On the Synthesis and Optical Characterization of Zero-Dimensional-Networked Perovskites

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ABSTRACT
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Jawaher Almutlaq

The three-dimensional perovskites are known for their wide range of interesting properties including spectral tunability, charge carrier mobility, solution-based synthesis and many others. Such properties make them good candidates for photovoltaics and photodetectors. Low-dimensional perovskites, on the other hand, are good as light emitters due to the quantum confinement originating from their nanoparticle size. Another class of low-dimensional perovskites, also called low-dimensional-networked perovskites (L-DN), is recently reemerging. Those interesting materials combine the advantages of the nanocrystals and the stability of the bulk. For example, zero-dimensional-networked perovskite (0-DN), a special class of perovskites and the focus of this work, consists of building blocks of isolated lead-halide octahedra that could be synthesized into mm-size single crystal without losing their confinement.

This thesis focuses on the synthesis and investigation of the optical properties of the 0-DN perovskites through experimental, theoretical and computational tools. The recent discovery of the retrograde solubility of the perovskites family (ABX₃), the basis of the inverse temperature crystallization (ITC), inspired the reinvestigation of the low-dimensional-networked perovskites.
The results of the optical characterization showed that the absorption and the corresponding PL spectra were successfully tuned to cover the visible spectrum from 410 nm for Cs₄PbCl₆, to 520 nm and 700 m for Cs₄PbBr₆ and Cs₄PbI₆, respectively. Interestingly, the exciton binding energies (E_b) of the 0-DNs were found to be in the order of few hundred meV(s), at least five times larger than their three-dimensional counterpart. Such high E_b is coupled with a few nanoseconds lifetime and ultimately yielded a high photoluminescent quantum yield (PLQY). In fact, the PLQY of Cs₄PbBr₆ powder showed a record of 45%, setting a new benchmark for solid-state luminescent perovskites.

Computational methods were used to calculate the bandgap and study the corresponding excitonic behavior. However, the unexpected mismatch between the calculated and experimental bandgaps questions the origin of the high luminescence, which to date, remains an area of scientific debate that needs further study. Until then, the high PLQY, together with the spectral tunability, insensitivity to particle size and stability all offer a new avenue for more sustainability in light-emitting materials.
ACKNOWLEDGMENTS

I would like to thank my advisor, Prof. Osman Bakr, for accepting me in his group, and all the support thereafter. My gratitude is extended to Prof. Omar Abdelsaboor and Prof. Lain-Jong Li for accepting my invitation to join my thesis committee. I was honored to work with Dr. Makhsud Saidaminov, my mentor, who set the bar very high, and it was rewarding. Indeed, surrounded by my colleagues in Functional Nanomaterials Materials Lab, I was able to grow up as a researcher. They were a great source of ideas and inspiration and my heartfelt gratitude goes to every one of them.

I would like to thank KAUST Gifted Student Program (KGSP) management, headed by Dr. Saham Alhusseini, for their support before and during my Master's degree.

I cherish the companionship of my friends, for their generosity and humor were priceless during my pivotal moments.

The words will not be enough to thank my family for their unconditional love and support.
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## LIST OF ABBREVIATIONS

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<tr>
<th>Acronym</th>
<th>Full Form</th>
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<tr>
<td>LED</td>
<td>light emitting diodes</td>
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<tr>
<td>TFT</td>
<td>thin film transistors</td>
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<tr>
<td>PSC</td>
<td>perovskite-based solar cells</td>
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<tr>
<td>NC</td>
<td>nanocrystals</td>
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<tr>
<td>Low-DN</td>
<td>low-dimensional-networked</td>
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<tr>
<td>0D</td>
<td>zero dimensional</td>
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<td>3D</td>
<td>three dimensional</td>
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<tr>
<td>PL</td>
<td>photoluminescence</td>
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<tr>
<td>XRD/PXRD</td>
<td>x-ray diffraction/Powder X-ray diffraction</td>
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<tr>
<td>SEM</td>
<td>transition electron microscopy</td>
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<tr>
<td>ITC</td>
<td>inverse temperature crystallization</td>
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<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
</tr>
<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>JDOS</td>
<td>joint density of states</td>
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<tr>
<td>PLQY</td>
<td>photoluminescence quantum yield</td>
</tr>
<tr>
<td>TRPL</td>
<td>Time-Resolved Photoluminescence</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>RPA</td>
<td>random phase approximation</td>
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<tr>
<td>BSE</td>
<td>Bethe–Salpeter equation</td>
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Figure 1.1 (A) the general structure of perovskite with the formula ABX3. (B) Spectral tunability of MAPbXnY3-n from 390 nm – 790 nm. (C) Perovskites have demonstrated color spaces covering a larger area than the National Television System Committee (NTSC). Reprinted by permission from ref. copyright (2015) with permission from Macmillan Publishers Ltd, Nature Photonics. (D) standard colloidal organometal halide perovskite CH$_3$NH$_3$PbX$_3$ (X = halides) nanoparticles shows a maximum luminous efficiency of 11.49 cd/A, a power efficiency of 7.84 lm/W, and an external quantum efficiency of 3.8%. Reprinted with permission from ref. Copyright (2016) American Chemical Society.

Figure 1.2 The electronic structures of lead iodide based low-dimensional crystals illustartes the bonding diagram of (A) [PbI$_4$]$^{4-}$ cluster of zero-dimensional system. (B) 3D crystal CH$_3$NH$_3$PbI$_3$ and 2D crystal (C$_4$H$_9$NH$_3$)$_2$PbI$_4$ at the top of the valence band and the bottom of the conduction band. (C)Crystal structures of inorganic parts of 3D crystal CH$_3$NH$_3$PbI$_3$ and 2D crystal (C$_4$H$_9$NH$_3$)$_2$PbI$_4$. Reprinted figure with permission from ref. Copyright (2003) by the American Physical Society.

Figure 1.3 The crystallographic and morphological differences between the low-dimensional networked and conventional low-dimensional perovskite. (A)A schematic representation presenting the structural variation between different low-dimensional networked perovskites through the connectivity of the metal-halide octahedral. Reprinted with permission from ref. Copyright (2016) American Chemical Society. (B) An SEM image of the zero-dimensional networked Cs$_4$PbBr$_6$. Figure reprinted from ref. with permission from John Wiley and Sons. (C) A schematic illustration showing the controllability of the nanocrystal dimension through a ligand-mediated process, in which the core of all different NCs is the conventional three-dimensional CsPbX$_3$. Reprinted with permission from ref. Copyright (2016) American Chemical Society.

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Figure 3.4 The PL spectrum of (A) Cs$_4$PbCl$_6$ (peak at 410 nm) (B) Cs$_4$PbBr$_6$ (peak at 520 nm), and (C) Cs$_4$PbI$_6$ (peak at 700 nm).

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Figure 5.2 (A) XRD spectra of trigonal phase Cs$_4$PbBr$_6$ NCs with R3c space group compared to the standard powder diffraction pattern of bulk Cs$_4$PbBr$_6$ (λCo-κα = 1.79 Å). (B) Absorption spectrum of Cs$_4$PbBr$_6$ NCs in hexane. Inset shows the
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Chapter 1

Introduction

1.1 The Dilemma

The annual report of the Directorate General for Energy of the European Commission estimated a 30% increase of the global energy demand by 2030. Out of all the current building electricity consumption, 20% goes for lighting. Thus, it became of paramount importance to find innovative and sustainable light emitting materials that are economically feasible and environmentally green. This leaves ethical and scientific obligations for the researchers and scientists to overcome the most difficult of challenges in the ever-expanding world.

