2015**, 6, 1461.
- [18] W. Känzig. *Journal of Physics and Chemistry of Solids*. **1960**, 17, 80.
- [19] C.-t. Kao, L. G. Rowan, L. M. Slifkin. *Physical Review B*. **1990**, 42, 3142.

- [20] C. C. Stoumpos, D. H. Cao, D. J. Clark, J. Young, J. M. Rondinelli, J. I. Jang, J. T. Hupp, M. G. Kanatzidis. *Chemistry of Materials*. **2016**, 28, 2852.
- [21] J. L. Knutson, J. D. Martin, D. B. Mitzi. *Inorganic Chemistry*. **2005**, 44, 4699.

Chapter 7

Conclusions and perspectives

This Chapter concludes the thesis by drawing general guidelines on the luminescence properties of 2D perovskites based on the findings of this thesis work. Implications of our findings for future studies of polaronic characteristics and development of new functional materials are commented. Finally, the impact of these materials for application in X-ray scintillators, solid-state lighting and metamaterials is discussed by presenting our preliminary results and future perspectives.

7.1 Impact and outcomes

Hybrid perovskites are the new frontier for solution-processed optoelectronic devices. Primarily based on self-assembled metal-organic frameworks with tunable composition, 3D perovskites have already set new benchmarks in solution processed photovoltaic and, concurrently, have been rapidly emerging for their exceptional light emitting properties.

Hybrid perovskites with reduced dimensionality, such as two-dimensional perovskites, expand the synthetic versatility of this class of materials, where the combination of different metals, halogens and organic cations allows the fine tailoring of the luminescence properties. The ability of controlling the optoelectronic properties in such perovskite systems through rational synthetic design is conditional to the understanding of the photophysical phenomena underlying their emissive properties in relation to the materials structure.

In this thesis work, we designed several two-dimensional perovskites and used them as model materials for the photophysical study of the interplay between perovskite structure and optoelectronic properties. The following outcomes were achieved:

1. *Crystal engineering of copper-based perovskites incorporating an optoelectronically active functional cation.*^{1,2} The development of lead-free perovskites is highly desirable to find suitable replacement to toxic lead-based materials, however lead-free perovskites for light emitting applications are still largely unexplored. Here, we have shown that the series $\text{MA}_2\text{CuCl}_x\text{Br}_{4-x}$ is characterized by green photoluminescence mediated by Cu^+ trap states. To further tune the luminescence properties while preserving the transport characteristics of the copper halide framework, we adopted a second-sphere coordination approach to design a novel functional perovskite incorporating a blue-emissive organic cation, whose luminescence properties are retained in the final hybrid material. This study set the bases for the tuning of optoelectronic properties of lead-free perovskites by tailoring the functional organic cation,

making copper perovskites an ideal platform to design materials with improved emissive properties.

2. *Elucidation of the white-light emission mechanism in two-dimensional lead-based perovskites.*^{3,4} In these systems, the interplay between excitonic and polaronic properties in relation to the perovskite structure allows, rather uniquely, to tune the luminescence from narrow linewidth to ultra-broad, highly Stoke-shifted “white” emission throughout the entire visible range. Although several 2D Pb-based perovskites with broadband emission have recently been demonstrated, the intrinsic nature of the mechanism underlying broadband luminescence have remained elusive. In this work, we developed an exciton relaxation model based on the formation of intra-gap polaronic emissive states. These involve the formation of self-trapped electrons (STEL: Pb_2^{3+}) and self-trapped holes (STH: Cl_2^- , Br_2^- , Pb^{3+}) responsible for the broadband and Stoke-shifted luminescence. The recent demonstration of white light emission also in perovskites with different dimensionalities suggests that the proposed model is not limited to 2D perovskites, and could be generalized to the whole class of perovskite materials.⁵⁻⁷

3. *Correlation between structural deformations and luminescence properties.*⁸ The careful choice of templating organic cations allows tuning the structural motif as well as the energetic landscape of the inorganic metal-halide framework. The structural properties of 2D perovskite can be rationalized in terms their different orientation, distortion of the PbX_6 octahedral coordination (X-Pb-X angle and Pb-X bond length) and of the octahedral connectivity (Pb-X-Pb bond angle). In this study, we have shown that strong octahedral distortion induced in corrugated $\langle 110 \rangle$ -oriented perovskites strongly affects the material defectivity assisting the formation of self-trapped charges. This is exemplified by the formation of V_F centres in $(\text{EDBE})\text{PbI}_4$, which are responsible for its photoluminescence broadening. On the other hand, we have shown that the Pb-X-Pb angle has a strong impact on the perovskite band-gap and can be exploited to engineer perovskite thermochromic materials with

phase transition close to room temperature. Overall, our conclusions on the impact of structural deformations on the perovskite's optical properties find good agreement with recent studies on broadband emission in low dimensional perovskites from different groups.^{5,9,10}

7.1.1 General trends of (EDBE)PbX₄ series

In this thesis, EDBE²⁺ was chosen as archetype cation because it allows the synthesis of model perovskites with broadband emission but with different structural properties by simply changing the halide. While (EDBE)PbCl₄ is a flat <100> perovskite, (EDBE)PbBr₄ and (EDBE)PbI₄ belong to the corrugated <110> type. The two undercoordinated halide atoms at the organic/inorganic interface characteristic of the <110> type favour the atomic displacement necessary to form X₂⁻ species and V_F centres.

Figure 7.1 Thin film X-ray diffraction patterns and steady state absorption and PL of a,d) (EDBE)PbCl₄; b,e) (EDBE)PbBr₄; c,f) (EDBE)PbI₄.

On the other hand, the halogen also influences the perovskite growth during the spin coating deposition towards specific preferential orientations, as clearly deduced by the few diffraction peaks visible in the thin films diffractograms: while (EDBE)PbCl₄ grows with the inorganic and organic layers parallel to the substrate (revealing only the (001) planes; Figure 7.1 a), both (EDBE)PbBr₄ and

(EDBE)PbI₄ grow with perpendicular orientation, mostly revealing the (*h*00) planes in their XRD patterns (Figure 7.1 b). While the effects of this different orientation were not investigated during this project, it might play an important role from an application perspective, since it is expected to influence the charge transport in the final device as observed in the case of copper perovskites. The octahedral distortion decreases in the series from Cl to I, in relation to the size of the halide (see section 3.5). The increased covalency from Cl to I also causes the redshift of the absorption band edge and excitonic peak from 330 to 470 nm, with the oscillator strength of the excitonic absorption being lower in the <110>-type than in the <100> perovskite (Figure 7.1 d-f). While the Cl and Br based perovskites show ultrabroad white light luminescence, the bandwidth of (EDBE)PbI₄ emission is considerably narrower (Figure 7.1 d-f). Indeed, our model suggests that, at room temperature, the formation of I₃⁻ V_F centres is favoured in the iodide perovskite, differently from (EDBE)PbCl₄ and (EDBE)PbBr₄ where the luminescence is dominated by the formation of Pb₂³⁺, X₂⁻, and Pb³⁺ species. However, the observation of similar ultrabroadband luminescence from (EDBE)PbI₄ below 100K (see Figure 6.4) suggests that the formation of similar polaronic species might dominate at low temperatures also in the iodide perovskite. Overall, these observations indicate that an interplay of multiple factors can affect the energetic landscape for the formation of self-trapped polaronic species: geometrical distortions of the inorganic framework (e.g. octahedral distortions), perovskite type (e.g. <100> vs <110>) and halogen used to assemble the perovskite structure.

