Lead Halide Perovskite Nanocrystals

A New Age of Semiconductive Nanocrystals

Quinten A. Akkerman
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Perovskite Nanocrystals: A New Age of Semiconductutive Nanocrystals

*About the cover:* One of the most important features of lead halide perovskite nanocrystals is that their photoluminescence can be easily tuned by simply altering their halide composition. The photograph on the cover, which was taken by the author, shows a series of cesium lead halide nanocrystal solutions emitting different colors across the visible spectrum of light.

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Chapter I

A general introduction to colloidal semiconducting nanocrystals
Chapter I: A general introduction to colloidal semiconducting nanocrystals

Abstract: Semiconductors are one of the most important types of materials in our daily lives, and they can be found in a wide range of applications such as solar cells, LEDs and circuit boards. Since society heavily relies on so many devices that use semiconductors, much research has been devoted to synthesize semiconductors with new and efficient compositions, and to discovering new ways of implementing them. One interesting way of implementing semiconductors is by producing them in the form of colloidal nanocrystals. This allows their properties to be easily tuned, due to the size depended quantum confinement effects. Furthermore, they can be simply processed in liquid form, allowing for simple and often room temperature device fabrication. This thesis will focus on a new type of colloidal semiconductor: lead halide perovskite nanocrystals. These nanocrystal have unparalleled optical properties but they currently lack in terms of size, shape and composition control. Furthermore, they suffer from several instability problems, limiting their use in devices. This thesis addresses these issues and aims to provide an overview of different syntheses methods and how to apply lead halide perovskite nanocrystal to optoelectronic based devices like solar cells and LEDs. This chapter will give a brief introduction to colloidal semiconducting nanocrystals including a description of their general properties and a brief historical overview. Finally, this chapter will present an outline of the main chapters.

1.1 Semiconductors and their influence on our lives

In the current age of electronics, we heavily depend on semiconductor based devices. Semiconductors are at the core of every diode, transistor, LED and processor. Therefore, many devices that we use on a daily basis, such as mobile phones, computers, credit cards etc. require semiconductors.\cite{1,2} Thus, they have a monumental impact on society. In addition to consumer electronics, semiconductors are also extremely important with regard to sustainable energy, as current solar energy technology is based on semiconductors.

A semiconductor’s properties lie somewhere between those of a conductor (like metals) and those of an insulator (glass, most plastics). The electric conductivity of a semiconductor thus also lies somewhat between that of conductors and insulators, hence the name “semi-conductor”. By combining semiconductors with different conductivities, which is often done by taking a single semiconductor and doping different regions with different elements, one can create a semiconductor junction. These semiconductor junctions direct the flow of electrons (electricity), and therefore can be used for the two most important components in electronics: diodes and transistors. In a diode, a semiconductor junction is used to create a near infinite resistance in one direction, and a near zero resistance in the other, thus ensuring that the conductivity can only flow in one direction. A transistor is a (multi) semiconductor junction which allows the direction of the current to be switched towards different “terminals”. Furthermore, a semiconductor junction can amplify the current in a transistor. Semiconductors are also excellent materials...
A general introduction to colloidal semiconducting nanocrystals

for converting light into electricity and vice versa, making them great materials for use in light emitting devices (LEDs, lasers) and light absorption devices (solar cells, light detectors etc.). Semiconductors can also exhibit other interesting properties. For example, they are heat sensitive which also allows them to be used in heat sensors.

Due to the extremely high demand for more powerful devices, and the desire to make them smaller, the research field of semiconductor materials is constantly looking for semiconductors with new compositions as well as new ways of implementing them. One approach to carrying out these goals is to make semiconductors in the form of colloidal nanocrystals (NCs), which not only decreases their size, allowing for smaller devices, but also allows for a new way of manipulating the properties of semiconductors.