Indeed, the advent of LED technology has contributed to the phase out of the incandescent light bulb and reshaped the solid-state lighting industry as the LEDs have been incorporated in indoor lighting, large displays, device backlighting and many others. In terms of commercial viability, LED has been voted as the most promising alternative by 2020 among all the clean technologies including photovoltaic solar cells and electric vehicles. Such success is attributed to the impressive efficiency of the blue LED back in the 1990s. Since then, the research has focused on expanding the emission spectrum to include the green and red components and eventually producing energy efficient white light LEDs. However, even after decades of research, the efficiency of the green component is barely exceeding the 30% mark, way behind the 80% efficient blue LED. In fact,
the green emission is obtained through the phosphor conversion from the blue LED. Such down conversion affects not only the efficiency and produces heat, but also leads to poor color purity. Moreover, despite the rapid economic growth, the tradeoff between the manufacturing cost and the quality of the LEDs limits the overall customer satisfaction. Thus, the second generation of LED will rely on the direct emission of different wavelengths across the visible spectrum, along with low-temperature low-cost manufacturing, high efficiency and high color purity. 

1.2 Perovskites as a Solution

Among the potential candidates for the realization of LEDs, a new class of hybrid perovskites-based materials has received recognition as they have proven competent properties for light-emitting applications. The recent successful fabrication of the one of the highest conversion efficiency LED keeps these hybrids perovskites at the top of the research interest with the end goal of commercialization. Although yet to reach the industrial stage, the perovskite-based optoelectronics have achieved the brightness and efficiency that other LEDs have accomplished over twenty years. Perovskites have an interesting research portfolio as they have dominated the field of photovoltaics and optoelectronic applications over the past few decades. The history of perovskites dates back to 1839, when the German mineralogist first discovers the calcium titanium oxide. The crystal structure of CaTiO$_3$ was later characterized by the Russian mineralogist Perovski, hence the name perovskite. Since then, perovskite has been
Figure 1.1 (A) the general structure of perovskite with the formula ABX$_3$. (B) Spectral tunability of MAPb$_n$Br$_{3-n}$ from 390 nm – 790 nm. (C) Perovskites have demonstrated color spaces covering a larger area than the National Television System Committee (NTSC). Reprinted by permission from ref. copyright (2015) with permission from Macmillan Publishers Ltd, Nature Photonics. (D) standard colloidal organometal halide perovskite CH$_3$NH$_3$PbX$_3$ (X = halides) nanoparticles shows a maximum luminous efficiency of 11.49 cd/A, a power efficiency of 7.84 lm/W, and an external quantum efficiency of 3.8%. Reprinted with permission from ref.13 Copyright (2016) American Chemical Society.
used to refer to any material adopting crystal structure ABX$_3$, where A and B are different cations counterbalanced by the X anion.\textsuperscript{17} Few years following its discovery, many breakthroughs have been witnessed, from the first report on halide-based perovskites investigating the optical properties of CsPbX$_3$ (X=Cl, Br, and I) in 1958 \textsuperscript{18}, to the first hybrid organic inorganic metal-halide resolved structure \textsuperscript{19}, and the first work on perovskite-based electronic devices featuring thin film transistors (TFTs) and light-emitting diodes (LEDs) in 1990s. \textsuperscript{20-23} However, in 2006, the photovoltaic community was astonished by the integration of perovskite into solar cells, and a new chapter in the history of perovskite had been written.\textsuperscript{13} The accelerated and intense research focusing on improving the stoichiometry, stability and device architecture of perovskite-based solar cells (PSC) resulted in a jump of the power conversion efficiency from merely 2.6\% in 2006 to a record of greater than 20\% in by the end of 2016. \textsuperscript{24-29} The attention that was given to study the photophysics of perovskites for photovoltaics led to parallel advancement in the optoelectronics as well, mainly due to the tunability of the PL spectrum upon halogen substitution, the excellent charge carrier mobility along with the improved solution-processed synthesis and growth of perovskite single crystals and thin films. \textsuperscript{30}
1.3 Conventional Low-Dimensional Perovskites

Initial attempts to integrate perovskite into the LED were not very encouraging since perovskite in general have low exciton binding energy (i.e. the energy necessary to generate an electron-hole pair) and therefore, low probability of radiative recombination.\(^{31}\) Until 2015, the work on the bulk ABX\(_3\), which ensembles an inorganic framework of metal octahalide extending in the three dimensions, was the center of the comprehensive studies. However, later that year, the realization of perovskites nanocrystals (NCs) received with excitement as halide-based multinary compounds have added another degree of freedom for compositional diversification compared to the metal chalcogenide nanocrystals, combining the advantages of both categories.\(^{32-33}\) The pioneer work on the colloidal CsPbX\(_3\) shows tunability of the bandgap between 410 nm (3.02 eV)– 700 nm (1.77 eV), covering the whole visible spectrum, with an impressive near-unity quantum yield and short lifetime in the nanoseconds, setting a starting point for low-dimensional perovskites.

Perovskites NCs have proven to be good candidates for many optoelectronic applications. Since then, the work on the compositional derivatives of low-dimensional perovskites has blossomed and, eventually, the work on the optimization of low-dimensional perovskite materials expanded the family to cover different shapes and sizes. Examples include the two-dimensional nanoplatelets \(^{34-36}\), one-dimensional nanowires, hybrid and all-inorganic perovskites.
To fully understand the distinction between the three-dimensional and low-dimensional perovskites, we need to think in terms of the density of states and electronic band structure. In bulk materials – that is in the macroscopic region - the electrical and optical properties are based on the quantum mechanical coupling of the electronic wavefunctions of thousands of atoms producing a continuous band structure. However, at the nanoscale, the motion of the charge carriers is confined in one or more dimensions and, consequently, the bulk quantum laws are no longer applied. Instead, the atoms experience size-dependent quantum effect. A direct implication of such spatial confinement is the size-dependent bandgap of semiconductors. Thus, the classical approach to the quantum confinement in semiconductors is through an external control of physical dimensionality by manipulating the physical size of the nanocrystals, affecting neither the local crystal structure nor the composition of the constituent atoms.

1.4 Low-Dimensional-Networked Perovskites

Alternatively, the quantum confinement could be accessed through internal structural modification. For example, in case of lead-based perovskites, another classification of lower dimensionally is realized based on the connectivity of the \([\text{PbX}_6]^{4-}\) octahedra. For the all inorganic cesium lead tri-halide perovskites, a more general formula could be written as \(A_n\text{PbX}_{n+2}\), with \(n=1\) corresponds to the three-dimensional perovskite, and \(n= 2 - 4\) to the low-dimensional perovskites, in which the octahedra could be arranged in sheets (two-dimensional)\(^{37}\) and chains (one dimensional)\(^{38}\) for \(n=2\) and \(n=3\), respectively. In the extreme case, when \(n= 4\), the
octahedra are completely isolated; hence, the zero-dimensional perovskite-related material nomenclature, which appeared for the first time in literature in 1999 \textsuperscript{21} in reference to the Isolated PI\textsubscript{6} ions in (CH\textsubscript{3}NH\textsubscript{3})\textsubscript{4}PbI\textsubscript{6}-2H\textsubscript{2}O. \textsuperscript{39} Figure 1.3 illustrates the structural and morphological difference between the low-dimensional networked and conventional low-dimensional perovskites. \textsuperscript{40}