7.2 Future work

From a broad fundamental standpoint, our findings highlight the important role of polaron formation in 2D perovskites, and prompt for a wider consideration of polaronic transport in perovskite with different dimensionalities, including 3D structures, with high relevance for both light emitting and photovoltaic applications. This is due to the “soft” nature of the metal halide framework,

highly prone to structural reorganization upon photoexcitation. In line with these considerations, polaron formation in methylammonium lead iodide is recently emerging as characteristic feature of this material.¹¹⁻¹⁴ To validate these models, experimental measurements will need to be performed to show direct evidence of the formation of polaronic species. In the near future, breakthrough results might be obtained combining electron paramagnetic resonance measurements (EPR) and neutron diffraction to probe formation of self-trapped charges and the induced local structural distortions. Infrared photoinduced absorption is also expected to reveal typical infrared active vibrational (IRAV) modes at low-energy spectral regions, characteristic of charged polaronic species,¹⁵ while time resolved photocurrent will allow to probe the polaron formation, relaxation and dynamics in 3D and low dimensional perovskites.

From the synthetic point of view, the main challenge consists in the design of truly functional materials whose final properties are superior respect to the individual characteristic of the separated organic and inorganic parts.¹⁶ Bulkier and highly conjugated cations with improved absorption and emissive properties could be explored in combination to the metal halide scaffold to provide better tunability (up to the red spectral region), luminescence yield and improved charge transport in low-dimensional structures. The interplay between structure and optoelectronic properties highlighted in this thesis will set the bases for the design of more efficient perovskite emitters, with either narrowband or white light emission, by modulation of the defectivity, polaronic and excitonic characteristics. Together with the incorporation of more complex organic cations, metal doping is a possible strategy to improve the perovskite optoelectronic properties, for instance to design 3 and 4 level systems for low-threshold lasers. Lead-free alternatives should also be designed and tested in actual light emitting devices to open up an easier commercialization pathway for perovskite-based technologies.

7.3 Application perspectives of 2D perovskites

In this thesis work, I showed how the luminescence properties of 2D hybrid perovskites can be synthetically tailored by structural design of the material. This approach allows achieving luminescence properties *on demand*, making 2D perovskites extremely attractive for a wide range of applications. The following paragraphs illustrate some first results we have achieved in this direction as well as challenges and future perspectives related to the use of such engineering strategies for the application of low dimensional structures in light emitting devices.

7.3.1 Lead-free vs lead-based perovskites for light emitting diodes (LEDs)

Lead toxicity poses several issues for the future commercialization of perovskite based devices; for example, the EU legislation restricts the use of hazardous substances (including lead) in electrical and electronic equipment, while the U.S. EPA sets low threshold levels for Pb^{2+} content in air and water.^{17,18} To overcome this bottleneck, the investigation of alternative lead-free materials it's a priority.¹⁹ In this dissertation, it was shown that copper perovskites are a valuable platform for the development of new materials with functional organic cations. This material engineering technique is very promising since it allows to tune the luminescence properties *on demand* in the visible spectral region. Moreover, it should be applicable to a various set of different metals beyond copper, and will help to overcome some of the limitations of these lead-free systems. Nevertheless, difficulties in the deposition of these functional materials in form of uniform thin films should be addressed before they become available for fabrication of light emitting devices. Further work will be also needed to experimentally evaluate and improve charge transport properties and luminescence quantum yield of these functional lead-free perovskites.

On the other hand, Pb-based perovskites possess unique optoelectronic properties and can be easily processed in form of smooth thin films or cm-scale single crystals. For example, accurate structural design allows to control the emission energy and bandwidth. While electroluminescent devices of 2D lead perovskites have already shown good efficiencies,²⁰ more work is needed to further improve their performance. In particular, multidimensional perovskites can combine high luminescence quantum yield with good charge transport properties, and might open the way to technologies which are out of reach with the current organic materials, such as electrically pumped lasers.²¹ Moreover, ultrabroadband polaronic emission offers the unique possibility to fabricate white light emitting diodes with a single-phase material, with the final target of achieving solid state lighting devices more efficient, stable and with better colour rendering than traditional incandescent and fluorescent lamps. Recently, D. Yuan *et al* have shown the use of microscale (EDBE)PbBr₄ microcrystals with 18% PLQY as phosphor for downconversion white light emitting diodes by pumping them with a 365 nm UV-LED chip.²² At this stage, the understanding of the origin of broadband emission developed in this thesis will be crucial to guide the chemical synthesis of more efficient emitters with improved colour rendering.

7.3.2 Single crystal X-ray detectors

X-ray detectors find application in scientific research (e.g. crystallography and astronomy) as well as medicine and inspection systems for safety controls.^{23,24} The current technologies are based on expensive materials, which so far has hampered the development of large-area detectors. Hybrid perovskites, thanks to the solution processability and the presence of heavy atoms which enhance their absorption cross section, are promising materials to lower the production costs and enhance the device performance. Two processes can be applied for the realization of X-ray detectors: one is based on the conversion of the incident

radiation into electrical current,^{25,26} while the other relies on the down-conversion of X-ray radiation by means of a scintillating material whose emission is measured by a low-energy photodetector.²⁷ The photon-to-current conversion approach was proven to be successful by using MAPbI₃ and MAPbBr₃ as active materials.²⁸⁻³⁰ Nevertheless, this method suffers from the limited carrier-diffusion length in the active material, which limits the film thickness as well as the responsivity at high energies. X-ray scintillation is an interesting alternative which allows to overcome these transport issues.

Figure 7.2 a-c) Luminescence measured on perovskite single crystals at different temperatures under X-Ray irradiation.³¹ d) Comparison of the temperature dependent light yield for the three different perovskite crystals.³¹

By following the crystal engineering strategies exposed in this thesis, we were able to design a 2D perovskite with ideal properties for X-ray scintillation.³¹

Specifically, compared to the archetype 3D perovskites MAPbI₃ and MAPbBr₃ (Figure 7.2 a, b), the white light emitting 2D dimensional perovskite (EDBE)PbCl₄ benefits of unique properties such as high exciton binding energy and large Stokes-shift, which reduce the negative effect of thermal quenching and the probability of radiation self-absorption. After being able to grow cm-scale crystals with suitable size for X-ray scintillation (Figure 7.2 c), we demonstrated that the white emitter (EDBE)PbCl₄ allows higher luminescence yields in the range 50-298 K (9,000 photons/MeV at room temperature) as compared to the standard 3D perovskites (Figure 7.2 d). Such encouraging performance might be further improved by increasing the luminescence quantum yield of the 2D perovskite through structural design and by doping with lanthanide ions such as Ce³⁺.