1.2 Small nanocrystals have a large impact

As is the case for semiconductors, our daily lives depend on material properties. For instance, we require conductive materials for electron transport, transparent materials for windows, and brightly colored materials for paintings. All these properties are material dependent. For instance, we use copper for conductive materials since copper is a good electron conductor, and we use silicon dioxide (SiO₂) for windows since SiO₂ is as transparent. We use other materials that strongly interact with light for instance in paintings, like The Great Wave off Kanagawa by Hokusai or the the Starry Night, by Vincent van Gogh, in which Prussian blue* (Fe₄[Fe(CN)₆]₃) is used to represent dark, deep blue. In all the aforementioned cases, the material properties, such as e.g. conductivity, melting point, colour, etc., do not depend on the size or shape of the used material. However, when one starts to look at material properties at the nano-scale (1-100 nm, or 0.000000001 - 0.0000001 meter), in a range where the amount of atoms start to be limited, certain material properties start to become size dependent, and they can differ greatly from the properties of their bulk sized counterparts. This extra property tunability has driven the scientific community, especially the field of semiconductors, to go “nano”, as it would allow for an extra tunability of the material properties. For instance, one can envision modifying the nano-size of materials in order to alter the optical and conductive properties, rather than having to change the composition of a metal, or the molecular structure of an organic molecule.

These colloidal semiconductor NCs have been synthesized and studied for at least the last three decades. Now, in 2018, we have an excellent understanding of how the nanoscale influences semiconductors, and we have access to a plethora of different compositions with a very great size and shape control on the nanoscale. Furthermore, the field has moved to colloidal NCs, meaning that the NCs can be synthesized as small, stable, solid NCs in a solution. This does not only allow for more control over the size during the synthesis (the NCs can be precisely tuned to the size of an atom), but also has a large processability advantage, as colloidal NC solutions can be deposited using simple deposition techniques like inkjet printing or spray painting. All these advancements have pushed these NCs from being the subject of fundamental lab studies to being employed in several types of applications today, such as light emitters in TVs (as is shown in figure 1.1). Current colloidal semiconductor NCs also have the capacity to be used in a wide range of applications in the future, such as solar cells, LEDs, lasers, luminescent solar concentrators⁶.

* Named after the Prussian army who used the blue pigment to dye their uniforms.
They are also extremely important with regard to advancements in nano-biotechnology, and they can be used in drug delivery techniques, in vivo imaging and photothermal cancer therapy treatments.

Figure 1.1: Semiconductor nanocrystals and their use in ultra-high definition TVs. (a) Example of solutions containing colloidal semiconductor NCs with different sizes, resulting in a range of different colors. (b) Samsung Ultra High Definition (SUHD) TV using InP NCs as emitters, resulting in one of the best TVs that is currently on the market in terms of color purity. Taken from ref. 5

1.3 A brief history of colloidal nanocrystals

Although the field of colloidal semiconductor NCs started to gain attention in the 1980s, particles with properties that are tunable on the nanoscale, especially metals, have been used for thousands of years. One of the most reported and visual examples is stained glass, which dates back to the middle ages. Medieval stained glass artists knew that baking their glass with gold and silver salts at different temperatures or for different amounts of times resulted in different colored stained glasses (even though the composition remained the same). Using silver salt, they could for instance produce every primary color (blue, yellow and red). Similarly, they created red, green and orange by using gold salts. Therefore, mixing silver and gold gave them access to any color that they needed to stain their windows. In a similar way, ceramics with different bright colors were made in Italy during the Renaissance period (i.e. during the 15th and early 16th century), using only different copper and silver salts, resulting in a wide variety of colors. These ceramics, called Deruta ceramics, were therefore a result of differently sized copper and silver NCs. Of course, at this time, the scientific reason behind the production of these different colors was not known. Nevertheless, this is a perfect example of the tunable properties of materials in NC form. In fact, the use of “nanoparticles” as single coloring agents can be traced back even earlier in history: lead sulfide NCs (about 5 nm) were used by the ancient Egyptians to dye their hair, and iron nanoparticles were used in the Bronze Age to dye pottery red. In retrospect, we now know that, in each of these cases, different reaction temperatures and times resulted in differently sized and shaped copper, silver, gold or iron NCs, all of which exhibited different colors due to their nano-size.