Recently, Bakr et al. suggested a new perspective on the terminology to distinguish between the two classes of low-dimensional perovskites, in which low-dimensional-networked (L-DN) was proposed to refer to the latter classification or “structurally formed potential barriers embedded in the crystal lattice.” \textsuperscript{41}
Figure 1.2 The electronic structures of lead iodide based low-dimensional crystals illustrate the bonding diagram of (A) $[\text{PbI}_6]^{4-}$ cluster of zero-dimensional system. (B) 3D crystal CH$_3$NH$_3$PbI$_3$ and 2D crystal (C$_4$H$_9$NH$_3$)$_2$PbI$_4$ at the top of the valence band and the bottom of the conduction band. (C) Crystal structures of inorganic parts of 3D crystal CH$_3$NH$_3$PbI$_3$ and 2D crystal (C$_4$H$_9$NH$_3$)$_2$PbI$_4$. Reprinted figure with permission from ref. Copyright (2003) by the American Physical Society.
Figure 1.3 The crystallographic and morphological differences between the low-dimensional networked and conventional low-dimensional perovskite. (A) A schematic representation presenting the structural variation between different low-dimensional networked perovskites through the connectivity of the metal-halide octahedral. Reprinted with permission from ref. 41 Copyright (2016) American Chemical Society. (B) An SEM image of the zero-dimensional networked Cs$_4$PbBr$_6$. Figure reprinted from ref. 40 with permission from John Wiley and Sons. (C) A schematic illustration showing the controllability of the nanocrystal dimension through a ligand-mediated process, in which the core of all different NCs is the conventional three-dimensional CsPbX$_3$. Reprinted with permission from ref. Copyright (2016) American Chemical Society.
1.5 Conventional vs. Low-Dimensional-Networked Perovskites

Although both classes of low-dimensional perovskites exhibit high exciton binding energy, the use of ligands in the colloidal quantum dots (CQDs) presented another challenge. Ligands are required to preserve the integrity and structural property of CQDs and to avoid the very-likely aggregation induced by the nanometric size. The loss of ligands leads to a major shortcoming as it introduces trap states that require further treatment. The CQDs also show low luminescence due to ligand aggregation when later made into thin films. In some applications, those ligands are necessary as they could be functionalized to serve more than just the mere confinement as in biomedical applications. However, there are other applications that the confinement, but not the ligands, is desired. In that sense, the low-dimensional networked perovskites have an advantage over the conventional nanocrystals as the confinement comes from their unique structure and not through encapsulation of ligands.

Another advantage of the L-DN perovskites is their insensitivity to particle size. The conventional low-dimensional perovskites have shown dependency of the PL spectrum on the thickness. Such correlation affects the particle size distribution and the reproducibility of the NCs of certain properties. However, the PL spectrum of the L-DN perovskites is independent of the thickness and gives only discrete options, rather than a continuous profile.
The work presented by Dou et al. provides an excellent case study for the correlation between the thickness and the PL properties of the 2-DN perovskites. In their work, the bulk 2-DN organic-inorganic hybrid (C$_4$H$_9$NH$_3$)$_2$PbI$_4$ perovskite was compared to atomically thin layers of the same material. The study revealed that 2-DN perovskite of 3–22 layers thick (average thickness between 1.6 nm–3.6 nm) and the bulk have PL peaks of 406 nm (3.01 eV) and 411 nm (2.97 eV), respectively. The slight blue shift of only 5 nm (40 meV) upon reducing the size as shown in Figure 1 proves that the confinement is an intrinsic property originating from the internal structure, independent of the size of the particle.

Figure 1.4 (A) The steady-state PL spectrum of the bulk and the few 2D sheets. (B) the optical image of the bulk crystal under excitation. Scale bar, 20 μm. (C-E) Optical images of the 2D sheets with 22 layers, 8 layers, and 3 layers. Scale bars, 2 μm. (F) SEM image of a 2D sheet. Scale bar, 2 μm. (G) The corresponding cathodoluminescence image showing the emission (with a 40-nm band pass filter centered at 415 nm). Figure reprinted from ref. copyright (2015) with permission from AAAS.
By contrast, the PL spectrum of the conventional low-dimensional perovskite is strongly dependent on the particle size. Figure 1.5 shows CsPbI$_3$ nanoplatelets, in which the bandgap could be tuned over a range of around 400 meV by reducing the size of the bulk that has an initial bandgap of 1.8 eV to 2.2 eV for a two-layer thick material.$^{43}$

![Figure 1.5](image)

**Figure 1.5** Tuning the optical properties by thickness control in the conventional low-dimensional perovskites. (a) UV/Vis absorption and PL spectra of CsPbI$_3$ NCs as a function of Cs$_2$CO$_3$/PbI$_2$ ratios (b-e) and the corresponding TEM images. (f) Calculated and experimental band gap energies of the perovskite NPLs as a function of the thickness. (g) The recorded lifetimes of a mixture of CsPbI$_3$ nanoplatelets with different thicknesses. Figure reprinted from ref.$^{43}$ copyright (2016)with permission from John Wiley and Sons.
1.6 Objectives and Outline

So far, the studies on the L-DN perovskites in literature have been mainly about the layered hybrid perovskites, with scared information on the all-inorganic L-DN materials. 41

Although L-DN perovskites seem very attractive, issues like synthesis and phase separation hinder their characterization and our understanding of the structure-property relation of those materials.44 Thus, the goal of this thesis is to unravel the structure and the optical properties of the all-inorganic Cs₄PbX₆ 0-DN perovskites. The initial stage of investigating the optical properties of these materials is synthesizing high quality samples. Chapter 1 reviews the synthesis methods attempted in literature and demonstrates the new technique adopted in this work, followed by Chapter 2 which deals with the structural and morphological verification of the compounds. In Chapter 3, the detailed results of the optical characterizations are presented and compared to the data reported in literature. Chapter 4 focuses on the high quantum efficiency of the 0-DN materials and correlates the optical properties to the lifetime and exciton binding energy. Chapter 5 is devoted to discuss the origin of the luminescence of the 0-DN perovskites highlighting the most probable explanations, mainly 3D inclusions and intrinsic behavior due to defects and trap states. This thesis concludes with Chapter 6 that summarizes the results and gives directions for future work.
Chapter 2

Synthesis and Structural Verification

This chapter deals with the synthesis and structural verification of Cs₄PbX₆ through XRD along with imaging from the optical microscope and SEM.

2.1 Introduction

There are three stable ternary compounds in CsBr-PbBr₂ phase diagram; CsPbBr₃, which melts congruently, and two that melt incongruently, Cs₂PbBr₅ and Cs₄PbBr₆.⁴⁵ In fact, Cs₄PbBr₆, one of the compounds under investigation in this thesis, has been reported in literature as an unavoidable co-phase of CsPbBr₃ in both the bulk and the thin films.

![Figure 2.1 The quasi-binary phase diagram of CsBr-PbBr₂ featuring three thermodynamically stable phases; CsPbBr₃, which melts congruently, and two that melt incongruently, Cs₂PbBr₅ and Cs₄PbBr₆. The incongruent melt of Cs₄PbBr₆ made growth techniques from the melt like Bridgman method unsuccessful.](image-url)
In literature, the bulk Cs$_4$PbBr$_6$ was grown from the melt by Bridgman method$^{46}$, and slow cooling of a saturated hot solution followed by a subsequent evaporation to form the thin film. $^{47-48}$ Both studies concluded the difficulty of separating the two phases due to the incongruent melting crystal growth process in the former method and relatively similar melting points in the latter. Another method to synthesize Cs$_4$PbBr$_6$ was through coating a CsBr single crystal with a thin layer of PbBr$_2$ and then annealing the crystal at elevated temperatures. Upon annealing, PbBr$_2$ diffuses into the crystals forming CsPbBr$_3$, Cs$_4$PbBr$_6$ and some randomly distributed Pb-aggregates.$^{49}$ Further efforts allowed the isolation of Cs$_4$PbBr$_6$ when prepared by annealing either a two-layer or an alternating-layer system of PbBr$_2$/CsBr/silica-glass at 500 K.$^{50}$ This method produced thin films of a single phase Cs$_4$PbBr$_6$ with excess of CsBr. The existence of CsBr, however, did not affect the optical properties study since the absorption spectrum of the two compounds do not overlap. Thus, to the best of our knowledge, the preparation of pure Cs$_4$PbBr$_6$ has not been reported without any co-product or leftover precursors.