7.3.3 Solid-state lighting

Figure 7.3 a) Representation of a light emitting perovskite FET with bottom gate, bottom contact architecture.³² b) Perovskite electroluminescence from the FET channel.³²

Recently, we have demonstrated the fabrication of MAPbI₃ light emitting field effect transistors (LE-FETs) where holes and electrons can be injected in the transistor channel resulting in the observation of electroluminescence (Figure 7.3).³² Such device concept, which favours the lateral charge transport, ideally suits the layered structure of 2D perovskites as demonstrated in the case of Sn-based perovskites.³³ Furthermore, the ability to modulate the interplay between polaronic and excitonic properties through structural design in layered

perovskites would allow the fabrication of light emitting devices with tunable narrowband emission or white light luminescence. Nevertheless, the insulating nature of 2D lead-based perovskites has so far hindered their successful application in FET devices. Further progresses in this direction are expected to come with targeted device engineering to solve charge injection issues at the source/drain electrodes, surface passivation of the FET dielectric and the use of multidimensional layered perovskites to improve the charge transport in the material.

7.3.4 2D Perovskite metasurfaces

By using the standard 3D perovskite methylammonium lead iodide MAPbI_3 we have shown that it's possible to fabricate solution processable, all-dielectric perovskite metasurfaces (Figure 7.4).³⁴ This concept exploits the perovskite as high refractive index dielectric material and modulate its interaction with light by patterning the perovskite film with nanostructures having size comparable to the wavelength of the incident radiation.³⁵⁻³⁷

Figure 7.4 a) Structural colouring of a MAPbI_3 film with nanoslits having different milling depth.³⁴ b) Purcell enhancement of the photoluminescence in the patterned perovskite.³⁴

By nanostructuring the perovskite films with nanogratings and nanoslits (patterned by focused ion beam milling) of different geometry and milling

depth, it was possible to enhance the reflectivity in selected spectral ranges and modulate the colour of the material (Figure 7.4 a). On the other hand, the increased light matter interaction provided by the nanopattern caused the enhancement of the perovskite photoluminescence, a phenomenon known as Purcell effect (Figure 7.4 b).^{38,39} Two dimensional perovskites are extremely attractive for this application, thanks to the unique optical properties and smooth morphology. Our preliminary results have shown that it's possible to nanostructure a white light emitting perovskite or couple the unstructured film to a nanopatterned metallic film to tune the materials colour and selectively enhance the broadband photoluminescence in specific spectral regions: this might ultimately allow the nanofabrication of the film to obtain pixels with different emissive properties from the same material, which is highly attractive for future implementation in light emitting diodes and transistors. Nevertheless, visible refractive index of 2D perovskites is generally lower than 3D perovskites, thus more work will be necessary to improve the resonance quality factor as well as the photoluminescence enhancement factor. In addition, the strong thermochromism observed in some narrowband emitting perovskite, such as (NBT)₂PbI₄, make them very attractive for the fabrication of reconfigurable metamaterials where temperature can be used as a parameter to modulate light-matter interaction by switching the perovskite structure and optical characteristics on demand.

7.4 Conclusions

In this thesis work, we studied the relation between structural and optoelectronic properties of two-dimensional hybrid perovskites, paving the way for their rational synthetic design and application in optoelectronic devices. Exploiting their great synthetic flexibility, we have demonstrated how to tailor the perovskite luminescence incorporating optoelectronically active functional cations, or by using organic cations as templating elements of the inorganic

framework and ultimately control defectivity and energetic landscape of the material. Using these strategies, the interplay between excitonic and polaronic properties can be tuned, rather uniquely, to control both the emission energy and bandwidth up to white light luminescence. Ultimately, we have shown that the ability to achieve a wide range of optoelectronic properties *on demand* makes 2D perovskites the materials of choice for several applications, ranging from X-ray scintillators to solid-state lighting and perovskite-based metasurfaces.

References

- [1] D. Cortecchia, H. A. Dewi, J. Yin, A. Bruno, S. Chen, T. Baikie, P. P. Boix, M. Grätzel, S. Mhaisalkar, C. Soci, N. Mathews. *Inorganic Chemistry*. **2016**, 55, 1044.
- [2] D. Cortecchia, C. Soci, M. Cametti, A. Petrozza, J. Martí-Rujas. *ChemPlusChem*. **2017**, 82, 681.
- [3] D. Cortecchia, J. Yin, A. Bruno, S.-Z. A. Lo, G. G. Gurzadyan, S. Mhaisalkar, J.-L. Bredas, C. Soci. *Journal of Materials Chemistry C*. **2017**, 5, 2771.
- [4] J. Yin, H. Li, D. Cortecchia, C. Soci, J.-L. Brédas. *ACS Energy Letters*. **2017**, 2, 417.
- [5] L. Mao, Y. Wu, C. C. Stoumpos, M. R. Wasielewski, M. G. Kanatzidis. *Journal of the American Chemical Society*. **2017**, 139, 5210.
- [6] Z. Yuan, C. Zhou, Y. Tian, Y. Shu, J. Messier, J. C. Wang, L. J. van de Burgt, K. Kountouriotis, Y. Xin, E. Holt, K. Schanze, R. Clark, T. Siegrist, B. Ma. *Nature Communications*. **2017**, 8, 14051.
- [7] C. Zhou, Z. Yuan, Y. Tian, H. Lin, R. Clark, B. Chen, L. J. v. d. Burgt, J. C. Wang, K. Hanson, Q. J. Meisner, J. Neu, T. Besara, T. Siegrist, E. Lambers, P. Djurovich, B. Ma. *arXiv:1702.07200*. **2017**.

- [8] D. Cortecchia, S. Neutzner, A. R. Srimath Kandada, E. Mosconi, D. Meggiolaro, F. De Angelis, C. Soci, A. Petrozza. *Journal of the American Chemical Society*. **2017**, *139*, 39.
- [9] M. D. Smith, A. Jaffe, E. R. Dohner, A. M. Lindenberg, H. I. Karunadasa. *Chemical Science*. **2017**, *8*, 4497.
- [10] S. Ahmad, J. J. Baumberg, G. V. Prakash. *Journal of Applied Physics*. **2013**, *114*, 233511.
- [11] T. Ivanovska, C. Dionigi, E. Mosconi, F. De Angelis, F. Liscio, V. Morandi, G. Ruani. *The Journal of Physical Chemistry Letters*. **2017**, 3081.
- [12] P.-A. Mante, C. C. Stoumpos, M. G. Kanatzidis, A. Yartsev. **2017**, *8*, 14398.
- [13] A. J. Neukirch, W. Nie, J.-C. Blancon, K. Appavoo, H. Tsai, M. Y. Sfeir, C. Katan, L. Pedesseau, J. Even, J. J. Crochet, G. Gupta, A. D. Mohite, S. Tretiak. *Nano Letters*. **2016**, *16*, 3809.
- [14] H. Zhu, M. T. Trinh, J. Wang, Y. Fu, P. P. Joshi, K. Miyata, S. Jin, X. Y. Zhu. *Advanced Materials*. **2017**, *29*, 1603072.
- [15] Z. Wang, J. Zhao, B. Frank, Q. Ran, G. Adamo, H. Giessen, C. Soci. *Nano Letters*. **2015**, *15*, 5382.
- [16] B. Saparov, D. B. Mitzi. *Chemical Reviews*. **2016**, *116*, 4558.
- [17] F. Giustino, H. J. Snaith. *ACS Energy Letters*. **2016**, *1*, 1233.
- [18] Z. Shi, J. Guo, Y. Chen, Q. Li, Y. Pan, H. Zhang, Y. Xia, W. Huang. *Advanced Materials*. **2017**, *29*, 1605005.
- [19] S. Chakraborty, W. Xie, N. Mathews, M. Sherburne, R. Ahuja, M. Asta, S. G. Mhaisalkar. *ACS Energy Letters*. **2017**, *2*, 837.
- [20] D. Liang, Y. Peng, Y. Fu, M. J. Shearer, J. Zhang, J. Zhai, Y. Zhang, R. J. Hamers, T. L. Andrew, S. Jin. *ACS Nano*. **2016**, *10*, 6897.
- [21] B. R. Sutherland, E. H. Sargent. *Nature Photonics*. **2016**, *10*, 295.
- [22] Z. Yuan, C. Zhou, J. Messier, Y. Tian, Y. Shu, J. Wang, Y. Xin, B. Ma. *Advanced Optical Materials*. **2016**, *4*, 2009.