† Derived from the name of the small town Deruta, in the region of Umbria, Italy
Although the use of NCs may go back centuries, the first reported scientific study on size dependent optical properties dates back to 1857, when Michael Faraday tried to study the relationship between gold (and other metal) layers of different thicknesses and light. In these experiments, he accidentally created different colored solutions while trying to mount gold leaf onto microscope slides. Based on these observations, he concluded that “known phenomena appeared to indicate that a mere variation in the size of its particles gave rise to a variety of resultant colors” and that “reflexion, refraction, absorption etc. depended upon such relations, there was reason to expect that these functions would change sensibly by the substitution of different sized particles”. Nowadays, we know that the different colors of metal particles stem from the so-called Localized Surface Plasmon Resonance (LSPR) effect, which, in turn, originates from the collective oscillation of electrons at the surface of the particles. This effect is highly sensitive to the surface of the NC, therefore it is highly size and shape dependent. The discovery that the electronic structure of NCs can change came a century later, when small nanometer-sized copper chloride and silver iodide, which will than were referred to as ‘crystallites’, were embedded into NaCl matrices in a very similar way as to how the medieval stained glass artists made their stain glass windows. For these crystallites, it was observed that the bandgap depended on their size, and, thus, on changes in the electronic structure of the NCs. One of the first theoretical models describing the relation between the electronic properties of semiconductors and size dates back to the 1960s, when Evens and Young correlated the changing optical properties of thin layered MoS2 with the changes in its electronic structure. Twenty years later, in the 1980s, the first models of small spherical semiconductor NCs, so called ‘Quantum dots (QDs)’, were published (figure 1.2a-c). One of the major breakthroughs with regard to linking the experimental data with theoretical models was achieved as a result of the quick pace at which advancements were made in the synthesis of colloidal PbS and CdSe NCs. One obstacle that was still limiting the linking of experimental data with theoretical models was the accurate determination of the NCs size (and shape), especially in the smaller size range of 1-10 nm. To this end, the discovery and development of the transmission electron microscope (TEM, which was first demonstrated by Max Knoll and Ernst Ruska in 1931, but it did not reach the required resolution until the 1970s-1980s) gave researchers the final boost they needed to link the experimental data with theoretical models, as it directly gave “images” of NCs (figure 1.2d). Another major breakthrough was in 1993, when the Bawendi’s group reported a synthetic procedure that was able to produce (nearly) monodisperse colloidal CdSe NCs, reaching near atomic precision (figure 1.2e-g). Over the following decades, the research field of colloidal semiconductor NCs quickly expanded and matured into a large research community. Today, the synthesis field has expanded to encompass different materials, such as PbSe, CuInS2, InAs, Cu2-xS, ZnS and many other semiconductors, and it has achieved a large range of sizes and shapes. Furthermore, highly complex binary NCs, consisting of multiple semiconductor domains, can be synthesized resulting in an extreme high tunability of the NC’s properties. Moreover, the field has matured and started to move from fundamental research towards applications, with NCs being studied for use in a wide range of applications such as LEDs, lasers, solar cells and cancer treatments.

\[\text{In 1986, Ernst Ruska was awarded the Nobel Prize in Physics “for his fundamental work in electron optics, and for the design of the first electron microscope.”}\]
Figure 1.2. Overview of some of the most important advancements in the history of colloidal semiconductor nanocrystals. (a) Absorption spectra of different sized CuCl NCs. (b) Plotted exciton absorption of CuCl vs. NC size. (c) Calculated quantum confinement effect of different semiconductors. (d) TEM image of 2 nm PbS cluster. (e) Optical absorption of 1.2 – 11.5 nm CdSe NCs in hexane. (f) High resolution TEM image of 8 nm CdSe NCs. (g) Monolayer of 5.1 nm diameter CdSe crystallites showing short-range hexagonal close packing. Taken with permission from ref. 19, 21, 24, 28

Lead halide perovskites (LHPs) are one of the latest materials to be added to the family of “colloidal semiconductor NCs”. Although perovskites have been studied for centuries, and are the most abundant type of mineral on earth (in the form of oxide perovskites), the LHPs have only made an impact on the scientific community in the past two decades, mainly driven by the photovoltaic community. One of the most profound properties of LHPs is their ease of obtaining high quality, defect free devices, something that is still challenging for silicon. This thus makes LHP promising contenders for replacing silicon in solar cells. With the solar panels being a billion dollar industry, it is therefore no surprise that many efforts have been put into developing LHPs, and that the first reports on LHPs NCs started to emerge in 2015. As a relatively ‘young’ research field, many aspects of LHPs NCs have yet to be understood.