Figure 2.2 shows a schematic illustration of the vertical Bridgman growth method.$^{51-52}$ Figure 2.3 reviews different thin film deposition technique usually attempted for perovskites.$^{53}$
Figure 2.2 (Left) Optical photograph of the as-grown CMT ingot grown by the vertical Bridgman technique. Figure reprinted from rdf.\textsuperscript{51} copyright (2016) with permission from Elsevier. (Right) Illustration of the Bridgman technique adopted to grow single crystals including perovskites. Figure reprinted from ref.\textsuperscript{52} copyright (2004) with permission from Elsevier.

Figure 2.3 Deposition methods for perovskite thin films. (a) single-step solution deposition, (b) two-step solution deposition, (c) two-step hybrid deposition, and (d) thermal vapor deposition. Figure reprinted with permission from ref.\textsuperscript{53} copyright (2009) Society of Photo Optical Instrumentation Engineers.
2.2 Inverse Temperature Crystallization

Generally the solubility of materials is directly proportional to the solvent temperature. However, there are few materials that do not follow the rule and instead precipitate upon increasing temperature displaying retrograde solubility behavior in the solvent. Such unusual solubility trend in hybrid organic-inorganic perovskites was first discovered in 2015 by Saidaminov and co-workers, and has been successfully employed to grow sizable single crystals of MAPbBr\textsubscript{3} and MAPbI\textsubscript{3} perovskites as illustrated in Figure 2.4. Fortunately, the relative low temperature solution-based rapid growth of the single crystals did not affect the quality of those crystals. All which inspired the adoption of this method to synthesize other compounds of the perovskite family, including the zero-dimensional networked perovskites.

![Figure 2.4](image_url)

**Figure 2.4** (A) The illustration of the ITC method. The solution vial is kept in a secondary container of silicon oil that is heated to 80 C. (B) The continuous growth of the single crystals is enabled by seeding. (C) Manipulation of the crystal morphology through the changing the geometry of the growth vessel. Reprinted with permission from ref. Copyright (2015) Nature Communications.
2.3 Synthesis Method

During the growth of CsPbBr₃ single crystals, we observed the formation of concomitant 0-D, Cs₄PbBr₆ perovskite phase. This yellow precipitate is difficult to dissolve and upon further increase of temperature transforms into orange precipitate of CsPbBr₃, which indicates the stability of the 0-DN phase at lower temperatures compared to 3D. Thus, we focused on synthesizing the Cs₄PbBr₆ powder separately. At high concentration of PbBr₂, the two phases coexist. However, increasing the CsBr:PbBr₂ ratio from 1:2 to 1:1 results in Cs₄PbBr₆ phase only as Cs-rich 0-DN phase needs more of CsBr precursor in the solution. In the optimized method, Cs₄PbBr₆ was synthesized through a one-step process at room temperature. To prepare the powder, (3 mmol) of PbBr₂ and (3 mmol) of CsBr were dissolved in 1 ml dimethyl sulfoxide (DMSO) and stirred for one hour at room temperature. Starting from 60 °C, the temperature was increased with a heating rate of 5 °C/30 mins. At 70 °C, the solution was decanted into new vials, and kept heating until 120 °C. The solution was filtered through a filter paper and the precipitate was then washed with DMSO. The collected powder was dried under vacuum and stored in ambient conditions.

To synthesize Cs₄PbCl₆, (3 mmol) of PbCl₂ and (3 mmol) of CsCl were dissolved in X mL of DMSO. The concentration of the solution and therefore the final yield is low due to the low solubility of CsCl in DMSO. After stirring, the solution was transferred into new vials and set directly at 100 °C. The Cs₄PbCl₆ powder was collected overnight. As for the Cs₄PbI₆, the precursors (3 mmol) of PbI₂ and
mmol) of CsI were dissolved in DMF and after stirring they were transferred into new vials where they were heated at 110 °C overnight.

**Figure 2.5** (A) Schematic illustration of the synthesis and purification of Cs₄PbBr₆. (B) The PXRD pattern for the powders before and after washing. The inclusion of the CsPbBr₃ before washing resulted in an extra peak in the PXRD pattern. The washing step eliminated the 3D phase as evidenced by the absence of the 3D diffraction peak and the brighter color of the powder. Reprinted with permission from ref. 44 Copyright (2016) American Chemical Society. (C) As-synthesized Cs₄PbI₆ in solution and after the extraction and washing with DMF.
2.4 Crystal Structure

There is a controversy in literature regarding the crystal structure of Cs$_4$PbCl$_6$ and Cs$_4$PbI$_6$. Petrov et al. proposed a monoclinic crystal structure with a space group of B2/b $^{56}$, while a more recent work by Andrew et al. reported a hexagonal one with a space group R-3c$^{47}$, supported later by the work from Nitsch et al.$^{57-58}$ However, both structures share the octahedron [PbX$_6$]$^{4-}$ as the building block which, as we will see later, controls the optical properties of zero-dimensional perovskites. Here, we adopted the hexagonal crystal structure for the initial phase identification, which then was confirmed by means of XRD and other characterization methods.

Figure 2.6 The crystal structure of the (left) three-dimensional perovskite, and (right) 0-DN. The structural difference lies in the connectivity of the [PbX$_6$]$^{4-}$ octahedral. Although Br-based perovskite presented here, similar crystal structures apply also to CsPbX$_3$ (X=Cl, I) and Cs$_4$PbI$_6$ (X= Cl, I). (Adapted from. Copyright 2014 American Chemical Society.). Reprinted with permission from ref.44 Copyright (2016) American Chemical Society.
2.5 Experimental Methods

2.5.1 Powder X-ray diffraction

Powder X-ray diffraction (PXRD) was the first characterization to run upon acquiring new materials. The powder X-ray diffraction was performed on a Bruker AXS D8 diffractometer using Cu-K radiation. Then generated patterns then compared to calculated patterns based on known crystal structures reported in literature.

2.5.2 Scanning Electron Microscopy

The SEM images were taken using Quanta 200 FEG instrument.

2.6 Results and Discussion

2.6.1 Powder X-Ray Diffraction

The PXRD pattern of the prepared sample confirms the phase purity of 0-DN Cs₄PbX₆ perovskite, which is also in a good agreement with the calculated PXRD pattern. Figure 2.7 shows the PXRD spectrum of the prepared and calculated Cs₄PbBr₆ along with the calculated XPRD pattern for CsPbX₃ for the sake of comparison. Thus, the single phase of Cs₄PbBr₆ was successfully produced through an easy, cost-effective and scalable method.