- [23] R. Rieder, T. Economou, H. Wänke, A. Turkevich, J. Crisp, J. Brückner, G. Dreibus, H. Y. McSween. *Science*. **1997**, 278, 1771.
- [24] M. Tegze, G. Faigel. *Nature*. **1996**, 380, 49.
- [25] P. Büchele, M. Richter, S. F. Tedde, G. J. Matt, G. N. Ankah, R. Fischer, M. Biele, W. Metzger, S. Lilliu, O. Bikondoa, J. E. Macdonald, C. J. Brabec, T. Kraus, U. Lemmer, O. Schmidt. *Nat Photon*. **2015**, 9, 843.
- [26] C. Szeles. *physica status solidi (b)*. **2004**, 241, 783.
- [27] N. Martin. *Measurement Science and Technology*. **2006**, 17, R37.
- [28] H. Wei, Y. Fang, P. Mulligan, W. Chuirazzi, H.-H. Fang, C. Wang, B. R. Ecker, Y. Gao, M. A. Loi, L. Cao, J. Huang. *Nat Photon*. **2016**, 10, 333.
- [29] S. Yakunin, M. Sytnyk, D. Kriegner, S. Shrestha, M. Richter, G. J. Matt, H. Azimi, C. J. Brabec, J. Stangl, M. V. Kovalenko, W. Heiss. *Nat Photon*. **2015**, 9, 444.
- [30] S. Yakunin, D. N. Dirin, Y. Shynkarenko, V. Morad, I. Cherniukh, O. Nazarenko, D. Kreil, T. Nauser, M. V. Kovalenko. *Nat Photon*. **2016**, 10, 585.
- [31] M. D. Birowosuto, D. Cortecchia, W. Drozdowski, K. Brylew, W. Lachmanski, A. Bruno, C. Soci. **2016**, 6, 37254.
- [32] X. Y. Chin, D. Cortecchia, J. Yin, A. Bruno, C. Soci. *Nat Commun*. **2015**, 6, 7383.
- [33] C. R. Kagan, D. B. Mitzi, C. D. Dimitrakopoulos. *Science*. **1999**, 286, 945.
- [34] B. Gholipour, G. Adamo, D. Cortecchia, H. N. S. Krishnamoorthy, M. D. Birowosuto, N. I. Zheludev, C. Soci. *Advanced Materials*. **2017**, 29, 1604268.
- [35] S. Jahani, Z. Jacob. *Nat Nano*. **2016**, 11, 23.
- [36] A. P. Vasudev, J. A. Schuller, M. L. Brongersma. *Opt. Express*. **2012**, 20, A385.
- [37] Y. Yang, I. I. Kravchenko, D. P. Briggs, J. Valentine. **2014**, 5, 5753.

- [38] Y. Gong, M. Makarova, S. Yerci, R. Li, M. J. Stevens, B. Baek, S. W. Nam, R. H. Hadfield, S. N. Dorenbos, V. Zwiller, J. Vučković, L. D. Negro. *Opt. Express*. **2010**, *18*, 2601.
- [39] M. Decker, I. Staude, I. I. Shishkin, K. B. Samusev, P. Parkinson, V. K. A. Sreenivasan, A. Minovich, A. E. Miroshnichenko, A. Zvyagin, C. Jagadish, D. N. Neshev, Y. S. Kivshar. **2013**, *4*, 2949.

APPENDIX A

A.1 Supplementary material to Chapter 4

Figure A.1 Pawley fit of MA_2CuBr_4 powder XRD: orthorhombic, Pbca , $a = 7.8013(9)$; $b = 7.6237(9)$; $c = 19.1287(4)$, with $R_B = 0.019$. The blue and red line represent the experimental data and fitting curve, while the gray line is the difference between the two. (*) shows diffraction peaks of a secondary phase unrelated to the bromide perovskite.

Figure A.2 Diffraction peak shift at smaller angles with increase bromine content.

Figure A.3 Projected density of states (PDOS) of the $\text{MA}_2\text{CuCl}_x\text{Br}_{4-x}$ series.

Figure A.4 In principle component fitting of NIR absorption of $\text{MA}_2\text{CuClBr}_3$, showing the presence of the 3 expected d-d transitions.

Figure A.5 X-ray photoelectron spectroscopy (XPS) measurements on MA₂CuCl_xBr_{4-x} films after annealing. a) The Cu 2p_{3/2} spectrum shows increasing content of Cu⁺ at higher Br/Cl ratios. b) the Cu 2p spectrum shows satellite peaks (typical of Cu²⁺) in chlorine-containing films, while these are absent in MA₂CuBr₄, indicating complete reduction to Cu⁺ at the film's surface.

Figure A.6 Powder X-ray diffraction of (H₂BPOA)CuCl₄ a) after synthesis and b) after 1 month of exposure to air. The data confirm the increased stability provided by the organic cation.

Table A1 Crystal data and structure refinement of BPOA•H₂O (C₂₄H₂₂N₂O₃), (H₂BPOA)Cl₂•2DMSO (C₂₈H₃₄Cl₂N₂S₂O₄), (H₂BPOA)Cl₂ (C₂₄H₂₂Cl₂N₂O₂) and (H₂BPOA)CuCl₄ (C₂₄H₂₂Cl₄Cu₁N₂O₂).

Formula	C ₂₄ H ₂₂ N ₂ O ₃	C ₂₈ H ₃₄ Cl ₂ N ₂ S ₂ O ₄	C ₂₄ H ₂₂ Cl ₂ N ₂ O ₂	C ₂₄ H ₂₂ Cl ₄ Cu ₁ N ₂ O ₂
Mr, g/mol	386.45	597.626	441.356	575.808
Cryst Syst	triclinic	triclinic	monoclinic	monoclinic
Space group	P-1	P-1	P21/c	P21/c
a, Å	5.6806(6)	5.6713(5)	4.7580(8)	23.499(4)
b, Å	7.9232(8)	8.2899(7)	44.664(10)	7.4335(12)
c, Å	21.668(2)	15.9733(14)	5.2176(7)	7.0455(10)
α, deg	93.567(7)°	85.385(7)°	90°	90°
β, deg	97.413(7)°	81.832(7)°	105.151(12)°	97.462(12)°
γ, deg	90.187(7)°	78.316(6)°	90°	90°
V, Å ³	965.161(7)	726.92(11)	1070.3(3)	1220.28(34)
Z	2	2	4	4
ρ, g/cm ³	1.323	1.365	1.301	1.567
T, K	296(2)	296(2)	296(2)	296(2)
reflection measured	3331	2459	1414	2128
independent reflections	2542	2107	649	1471
parameters	262	175	137	152
restraints	0	0	0	0
R ₁ , [I>2σ(I)]	0.0845	0.0354	0.105	0.0986
wR ² , [I>2σ(I)]	0.2909	0.0935	0.2525	0.2641

Figure A.7 Transformed Kubelka-Munk function of powder reflectance spectra of a) (H₂BPOA)Cl₂ and b) (H₂BPOA)CuCl₄ for band-gap determination.

APPENDIX B

B.1 Supplementary material to Chapter 5

Figure B.1 a,b) X-ray diffraction patterns of spin-coated thin films and corresponding Pawley fit with refined parameters a) monoclinic, C2, $a = 7.7403 \text{ \AA}$, $b = 7.4418 \text{ \AA}$, $c = 13.3583 \text{ \AA}$ for (EDBE)PbCl₄ and b) monoclinic, P21/c, $a = 6.1011 \text{ \AA}$, $b = 28.7912 \text{ \AA}$, $c = 8.8547 \text{ \AA}$, $\beta = 91.96^\circ$ for (EDBE)PbBr₄. The diffraction patterns are consistent with the formation of the crystal structures of the $\langle 100 \rangle$ perovskite (EDBE)PbCl₄ and $\langle 110 \rangle$ perovskite (EDBE)PbBr₄ with strong preferential orientation along the $00l$ and $h00$ direction, respectively. c,d) AFM characterization of thin films spin-coated from 0.25M DMSO solutions: c) (EDBE)PbCl₄, thickness = $107 \pm 11 \text{ nm}$ and roughness $R_{\text{RMS}} = 7 \text{ nm}$; d) (EDBE)PbBr₄, thickness = $80 \pm 10 \text{ nm}$ and $R_{\text{RMS}} = 6 \text{ nm}$.

Figure B.2 Exciton binding energy (EBE) extraction for a) (EDBE)PbCl₄ and b) (EDBE)PbBr₄. The EBE was determined as the distance between the perovskite band-edge and the 0-0 transition of the excitonic absorption as determined from Frank-Condon Fitting (E_0).

Figure B.3 Time resolved photoluminescence decay ($E_{\text{probe}} = 2.34$ eV) of a) (EDBE)PbCl₄ and b) (EDBE)PbBr₄ measured at different excitation energy: 4.66 eV (blue lines); 3.76 eV and 3.26 eV (red lines).

Table B.1 Fitting parameters of the time resolved photoluminescence decays at the probing energy 2.34 eV.

Material	Excitation Energy (eV)	τ 1 (ns)	A1	τ 2 (ns)	A2	τ 3 (ns)	A3
(EDBE)PbCl ₄	4.66	0.04	0.93	0.15	0.06	3.8	0.01
	3.76	0.04	0	0.15	0.06	3.8	0.94
(EDBE)PbBr ₄	4.66	0.04	0.79	0.74	0.04	3.2	0.17
	3.26	0.04	0	0.74	0.09	3.2	0.91

Figure B.4 a) Temperature dependent time resolved photoluminescence spectrum of (EDBE)PbCl₄ (E_{exc} 3.76 eV). b) PL activation energy extraction from the luminescence temperature dependence of (EDBE)PbCl₄ (upper panel) and (EDBE)PbBr₄. The fitting of the integrated PL intensity (I) vs T was performed with the Arrhenius formula $I = I_0/[1 + a \exp(-E_a/kT)]$: E_a = activation energy, k = Boltzmann constant, I_0 = zero-temperature PL intensity, a = quenching strength.

Figure B.5 PL analysis of (EDBE)PbBr₄. a, In principle component fitting of the PL profile at 78 K; b) total PL intensity and c) emission of individual PL components W1, W2, W3 vs temperature. d) Peak position of individual component vs temperature.

Figure B.6 PL analysis of (EDBE)PbBr₄. a, In principle component fitting of the PL profile at 78 K; b) total PL intensity and c) emission of individual PL components W1, W2, W3 vs temperature. d) Peak position of individual component vs temperature.

Figure B.7 a) Transient absorption spectra and b) spectral dependence of the decay dynamics of (EDBE)PbCl₄ under excitation energy 3.76 eV.

Table B.2 Fitting parameters of transient absorption decay dynamics under excitation resonant to the excitonic absorption. Global fitting of the decays at different wavelengths was performed on the datasets of the two perovskites.

Material	Excitation Energy (eV)	Probe Energy (eV)	τ_1 (ps)	A1	τ_2 (ps)	A2
(EDBE)PbCl ₄	3.76	2.76	11.1	0.08	296.4	0.92
		2.48		0.07		0.93
		2.25		0.00		1.00
		2.07		0.04		0.96
		1.91		0.05		0.95
(EDBE)PbBr ₄	3.26	2.76	9.8	0.46	741	0.54
		2.48		0.51		0.49
		2.25		0.46		0.54
		2.07		0.41		0.59
		1.91		0.19		0.81

Figure B.8 Charge density distribution of (EDBE)PbCl₄ at PBE/wSOC level for unperturbed and perturbed structures.

Figure B.9 Charge density distribution of (EDBE)PbBr₄ at PBE/wSOC for unperturbed and perturbed structures.

Figure B.10 Calculated energies of unperturbed and perturbed structures of (EDBE)PbCl₄ and b, (EDBE)PbBr₄.

APPENDIX C

C.1 Supplementary material to Chapter 6

Figure C.1 Pawley fit of thin film X-ray diffraction patterns. The refined parameters are a) orthorhombic, Pbca , $a = 8.8854 \text{ \AA}$, $b = 8.6249 \text{ \AA}$, $c = 27.4588 \text{ \AA}$ for $(\text{NBT})_2\text{PbI}_4$ and b) monoclinic, P21/c , $a = 6.5459 \text{ \AA}$, $b = 29.3190 \text{ \AA}$, $c = 9.3356 \text{ \AA}$, $\beta = 92.46^\circ$ for $(\text{EDBE})\text{PbI}_4$. The two films show preferential orientation along the $00l$ and $h00$ direction, respectively.

Figure C.2 a) Raman spectra measured on perovskite films; b-d) photoluminescence of (EDBE)PbI₄ measured on films with different thickness obtained increasing the concentration of spin coating solution: b) 0.25M, 86±8 nm; c) 0.5M, 227±26 nm; d) 1M, 500±33 nm. Only thin films allow to resolve well the excitonic luminescence.