To investigate the possibility of phase transitions upon cooling, non-ambient PXRD was run for all samples. The results presented in Figure 2.8 confirms the absence of any phase transition below room temperature. Such finding will be useful for the analysis of temperature-dependent PL presented in Chapter 4.
Figure 2.7 The PXRD patterns for (A) Cs₄PbCl₆, (B) Cs₄PbBr₆, and (C) Cs₄PbI₆. The powders obtained in this work through ITC method were compared to the calculated pattern generated through a crystal visualization software and the crystal structure from the MaterialsSpringer database. The PXRD patterns for the three-dimensional CsPbX₃ were also included for comparison and to conform the absence of evidence to the existence of those phases in the powders.
Figure 2.8 Temperature PXRD results for Cs$_4$PbI$_4$, from 98 K (-175 °C) to 308 K (35 °C). The absence of the appearance of new diffraction peaks and the disappearance of the already existed ones exclude any low-temperature phase transitions.
2.6.2 Scanning Electron Microscopy

Figure 2.9 SEM images of (A-C) Cs$_4$PbBr$_6$, (D) Cs$_4$PbI$_6$. The particles ensemble the hexagonal crystal structure with irregular particles probably due to washing and grinding.
2.7 Conclusion

The all-inorganic 0-DN perovskites Cs$_4$PbX$_6$ (x = Cl, Br and I) were successfully synthesized through inverse temperature crystallization (ITC). Powder XRD patterns of synthesized materials confirmed phase purity and compared to calculated patterns based on previously reported crystals structures. Initial characterizations showed inclusions of CsPbX$_3$ that were eliminated later through washing with the same solvent used in the synthesis. Results from the non-ambient PXRD showed no evidence of phase transitions at low temperature, up to 98 K. The images obtained from SEM show some particles with hexagonal crystal structure along with the irregular particles. Next, the optical properties will be investigated.
Chapter 3

Optical Characterization

Next, the optical properties of zero-dimensional perovskite-related materials have been investigated. This chapter presents the experiments and results of the steady-state photoluminescence and optical absorption measurements, and compares the results from this work to similar light-emitting materials in literature.

3.1 Experimental Methods

3.1.1 Absorption

Halide-based perovskites being direct bandgap semiconductors are known for their strong optical absorption. Thus, the first step after the synthesis was studying the absorption spectrum. In this work, the optical absorption spectrum was measured using Cary 6000i UV-Vis-NIR spectrophotometer supplied with integrating sphere.

3.1.2 Steady-State Photoluminescence (PL)

The steady state PL measurements were performed using an Edinburgh Instruments FLS920 Fluorescence Spectrometer equipped with 450 W continuous wavelength xenon lamp. The excitation wavelengths varied based on the material and specified under each PL spectrum.
3.2 Results and Discussion

3.2.1 Absorption

Perovskites, and Lead halide perovskites in particular, have strong absorption that is attributed to the high lead p-p transition probability. First-principle calculations revealed that the absorption spectrum of the halide perovskite materials is ultimately determined by two components. First, the transition matrix elements, which measures probability of all the photoelectric transitions between the valence band and conduction band states. The other is the joint density of states (JDOS) of the interband transitions represented by the product of the density of states (DOS) of the valence and conduction bands. 59-61

To understand the absorption mechanism in perovskites, a comparison between MAPbI₃, GaAs and Si, the absorber layers of the three generations of solar cells presented in Figure 3.1. Starting with silicon, the absorption near the band edge is coming from the transition between the valence band formed by the p orbital to p and s orbitals in the conduction band. Being indirect bandgap the transition probability is weak which implies thicker layer is needed, adding to the expenses of this material. GaAs and perovskites, on the other hand, are marked by their strong absorption due to their direct bandgaps. However, perovskites have significantly higher absorption since the lower part of the conduction band is formed by the degenerate b orbital of Pb, which is less dispersive than the degenerate s orbital in
GaAs. Consequently leading to higher DOS of the former, hence the order of magnitude difference in the optical absorption coefficient.\textsuperscript{60, 62}

\textbf{Figure 3.1} The schematic optical absorption of (a) first-generation, (b) second-generation, and (c) halide perovskite solar cell absorber. GaAs has been chosen as a prototypical second-generation solar cell absorber. Reprinted with permission from ref.\textsuperscript{62} Copyright (2015) Royal Society of Chemistry.
Since the bandgap and the subsequent optical transitions is determined by the $[\text{PbX}_6]^{4-}$ ocraedra,$^{23}$ the aforementioned argument holds true when applied to other lead-halide perovskites, including the zero-dimensional-networked materials. The absorption spectra of the three halide compounds are presented in Figure 3.2.

The UV-vis absorption spectra feature absorption edges at 400 nm, 520 nm and 690 nm for $\text{Cs}_4\text{PbCl}_6$, $\text{Cs}_4\text{PbBr}_6$ and $\text{Cs}_4\text{PbI}_6$, respectively. The three curves have similar shape, with saturated spectra for wavelengths shorter than 450 nm and absorption edge at the other end of the spectra. The data represented here is consistent with values reported in literature for the $\text{Cs}_4\text{PbBr}_6$ powders$^{63-64}$ and NCs.$^{65}$ However, the latter also reported a strong absorption peak at 315 nm, highlighting the controversy in literature regarding the origin of the optical properties of those materials. In fact, there are groups that attributed the green emission to the inclusions of $\text{CsPbBr}_3$ and assigned the longer wavelength absorption edge to those 3D nanoparticles, while the shorter peak to the isolated octahedra, and a more recent work show their clear and transparent solution with absorbance peaks at 220 nm and 313 nm.$^{66}$ Similarly, the absorption peaks of $\text{Cs}_4\text{PbCl}_6$ and $\text{Cs}_4\text{PbI}_6$ were assigned to the 3D aggregates embedded in the matrix of the zero-dimensional materials.$^{67-70}$ These peaks were linked to the halide $s_{1/2}-p_{1/2}$ transitions within the isolated octahedral, in favor of the data from the earliest work on those materials.$^{46, 50, 71}$ More on this discrepancy will be discussed in Chapter 5.
Figure 3.2 The optical absorption spectra featuring absorption edges of (A) Cs₄PbCl₆ (400 nm), (B) Cs₄PbBr₆ (520 nm), and (C) Cs₄PbI₆ (690 nm).
3.2.2 Steady-State Photoluminescence (PL)

Perovskites, as many other semiconductors, lose their energy through spontaneous emission after being excited to higher energy levels. For the emission to take place, the injected electrons must relax back to the ground state, which could be either the bottom of the conduction band or another discrete level, in which the emission occurs. Since having more than one electron with the same quantum state violates Pauli Exclusion Principle, the lower state must be empty.\textsuperscript{72} Recall that for the halide-based perovskites, the substitution of the halide component allows for spectral tunability in the visible range. The conduction band and valence band are determined by the lead and halide orbitals, respectively. Thus, by fixing all other sites, the X-site determines the band gap by changing the valence band composition from 3p for Cl, to 4p for Br and 5p for I we decrease the negative overlap between the lead and halide orbitals, and consequently, shrinking the bandgap.\textsuperscript{73}

However, not all excitation-relaxation processes involve radiative emission as shown in Figure 3.3.\textsuperscript{74} The material could undergo a non-radiative emission in which the excess of energy is released as local vibrations of the surrounding atoms producing excess of heat (phonons) or transfer as a kinetic energy to another electrons as in Auger recombination.
Figure 3.3 A schematic of the photophysical processes and loss mechanisms in perovskites following photoexcitation. Efficient (or strong) pathways and suppressed (or weak) pathways are denoted by the black and grey lines, respectively. Monomolecular recombination is charge carrier density independent, while bimolecular and Auger recombination are charge carrier density dependent processes that would typically be present under high intensity photoexcitation. In fact, under even higher photoexcitation densities, amplified spontaneous emission (ASE) will out-compete Auger recombination. However, under solar light intensities (low intensity excitation), these latter processes will be strongly suppressed. Reprinted with permission from ref. 74 Copyright (2014) Royal Society of Chemistry.
Figure 3.4 shows the PL spectrum was successfully tuned from 410 nm for Cs$_4$PbCl$_6$ to 520 nm for Cs$_4$PbBr$_6$ and finally to 700 nm for Cs$_4$PbI$_6$. The PL peak position of the Cs$_4$PbBr$_6$ agrees well with the recent reports in literature.$^{44, 63, 65}$ Those peaks are blue-shifted by around 20 nm – 30 nm compared to the three-dimensional perovskite crystals counterpart. By comparing Figure 16 and Figure 18, we can clearly see that the PL peaks are located at the tail of the absorption edge.

The disagreement in the absorption data between this work and some reports extends to the PL results since the absence of the absorption edge is also coupled with the blue shift in the PL peak. The Cs$_4$PbBr$_6$ PL was centered at 375 nm upon 313 nm excitation. $^{40, 66}$ On the same note, in literature, the 410 nm PL peak of Cs$_4$PbCl$_6$ and the 700 nm peak of Cs$_4$PbI$_6$ was assigned to the three-dimensional CsPbCl$_3$ and CsPbI$_3$, respectively.$^{58, 68, 71}$

Interestingly, in both materials, the shape and peak position of the PL spectra are independent on the excitation wavelength, indicating the absence of defects and trap-states, as such defects could introduce sub-bandgap states and, in turn, induce deformations and/or new PL peaks in the longer wavelength side of the spectrum.$^{46}$
Figure 3.4 The PL spectrum of (A) Cs₄PbCl₆ (peak at 410 nm) (B) Cs₄PbBr₆ (peak at 520 nm), and (C) Cs₄PbI₆ (peak at 700 nm)
3.3 Conclusion

The optical properties of Cs₄PbX₆ have been investigated through the absorption and photoluminescence spectroscopies. The absorption edges were found to be at 400 nm, 520 nm and 690 nm for Cs₄PbCl₆, Cs₄PbBr₆ and Cs₄PbI₆, respectively. The PL spectrum was also successfully tuned with PL peaks from 410 nm for Cs₄PbCl₆, to 520 nm and 700 nm for Cs₄PbBr₆ and Cs₄PbI₆. Although the results are consistent with some of the recent reports, but there is also a large discrepancy that could not be ignored. A detailed study of the underlying science behind the origin will be discussed in Chapter 5. Next, the high photoluminescence quantum yield of the zero-dimensional-networked will be investigated.
Chapter 4

Luminescent Properties

4.1 Introduction

The bulk three-dimensional APbX₃ have corner-shared octahedra where the electronic wavefunctions overlap leading to a continuous band structure analogous to any other bulk semiconductor. In contrast, the quantum confinement in LDN perovskites is prevalence and has a direct impact on their optical and optoelectronic properties. As a consequence of their structure, the low dimensional 0-DN perovskites exhibit a unique behavior arising from the quantum confinement effect, which is directly reflected on their electrical and optical properties. Figure 4.1 shows a comparison between CsPbBr₃ and Cs₄PbBr₆ powders under a UV lamp. We can clearly see that three-dimensional CsPbBr₃ shows no luminescence characteristic when exposed to UV light at 365 nm, while the zero-dimensional perovskite is bright green.

Figure 4.1 CsPbBr₃ and Cs₄PbBr₆ powders under a 365 nm UV lamp. Reprinted with permission from ref. 44 Copyright (2016) American Chemical Society.
Such property is worth investigating, as it has direct implications when it comes to the use of those materials in optoelectronic devices. This chapter will address the effect from the exciton binding energy and lifetimes on the outstanding photoluminescence quantum yield (PLQY) of these materials.

4.2 Experimental Methods

4.2.1 Time-Resolved microscopy

As discussed in Chapter 3, the zero-dimensional perovskites with the bound-excitons undergo a spontaneous radiative recombination. Einstein coefficient $A$ allows calculating the spontaneous emission rate for radiative transition between two levels, which depends on the upper-level population of the electrons $N$ at time $t$:

$$\frac{dN}{dt} = NA$$  \hspace{1cm} (1)

By solving the equation above, we get:

$$\left(\frac{dN}{dt}\right)_{\text{total}} = \frac{-N}{\tau_R} - \frac{N}{\tau_{NR}} = -N\left(\frac{1}{\tau_R} - \frac{1}{\tau_{NR}}\right)$$  \hspace{1cm} (2)

Where $n$ is the luminescence efficiency $\tau_R$ and $\tau_{NR}$ are the lifetimes for the radiative and non-radiative recombinations, respectively. The coefficient $A$ is directly proportional to the absorption coefficient $B$ and inversely proportional to the lifetime of radiative recombination, which has two implications. First, the high
efficient light-emitting materials have shorter lifetimes; and second, good absorbents are potentially good emitters.

By Dividing Equation 2 by Equation 1, we get:

\[
\eta = \frac{AN}{N(1/\tau_R + 1/\tau_{NR})} = \frac{1}{1 + (\tau_R / \tau_{NR})} \quad (3)
\]

Thus, when the radiative recombinations have shorter lifetime, the efficiency or the PLQY increases until it reaches unity when the radiative recombination completely dominates. In this work, the lifetime has been recorded using Ultrafast system HALCYONE femtosecond fluorescence spectrometer.

4.2.2 Steady-State PL with Integrating Sphere

Following the method reported by de Mello et al, the absolute quantum yield was measured through the Edinburgh instrument FLS920, equipped with integrating sphere. Initially, the excitation-emission map was generated for each material, and then the excitation wavelength that gave the highest intensity peak was used in the PLQY measurement. The PLQY was then calculated based on the following equation\(^7\):

\[
\eta = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}} = \frac{L_{\text{sample}}}{E_{\text{reference}} - E_{\text{sample}}} \quad (4)
\]

Where \(L_{\text{sample}}\) is the emission intensity of the sample, and \(E_{\text{reference}}, E_{\text{sample}}\) refer to the scattered emission from the reference and sample, respectively.
4.2.3 Temperature-Dependent PL

The temperature-dependent PL was measured using Horiba JY LabRAM Aramis spectrometer equipped with an Olympus 50x lens in a Linkam THMS600 stage. From the TDPL, the exciton binding energy can be estimated from the following equation:

\[ I(T) = \frac{I_0}{1 + A e^{-E_b/k_b T}} \]  

(5)

where \( I_0 \) is the integrated PL intensity at 6 K, \( E_b \) is the exciton binding energy, and \( k_b \) is the Boltzmann constant. Two distinct features were observed: the blue shift as the temperature increase and the increase of the FWHM as a function of temperature.
4.3 Results and Discussion

4.3.1 Photoluminescence Quantum Yield (PLQY)

A high quantum yield is an attractive advantage of some semiconductors that unlock applications for lasers, light converters, LEDs, and many others. The photoluminescence quantum yield (PLQY) is defined as the ratio between the photons emitted to the photons absorbed.