Figure C.3 PL power dependence of (EDBE)PbI₄ single crystals.

Table C.1 Calculated band-gaps at PBE/GGA level

EDBE			NBT	
Perf. Cryst.	Rel. En.	Gap	Rel. En.	Gap
VAC Pb*	-	1.40	-	1.25
VAC I	ap. External	0.00	0.00	1.69
	ap. Inner	0.31	-	-
	eq.	0.26	0.04	1.48
INT I	ap. External	0.26	0.04	1.49
	ap. Inner	0.00	-	-

Figure C.4 Relaxed crystal structures from experimental coordinates at GGA level, 25/200 Ry for a) (EDBE)PbI₄ and b) (NBT)₂PbI₄.

Figure C.5 Small angle X-ray scattering (SAXS) signal of (NBT)₂(MA)[Pb₂I₇] powders showing the shift of the 001 diffraction peak during the two low-temperature phase transitions.

Figure C.6 Differential scanning calorimetry (DSC) measurements performed on a) $(\text{NBT})_2\text{PbI}_4$ and b) $(\text{NBT})_2(\text{MA})[\text{Pb}_2\text{I}_7]$.

Table C.2 Crystal data and structure refinement from single crystal X-ray diffraction of $(\text{NBT})_2(\text{MA})[\text{Pb}_2\text{I}_7]$, $(\text{C}_9\text{H}_{30}\text{N}_3\text{Pb}_2\text{I}_7)$.

Formula	$\text{C}_9\text{H}_{30}\text{N}_3\text{Pb}_2\text{I}_7$
M_r , g/mol	1483.09
Cryst Syst	triclinic
Space group	P-1
a, Å	8.6397(9)
b, Å	9.0767(9)
c, Å	19.5071(18)
α , deg	103.152(8)°
β , deg	95.000(8)°
γ , deg	91.764(7)°
V, Å ³	1481.9(3)
Z	4
ρ , g/cm ³	3.303
T, K	100(2)
reflection measured	4164
independent reflections	2882
parameters	120
restraints	0
R_1 , [$I > 2s(I)$]	0.1003
wR^2 , [$I > 2s(I)$]	0.2573

Figure C.7 Pawley fit of a,b) $(\text{NBT})_2\text{PbI}_4$ and c,d) $(\text{NBT})_2(\text{MA})[\text{Pb}_2\text{I}_7]$ powders at a,c) 298 K and b,d) 100 K. Refined parameters a) orthorhombic, *Pbca*, $a=8.8860(1) \text{ \AA}$, $b=8.6676(5) \text{ \AA}$, $c=27.4536(2) \text{ \AA}$; b) orthorhombic, *Pbca*, $a=8.4184(7) \text{ \AA}$, $b=9.0173(3) \text{ \AA}$, $c=26.1838(6) \text{ \AA}$; c) orthorhombic, *Cc2m*, $a=8.8963(2) \text{ \AA}$, $b=39.2881(2) \text{ \AA}$, $c=8.8287(8) \text{ \AA}$; d) triclinic, *P-1*, $a=8.5731(1) \text{ \AA}$, $b=8.9223(7) \text{ \AA}$, $c=19.6484(7) \text{ \AA}$, $\alpha=102.832(4)^\circ$, $\beta=93.252(8)^\circ$, $\gamma=94.831(8)^\circ$.

Publications and Conference List

Journals

- 1 D. Cortecchia, J. Yin, A. Bruno, S-Z A. Lo, G. Gurzadyan, S. Mhaisalkar, J-L Brédas, C. Soci, Polaron Self-localization in White-light Emitting Hybrid Perovskites, *J. Mater. Chem. C* **2017**, 5, 2771-2780. **(Highlighted in Journal Cover)**
- 2 D. Cortecchia, S. Neutzner, A. R. S. Kandada, E. Mosconi, D. Meggiolaro, F. De Angelis, C. Soci, A. Petrozza, Broadband Emission in Two-Dimensional Hybrid Perovskites: The Role of Structural Deformation, *J. Am. Chem. Soc.* **2017**, 139 (1), 39–42.
- 3 D. Cortecchia, C. Soci, M. Cametti, A. Petrozza, J. Martí-Rujas, Crystal Engineering of a 2D Lead-free Perovskite with Functional Organic Cation by Second Sphere Coordination, *ChemPlusChem* **2016**, 81, 1–6. **(Highlighted in Journal Cover)**
- 4 D. Cortecchia, H. A. Dewi, J. Yin, A. Bruno, S. Chen, T. Baikie, P. P. Boix, M. Grätzel, S. Mhaisalkar, C. Soci, N. Mathews, Lead-Free MA₂CuCl_xBr_{4-x} Hybrid Perovskites, *Inorganic Chemistry* **2016**, 55, 1044.
- 5 A. Bruno, D. Cortecchia, X. Y. Chin, K. Fu, P. P. Boix, S. Mhaisalkar, C. Soci, Temperature and electrical poling effects on ionic motion in MAPbI₃ photovoltaic cells, *Adv. Energy Mater.* **2017**, 1700265.
- 6 J. Yin, H. Li, D. Cortecchia, C. Soci, J-L Brédas, Excitonic and Polaronic Properties of 2D Hybrid Organic-Inorganic Perovskites, *ACS Energy Lett.* **2017**, 2 (2), 417–423.
- 7 B. Gholipour, G. Adamo, D. Cortecchia, H. Krishnamoorthy, N. Zheludev, C. Soci, Organometallic Perovskite Metasurfaces, *Adv. Mater.* **2017**, 1604268. **(Highlighted in Journal Back Cover)**
- 8 M. D. Birowosuto, D. Cortecchia, W. Drozdowski, K. Brylew, W. Lachmanski, A. Bruno, and C. Soci, X-ray Scintillation in Two-

- Dimensional Lead Halide Perovskite Crystals, *Scientific Reports* **2016**, 6, 37254.
- 9 X. Y. Chin, D. Cortecchia, J. Yin, A. Bruno, C. Soci, Lead iodide perovskite light-emitting field-effect transistor, *Nat. Commun.* **2015**, 6, 7383.
  - 10 J Yin, D. Cortecchia, A. Krishna, S. Chen, N. Mathews, A. C. Grimsdale, C. Soci, Interfacial charge transfer anisotropy in polycrystalline lead iodide perovskite films, *J. Phys. Chem. Lett.* **2015**, 6 (8), 1396–1402.
  - 11 I. Neogi, A. Bruno, D. Bahulayan, T. W. Goh, B. Ghosh, R. Ganguly, D. Cortecchia, T. C. Sum, C. Soci, N. Mathews, S. G. Mhaisalkar, Broadband emitting 2D-hybrid organic inorganic perovskite based on cyclohexane-bis(methylammonium) cation, *ChemSusChem*, *accepted*.