The trap-state density is often thought to correlate with the high PLQY such that materials with low trap density should have near ideal quantum yield.\(^76\) However, such correlation does not hold true in case of three-dimensional perovskite CsPbBr\(_3\) that have trap density as low as \(10^{-3} \text{ cm}^{-1}\), and yet, their quantum yield barely exceeds 0.1%.\(^77-78\)

Recently, the two-dimensional Cs\(_2\)PbBr\(_5\) has been reported to have a PLQY of 87% in solution, and although not reported, the value is expected to still be high in solid state.\(^79\) In fact, a close examination of perovskite materials with high quantum yield reveals that those materials are low dimensional and have an outstandingly high exciton binding energy. Recall that the high exciton binding energy means the photoexcitation of the optical band-gap charge carriers are bound-exciton, rather than free-excitons or free carriers. Consequently, the probability that the bound-pair will recombine rather than dissociate is higher. As for the origin of such high exciton binding energy, it could be explained in terms of quantum confinement.
The structural difference between the 3D and low-dimensional materials lies in the coordination of the octahedron. In case of 2D perovskites, the octahedra are arranged in isolated planes rather than a connected matrix. Indeed, the 0D presents the extreme case of confinement where the octahedra are completely isolated preventing the extension of the electronic states of their corresponding atoms, forcing the charge carriers to recombine radiatively. This theoretical explanation is not only consistent, but also correlates the PLQY to the exciton binding energy. 80-82

Similar phenomenon has also been realized for the perovskite quantum dots as perovskite QDs possess near ideal PLQY in solution. Yet, one major drawback is the lack of it once they are made into solids, such as powders and thin films. The sharp decrease is due to the complications of ligand aggregations and stability in ambient conditions. Once those solutions are deposited to make the thin films, they start forming aggregations leading to dispersion and film uniformity issues. As a result, their photoluminescence quantum yield drops significantly from 50-90% to as low as 20%. 83 Thus, the loss of the luminescence characteristic in perovskite quantum dots presents a challenge that holds back the use of those particles in a solid-state form. The goal of this chapter is to investigate the luminescence characteristics of the 0-DN perovskites, including their PLQY.
The PLQY results from the direct measurement through the integrating sphere shows 45% QY for Cs$_4$PbBr$_6$, a record for solid-state perovskites. PLQY of 14% and < 1% were recorded for Cs$_4$PbI$_6$ and Cs$_4$PbCl$_6$, respectively. The high exciton binding energy for Cs$_4$PbBr$_6$ is consistent with the recent reports in literature.$^{64-65}$ Figure 20 shows the TDPL of Cs$_4$PbX$_6$ in which the PL was measured over a temperature range from 6 K – room temperature. Clearly, the singularity of the peak for all temperatures indicates the excitonic origin of the emission along with the absence of any phase transitions, which was already confirmed by non-ambient PXRD in Chapter 2. The PLQY was estimated from the temperature-dependent PL by taking the ratio of the integrated intensity for the PL peak at room temperature to the peak at 6 K. In this method, two major assumptions were made. First, the materials are defect-free and the, therefore, the PLQY is unity at 6K. $^{84}$ The calculated PLQY from TDPL of Cs$_4$PbBr$_6$ was the highest at 40%, followed by 27% for Cs$_4$PbI$_6$. Unfortunately, it was not technically possible to measure the PLQY for Cs$_4$PbCl$_6$ due to a rather complicated TDPL curve.
Figure 4.2 TDPL for (A) Cs$_4$PbBr$_6$, and (B) Cs$_4$PbI$_6$. 
4.3.2 Time-Resolved Photoluminescence (TRPL)

PL decay curves of Cs$_4$PbX$_6$ are fitted by the bi-exponential function. Figure 4.3 shows the lifetimes of Cs$_4$PbCl$_6$ and Cs$_4$PbI$_6$ materials upon excitation. All lifetimes were in the nanoseconds, with the shortest for Cs$_4$PbCl$_6$ ($t_1 = 0.175$ ns and $t_2 = 1.46$ ns) and similar lifetimes for Cs$_4$PbBr$_6$ ($t_1 = 4.7$ ns and $t_2 = 24.3$ ns) and Cs$_4$PbI$_6$ ($t_1 = 3.8$ ns and $t_2 = 30.8$ ns). The lifetime of Cs$_4$PbBr$_6$ is consistent with the data reported in literature for powders$^{63}$ and nanocrystals$^{65}$, and single crystals.$^{64}$ These lifetimes are 2 orders of magnitude faster than those of 3D perovskite analogues.$^{77, 85}$ These fast radiative recombination rates may be attributed to the dramatic increase in the exciton binding energy.

![Figure 4.3 TRPL results for (a) Cs$_4$PbCl$_6$ and (b) Cs$_4$PbI$_6$. $t_1$ and $t_2$ refer to the long and short lifetimes, respectively. Units in nanoseconds.](image)
Chapter 5

The Origin of the Luminescence

5.1 Introduction

From the findings of Chapters 2, 3 and 4, a significant question concerning the origin of the optical property needs to be addressed. In this chapter, the focus will be on the two most probable answers, mainly the 3D inclusions and the intrinsic property of the material.

Two possible interpretations behind what initially thought to be an intrinsic behavior of the zero-dimensional-networked perovskites. First, according to the quantum confinement rules, the size of the individual octahedra and the blue shift of the photoluminescence between the 3D and 0D of only 30 nm are not consistent. Figure 5.1 shows how large the shift would be if it were coming from the 0-DN perovskites,\(^6\) keeping in mind that the radius of the corresponding octahedral is in the order of 0.5 nm.

The other motivation is the recent synthesis of colorless 0D nanocrystals with photoluminescence and absorption spectra evolving in the UV region. The structure of these NCs matches with the structure attributed to Cs\(_4\)PbBr\(_6\) from the PXRD (as shown in Figure 5.2), however the optical properties do not match with the already reported properties for 0-DN.\(^{6}\)
Figure 5.1 Comparison between experimental and calculated effective band-gap energies for CdSe semiconductor Qds, as functions of the dot radius. The experimental data are plotted with symbols and the theoretical predictions with solid curves. We can clearly see the large confinement energy of 2 eV upon decreasing the radius to 0.5 nm. Although the 0-DN perovskites would have a different confinement energies range, the exponential correlation is expected to still hold. Reprinted with permission from ref.86 Copyright (2006) AIP Publishing.

Figure 5.2 (A) XRD spectra of trigonal phase Cs$_4$PbBr$_6$ NCs with R3c space group compared to the standard powder diffraction pattern of bulk Cs$_4$PbBr$_6$ (λCo-κα = 1.79 Å). (B) Absorption spectrum of Cs$_4$PbBr$_6$ NCs in hexane. Inset shows the photograph of the colorless Cs$_4$PbBr$_6$ NCs hexane solution. Reprinted with permission from ref.66 Copyright (2017) American Chemical Society.
5.2 Inclusions of CsPbX3

Recall that the early work from literature assigned the absorption and PL peaks at higher energies to the 0D, while the peaks in the visible spectrum were assigned to the 3D. The basis of this argument relies on the similarities between the 3D and 0D PL peaks. Recently, the ability to synthesize 0D materials with peaks in the UV region that are not emissive in the visible spectrum supported such correlation.

From these findings, the groups correlate the optical properties and the lack of them thereof to the presence of 3D nanocrystals embedded in the matrix of 0D. In Chapter 2, the PXRD peaks pattern, showed no peaks that could possibly indicate the presence of 3D. Although we acknowledge that XRD cannot fully assess the purity of the materials due to technical limitations, the calculated the particle size of 3D QDs that should give a PL peak at 520 nm and found the size to be around 10 nm. The same size of the particles is predicted by calculation in a recent report on the zero-dimensional-networked perovskites. Such particles would be hard not to be detected by PXRD. In addition, the FWHM of the XRD peak at (121) of CsPbBr3 ($\Delta(2\theta) \sim 0.2^\circ$), which is too small for 10 nm particle size. While this thesis does not rule out the possibility of having traces or QDs of 3D perovskites, such claim will need a more concrete and direct evidence, perhaps a simultaneous measurement with a local PXRD coupled with electron diffraction (ED) and atomic force microscopy (AFM) that would correlate the local structure to the emission wavelength and the luminescence origin.
5.3 Computation results

To shed light on the properties characteristic of the 0D perovskites under investigation, density functional theory (DFT) and many-body calculations were used to calculate the bandgap and the excitonic feature of the 0D materials. By this method, the optically allowed transitions were calculated by both random phase approximation (RPA) and Bethe–Salpeter equation (BSE). The results of the computation shows higher absorption bands due to interband transitions of Pb$_2^+(6s)$Br$^-(4p)\rightarrow$Pb$_2^+(6p)$. As shown in Figure 5.3, the calculated absorption spectra are matching with those reported in literature form the early work on 0D perovskites. The exciton binding energies of the 0D materials are calculated based on the difference between the absorption band with and without the electron-hole interaction. However, the calculated binding energy of these calculation may not be compared to the experimental binding energies since the exciton binding energy calculated through TDPL is peak specific and the absorption spectra from the calculation and the experiment are not matching. However, a key feature that could be observed is the localization of excitons of the Cs$_4$PbX$_6$ in the individual octahedra, with exception to the Cs$_4$Pbl$_6$ excitons. One direct conclusion of the exciton localization and exciton binding energy is that the higher the exciton energy the more localized are the electron-hole pair, which leads to higher recombination probability and therefore higher the PLQY. This new findings agree well with the previous results on the PLQY and exciton binding energy trend reported in Chapter 4.
Figure 5.3 (A,B) the absorption spectrum with and without the exciton interaction for Cs$_4$PbCl$_6$ and Cs$_4$PbI$_6$, respectively. (C,D) a visualization of the exciton localization of Cs$_4$PbCl$_6$ and partial delocalization in Cs$_4$PbI$_6$. 
Figure 5.4 Crystals structures and corresponding electronic band structures for \( \text{Cs}_4\text{PbCl}_6 \), \( \text{Cs}_4\text{PbBr}_6 \) and \( \text{Cs}_4\text{PbI}_6 \).
5.4 Intrinsic Property

The octahedral sizes and their isolation strongly support the idea of an elevated quantum confinement, as well in agreement with theoretical calculations. However, the evidence that the predicted bandgap for 0-DN does not match with the predicted calculations, neither means it is coming from the 3D nor it excludes the possibility of other intrinsic defects and trap states that could control the optical behavior. Thus, a second interpretation suggests that the emission is coming from some defects and trap states such as interstitial and/or the vacancies of the halides.

The proposed defects are mainly halide interstitials and vacancies. This idea was inspired by the above-bandgap luminescence observed in CsPbBr$_3$ in which two emission PL peaks with energies of 2.33 and 2.29 eV at 10 K, persisting up to room temperature. Results from DFT calculations showed that the states of $\sim$0.23 eV and $\sim$0.24 eV above the bandgap are due to Br vacancies, $^{87}$ and in agreement with previous calculations. $^{86}$ Therefore, the emission at around 2.38 eV was correlated to the recombination of the bound excitons at those defects. Thus, to fully prove the energy and mechanism of native defects formation in Cs$_4$PbX$_6$, similar study and calculations should be conducted in analogues to the presented calculations based on the three-dimensional CsPbX$_3$. 
Figure 5.5 Calculated defect formation energies in the CsPbBr₃ are plotted as a function of Fermi level. Left and right panels correspond to Cs-poor and Br-poor conditions, respectively. The middle panel is plotted for the midcondition between Cs-poor and Br-poor. Equilibrium Fermi level $E_{\text{eqF}}$ is plotted as black vertical dotted line. (b) Defect levels for vacancy and antisite defect of CsPbBr₃ are summarized. Defect levels are presented with respect to the valence band maximum. Blue and red text at the bottom of figure indicates acceptor and donor defects, respectively. Reprinted with permission from ref.⁸⁷ Copyright (2015) The American Physical Society.
5.5 Conclusion

The mismatch between the optical properties presented in this thesis and others results present in literature inspired the writing of this chapter. Only through a thorough investigation on the optical properties of low dimensional perovskite will be possible to define an explanations to either the presence of CsPbX$_3$ NCs or native defects. While the former is more popular, there is no solid evidence to back the claim. Further, to date, there are no reported work on the native defects in the zero-dimensional-networked perovskites. Therefore, the origin of the emission is still an open question.
Chapter 6

Conclusion and Outlook

6.1 Summary

In summary, zero-dimensional-networked perovskites have been successfully synthesizes through the ITC method. The structural and optical properties are summarized in Table 1. Among all, the high PLQY, a crucial criterion for light-emitting materials, is inherited in zero-dimensional-networked perovskites due to their high exciting binding energy. This property is attributed to their structure rather than their physical size, which highlights the difference between the conventional low-dimensional and L-DN perovskites. With many compositions to be discovered under this family, the future is promising and holds exciting opportunities for white light applications, including LEDs.

Table 1 Summary of the structural and optical properties of Cs$_4$PbX$_6$

<table>
<thead>
<tr>
<th>Property</th>
<th>Cs$_4$PbCl$_6$</th>
<th>Cs$_4$PbBr$_6$</th>
<th>Cs$_4$PbI$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>R3c</td>
<td>R3c</td>
<td>R3c</td>
</tr>
<tr>
<td>Absorption (nm)</td>
<td>400</td>
<td>520</td>
<td>690</td>
</tr>
<tr>
<td>Photoluminescence (nm)</td>
<td>410</td>
<td>520</td>
<td>700</td>
</tr>
<tr>
<td>PLQY (%) (Integrating Sphere)</td>
<td>&lt; 1%</td>
<td>45%</td>
<td>14%</td>
</tr>
<tr>
<td>PLQY (%) (TDPL)</td>
<td>NA</td>
<td>40%</td>
<td>27%</td>
</tr>
<tr>
<td>$E_b$</td>
<td>&gt; 400 meV</td>
<td>180 meV</td>
<td>47 meV</td>
</tr>
</tbody>
</table>
6.2 Moving Forward

**Integrating the materials into devices.** This thesis started with a call for the scientific community to find innovative solutions for the energy crisis. Now that we were able to successfully synthesize the 0-DN materials and show their outstanding optical properties, the next step would be using those materials in light-emitting devices. In order to do so, high quality thin films and, hopefully, thin crystals will be needed. Fortunately, our preliminary results of thin film fabrication are promising.

**Replacing lead with safe elements.** So far, lead has been the most popular choice for B-cite in perovskites as it fits nicely in the octahedra, stabilizing the structure, and contributing the right optical bandgap. However, we cannot ignore the health and environmental risks imposed by using lead. In fact, the human exposure of even small amounts of lead could lead to serious health risks ranging from mental disorder to death. The real risk lies in the lack of any known method to free the body from lead once contaminated. Lead also imposes danger on the environment and the living creatures at large.

Potential solutions include using a double alternating cations with 1+ and 3+ oxidation states, and substituting with its neighbor, tin. The sooner the replacement, the closer we are to achieve the optimum solutions that are both efficient and safe.
Mixed halides for further tunability. Recall the insensitivity of the zero-dimensional networked perovskites. Thus, the currently available approach to access the different emissions in the visible spectrum is through halide mixing.

Identifying the origin of the optical properties. This point was left at the bottom of the list intentionally, not to underestimate the significance of the science behind these properties, but rather to open the doors for applications. Hopefully through implementing these materials in devices we could gain some clues that would facilitate the efforts to understand the corresponding photophysics.


53. Song, Z.; Watthage, S. C.; Phillips, A. B.; Heben, M. J., Pathways toward high-performance perovskite solar cells: review of recent advances in orga-