In preparation:

- 12 D. Cortecchia,* L. K. Cheng,* A. Bruno, C. Soci, Cathodoluminescence of self-organized heterogeneous phases in multidimensional perovskite thin films, *in preparation*. (***Co-first Authors**)
- 13 D. Cortecchia, S. Neutzner, A. Bruno, J. Martí-Rujas, T. Salim, J. Yin, L. Y. Ming, A. Petrozza, C. Soci, Structure induced thermochromism in multidimensional perovskites, *in preparation*.
- 14 S-Z A. Lo, D. Cortecchia, A. Bruno, X. Li, G. Gurzadyan, C. Soci, Self-trapped polaron dynamics in two-dimensional hybrid perovskite, *to be submitted*.
- 15 F. Maddalena, X. Y. Chin, D. Cortecchia, A. Bruno, C. Soci, AC-Driven perovskite light-emitting field-effect transistors, *to be submitted*.

Patents

- 1 Scintillation in lead halide perovskite crystal, M.D. Birowosuto, D. Cortecchia, C. Soci, Singapore provisional application number

- 10201606250W. (July 28, **2016**)
- 2 Device including halide perovskite structure, methods of forming and operating the same, C. Soci, B. Gholipour, G. Adamo, D. Cortecchia, US Patent Application 15/471,694. (28 March, **2017**).
  - 3 Light-emitting device, method of forming and operating the same, C. Soci, X.Y. Chin, D. Cortecchia, A. Bruno, J. Yin, F. Maddalena, US 15/199,185. (30 June, **2016**)
  - 4 Perovskites for optoelectronic applications, S.G. Mhaisalkar, T. Baikie, N. Mathews, P.P. Boix, C. Soci, D. Cortecchia, US 2106/0149145 A1. (May 26, **2016**).

Conference presentations

Talks:

- 1 D. Cortecchia, J. Yin, M. D. Birowosuto, S.-Z. A. Lo, G. Gurzadyan, A. Bruno, J-L Brédas, C. Soci, Small polarons in 2D perovskites, CLEO/EUROPE, Munich, 25-29 Jun **2017**. **(Talk)**
- 2 F. Maddalena, X. Y. Chin, D. Cortecchia, A. Bruno, C. Soci, AC-Driven perovskite light-emitting field-effect transistors, CLEO/EUROPE, Munich, 25-29 Jun **2017**. **(Talk)**
- 3 D. Cortecchia, J. Yin, S-Z A. Lo, G. G. Gurzadyan, A. Bruno, J-L Brédas, C. Soci, Small polarons in layered hybrid perovskites, ICMAT, Singapore 18-23 Jun **2017**. **(Talk, Presenting)**
- 4 A. Bruno, D. Cortecchia, X. Y. Chin, F. Maddalena, S. Mhaisalkar, C. Soci, Controlling ionic motion in hybrid perovskites solar cells by temperature and electrical poling, ICMAT, Singapore 18-23 Jun **2017**. **(Talk)**
- 5 S.-Z. A. Lo, D. Cortecchia, A. Bruni, C. Soci, Ultrafast polaron dynamics in two-dimensional perovskites, ICMAT, Singapore 18-23 Jun **2017**.

(Talk)

- 6 F. Maddalena, X. Y. Chin, D. Cortecchia, A. Bruno, C. Soci, Hybrid perovskites AC-driven light-emitting field-effect transistors, ICMAT, Singapore 18-23 Jun **2017. (Talk)**
- 7 D. Cortecchia, Light emitting properties of hybrid perovskites, Ceramics for Energy – Cen 2017, Faenza 7-9 Jun **2017. (Invited Talk, Presenting)**
- 8 D. Cortecchia, J. Yin, S-Z A. Lo, G. G. Gurzadyan, A. Bruno, J-L Brédas, C. Soci, Small polarons in white-emitting 2D perovskites, IPS Meeting, Singapore 22-24 Feb **2017. (Invited Talk, Presenting)**
- 9 A. Bruno, D. Cortecchia, C. X. Yu, F. Maddalena, S. Mhaisalkar, C. Soci, Temperature and electrical poling effects in hybrid Perovskite solar cells, IPS Meeting, Singapore 22-24 Feb **2017. (Talk)**
- 10 K. C. Lew, D. Cortecchia, J. So, A. Bruno, C. Soci, Cathodoluminescence spectroscopy of multidimensional organic-inorganic perovskites, IPS Meeting, Singapore 22-24 Feb **2017. (Talk)**
- 11 F. Maddalena, X. Y. Chin, D. Cortecchia, A. Bruno, C. Soci, Hybrid perovskite light-emitting field-effect transistors, IPS Meeting, Singapore 22-24 Feb **2017. (Talk)**
- 12 G. Adamo, B. Gholipour, K. C. Lew, D. Cortecchia, H. N. S. Krishnamoorthy, A. Bruno, J. So, M. D. Birowosuto, N. I. Zheludev, C. Soci, Control of luminescence in perovskite metamaterials, IPS Meeting, Singapore 22-24 Feb **2017. (Invited Talk)**
- 13 D. Cortecchia, S. Neutzner, A. R. S. Kandada, E. Mosconi, F. De Angelis, C. Soci, A. Petrozza, Strain-assisted broadband photoluminescence in two-dimensional hybrid perovskites, MRS, Boston, 27 Nov-2 Dec **2016. (Talk)**
- 14 D. Cortecchia, C. Soci, M. Cametti, A. Petrozza, J. Martí-Rujas, Crystal Engineering of a Copper-based layered perovskite using an optoelectronically active functional cation, SICCC9, Singapore 11-14 Dec **2016. (Talk, Presenting)**

- 15 D. Cortecchia, J. Yin, S-Z A. Lo, A. Bruno, C. Soci, Lattice-induced exciton localization in 2D organometallic perovskites, APC2016, Singapore, 4-8 Dec **2016. (Invited Talk, Presenting)**
- 16 D. Cortecchia, N. Mathews, J. Martí-Rujas, A. Petrozza, C. Soci, Copper-based layered perovskites for light-emitting applications, APC2016, Singapore, 4-8 Dec **2016. (Talk, Presenting)**
- A. Bruno, D. Cortecchia, X. Y. Chin, F. Maddalena, P. P. Boix, S. Mhaisalkar, C. Soci, Temperatures dependence of $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells performances, APC2016, Singapore, 4-8 Dec **2016. (Talk)**
- 17 Bruno, D. Cortecchia, X. Y. Chin, K. Fu, F. Maddalena, P. P. Boix, S. Mhaisalkar, C. Soci, MAPbI_3 Solar cells efficiencies at cryogenic temperatures, PVSEC, Singapore, 24-28 Oct **2016. (Talk)**
- 18 F. Maddalena, X.Y. Chin, K.C. Lew, D. Cortecchia, U.S. Binte Eliase, A. Bruno, C. Soci, Effect of precursor stoichiometry and device architecture on the characteristics of methylammonium lead iodide perovskite field-effect transistors, (PVSEC), Singapore 24-28 October **2016. (Talk)**
- 19 D. Cortecchia, J. Yin, P. Lova, S. Mhaisalkar, G. Gurzadyan, A. Bruno, C. Soci, Role of polaronic excitons in white-light emitting hybrid perovskites, HOPV, Swansea 28 Jun – 1 Jul **2016. (Talk, Presenting)**
- A. Bruno, D. Cortecchia, X. Y. Chin, P. F. Kunwu, P. Boix, S. Mhaisalkar, C. Soci, Efficiency enhancement of MAPbI_3 mesoporous solar cells, HOPV, Swansea 28 Jun – 1 Jul **2016. (Talk)**
- 20 X. Y. Chin, D. Cortecchia, J. Yin, A. Bruno, and C. Soci, Perovskite Light Emitting Transistor, 1st International Conference on Perovskite Solar Cells and Optoelectronics (PSCO), 27-29 Sep, Lausanne, Switzerland **2015. (Talk, Presenting)**
- 21 D. Cortecchia, A. Bruno, A. H. Dewi, J. Yin, S. Chen, T. Baikie, P. P. Boix, S. Mhaisalkar, N. Mathews, C. Soci, Lead-free two-dimensional perovskite $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_x\text{Br}_{4-x}$ for solar cells applications, IPS Meeting, Singapore 4-6 March **2015. (Talk, Presenting)**

- 22 X. Y. Chin, D. Cortecchia, J. Yin, A. Bruno, C. Soci, Light emitting perovskite field-effect transistor, IPS Meeting, Singapore 4-6 March **2015. (Talk)**
- 23 D. Cortecchia, A. Bruno, A. H. Dewi, J. Yin, S. Chen, T. Krishnamoorthy, R. R. Prabhakar, T. Baikie, P. P. Boix, S. Mhaisalkar, N. Mathews, C. Soci, Synthesis and characterization of two-dimensional copper-based hybrid perovskites, MRS Spring Meeting, San Francisco 6-10 April **2015. (Talk, Presenting)**
- 24 X. Y. Chin, D. Cortecchia, J. Yin, A. Bruno, C. Soci, CH₃NH₃PbI₃ Perovskite Light Emitting field-effect transistor, E-MRS Spring Meeting, Lille 21-25 June **2015. (Talk)**
- 25 X. Y. Chin, D. Cortecchia, J. Yin, A. Bruno, C. Soci, Perovskite field-effect transistor, ICMAT, Singapore 28 June - 03 July **2015. (Talk)**
- 26 D. Cortecchia, A. Bruno, A. H. Dewi, J. Yin, S. Chen, T. Baikie, P. P. Boix, S. Mhaisalkar, C. Soci, N. Mathews, Lead-free (CH₃NH₃)₂CuCl_xBr_{4-x} hybrid perovskites, ICMAT, Singapore 28 June - 03 July **2015. (Talk, Presenting)**
- 27 D. Cortecchia, A. H. Dewi, S. Dharani, T. Baikie, C. Soci, N. Mathews, “Green” 2D hybrid perovskites for perovskite-based solar cells, EOSAM, Berlin 15-19 September **2014. (Talk, Presenting)**
- 28 J. Yin, D. Cortecchia, S. Chen, C. Soci, Interfacial modeling of lead iodide perovskite and organic charge transporting heterostructures, EOSAM, Berlin 15-19 September **2014. (Talk, Presenting)**

Posters:

- 29 W. P.D. Wong, D. Cortecchia, Y. Jun, X. Yu Chin, C. Soci, A. C. Grimsdale, Polaron formation and transport dynamics in MAPbI₃, IPS Meeting, Singapore 22-24 February **2017. (Poster)**
- 30 S-Z A. Lo, D. Cortecchia, A. Bruno, C. Soci, Ultrafast dynamics of self-

- trapped Carriers in two-dimensional hybrid perovskites, IPS Meeting, Singapore 22-24 February **2017. (Poster)**
- 31 K. C. Lew, D. Cortecchia, X. Y. Chin, C. Soci, Controlled synthesis of perovskite nanostructures and their optical characterization, SICC9, Singapore 11-14 Dec **2016. (Poster)**
  - 32 M. D. Birowosuto, D. Cortecchia, W. Drozdowski, K. Brylew, W. Lachmanski, A. Bruno, Cesare Soci, X-Ray scintillation in lead halide perovskite crystals, APC2016, Singapore, 4-8 Dec **2016. (Poster)**
  - 33 D. Cortecchia, S. Neutzner, A. R. S. Kandada, E. Mosconi, D. Meggiolaro, F. De Angelis, C. Soci, A. Petrozza, Role of structural distortion in photoluminescence broadening of hybrid perovskites, PSCO, Genova, 26-28 Sep **2016. (Poster)**
  - 34 B. Gholipour, G. Adamo, D. Cortecchia, H. Krishnamoorthy, J. Yin, A. Bruno, N. Zheludev, C. Soci, Tunable photonic response of lead iodide perovskites metamaterials, Nanophotonics in Asia 2015, Nakanoshima Center, Osaka University, Japan 10-11 Dec **2015. (Poster)**
  - 35 D. Cortecchia, Z. Wang, Y. M. Joshua, Y. Jun, C. Shi, P. Lova, G. Gurzadyan, A. Bruno, S. Mhaisalkar and C. Soci, (EDBE)PbX₄ perovskite white emitting devices, 1st International Conference on Perovskite Solar Cells and Optoelectronics (PSCO), Lausanne, Switzerland 27-29 Sep **2015. (Poster, Presenting; Materials Horizons Best Poster Award)**
  - 36 P. Lova, D. Cortecchia, C. Bastianini, H.N.S. Krishnamoorthy, D. Comoretto, A. Bruno, C. Soci. Solution processable perovskite-polymer microcavities, PSCO 2015 - 1st International Conference on Perovskite Solar Cells and Optoelectronics, Lausanne, Switzerland 27-29 Sep **2015. (Poster, Presenting)**
  - 37 J. Yin, D. Cortecchia, A. Krishna, S. Chen, N. Mathews, A. C. Grmsdale, C. Soci, Interfacial charge transfer anisotropy in polycrystalline lead iodide perovskite films, MRS Spring Meeting, San Francisco 6-10 April

2015. (Poster, Presenting)

- 38 X. Y. Chin, D. Cortecchia, J. Yin, A. Bruno, C. Soci, Lead iodide perovskite light emitting field effect transistors, MRS Spring Meeting, San Francisco 6-10 April **2015. (Poster, Presenting)**
- 39 X. Y. Chin, D. Cortecchia, J. Yin, A. Bruno, C. Soci, Electroluminescence from $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite light emitting devices, E-MRS Spring Meeting, Lille 11-15 May **2015. (Poster)**
- 40 D. Cortecchia, H. A. Dewi, S. Dharani, T. Baikie, C. Soci, N. Mathew, 2D hybrid perovskites for photovoltaic application, OCPA8, Singapore 23-27 Jun **2014. (Poster, Presenting)**
- 41 D. Cortecchia, D. G. F. Del Valle, I. Kriegel, T. He, J. Yin, M. Panahandeh-Fard, M. Kumar, H. Sun, F. Scotognella, C. Soci, Study on the transient absorption of CuO/ZnO thin film heterojunction, EOSAM, Berlin 15-19 September **2014. (Poster, Presenting)**
- 42 D. Cortecchia, D. G. F. Del Valle, I. Kriegel, T. He, J. Yin, M. Panahandeh-Fard, M. Kumar, H. Su, F. Scotognella, C. Soci, CuO/ZnO heterojunctions, IPS Meeting, Singapore 26-28 February **2014. (Poster, Presenting)**