1.4 Aim of this thesis

This thesis will mainly focus on the synthesis and characterization of colloidal LHPs NCs. It will also shed light on many synthetic aspects of these NCs, such as their size, shape and compositional control, as well as on how to increase their stability and processability, allowing the use of LHP NCs in devices. Furthermore, this thesis will present several nano-scaled reactions using lead halide NCs, which result in so-called “nanocrystal transformations”. To bridge the gap between the fundamental synthetic work and the application of these NCs, several proof-of-principle devices have been made with LHP NCs, including solar cells and LEDs and will all be demonstrated herein. Finally, several new halide based NCs have been synthesized and will be discusses, broadening the scope of this work not only to LHP NCs, but also to halide based NCs in general.
1.5 **Outline of this thesis**

This thesis is divided into 12 chapters. This first chapter gives a general introduction, *chapters 2 to 4* describe the necessary background theory, and *chapters 5-11* discuss the obtained results. The final chapter, *chapter 12*, will conclude the work that is presented in this thesis and will offer an overview of the future directions that this field might take. Overall, the following chapters are divided as follows:

*Chapter 2: The physics behind semiconductor nanocrystals* will describe the theory behind the physical properties of semiconductors and semiconductor NCs.

*Chapter 3: The chemistry behind semiconductor nanocrystals* will provide a chemical description of colloidal semiconductor NCs, as well as the theory behind their synthesis.

*Chapter 4: An introduction to lead halide perovskites* will offer a general description of LHPs and their properties, since this is the main semiconductor material that has been researched in this thesis.

*Chapter 5: Shape control of CsPbBr$_3$ nanocrystals* will present a synthesis method for obtaining anisotropically shaped CsPbBr$_3$ nanoplatelets. It will also propose the mechanism behind their formation.

*Chapter 6: Alloying CsPbX$_3$ nanocrystals with Mn$^{2+}$* will discuss the effect of introducing Mn$^{2+}$ to CsPbCl$_3$ and CsPbI$_3$ NCs.

*Chapter 7: Ruddlesden Popper Cl-I and Cl-Br-I lead halide perovskite nanocrystals* will discuss the synthesis and properties of Cs$_2$PbI$_2$Cl$_2$ and CsPb(Cl:Br:I)$_3$ NCs which exhibit full or partial Ruddlesden-Popper crystal lattices.

*Chapter 8: Zero dimensional Cs$_4$PbX$_6$ nanocrystals* will cover the synthesis and properties of Cs$_4$PbX$_6$ NCs, as well as their transformation reactions into CsPbX$_3$ NCs.

*Chapter 9: A case study on the optical properties of Cs$_4$PbBr$_6$* will cover a literature study on the controversial optical properties of Cs$_4$PbBr$_6$ in both bulk and NC form.

*Chapter 10: A novel synthesis approach for iodide based nanocrystals* will discuss the synthesis and optical properties of several other halide based NCs, including KI, RbI, CsI, Cs$_3$Bi$_2$I$_9$, AgI and RbAg$_4$I$_5$ based ones.

*Chapter 11: Towards applications of lead halide perovskite nanocrystals* will present several different devices that have been made using lead halide perovskite NCs, including solar cells and LEDs.

*Chapter 12: Summary and outlook.* The final chapter will give a summary of the work that is presented herein, as well as provide an overview of some future directions that the field of LHP NCs might take.

**References**


Chapter I


Chapter II

The physics behind semiconductor nanocrystals
Chapter II: The physics behind semiconductor nanocrystals

Abstract: Although the majority of this thesis focuses on the chemistry and synthesis of colloidal semiconductor nanocrystals, it is necessary to have a basic understanding of the physical properties of atoms and semiconductors. Although more rigorous and detailed descriptions can be found in classical textbooks, it is useful here to recall some basic concepts used throughout this thesis. This chapter will focus on the fundamental descriptions of semiconductors and semiconductor nanocrystals as well as the basic concepts behind how the changes in the size and shape of semiconductor nanocrystals can alter their electronic properties.

2.1 Introduction

One of the most important terms that is associated with semiconductor NCs is ‘Quantum Confinement’. To fully understand what the quantum confinement effect is, and how it affects the electronic structure of semiconductor NCs, one has to first look at the electronic structure of a semiconductor. Furthermore, an understanding of the relationship between the electronic structure and the electronic shape (orbitals) of single atoms is also needed to describe and predict the electronic structure of, for instance, LHP NCs. Thus, this chapter will first describe the electronic structure of single molecules, starting from their atomic orbitals. From this description, the electronic structure of small molecules can be predicted by combining several atomic orbitals to form molecular orbitals in such a way that they start to build larger electronic structures. From these larger structures, the general electronic structure of a semiconductor can be derived. By the end of this chapter, the terms “semiconductor” and “bandgap” will be derived as well as the concept of light absorption and emission with regard to semiconductors. This should result in a clear idea why semiconductors are used in devices such as solar cells and LEDs. Finally, the last part of this chapter discusses the quantum confinement effect in relation to semiconductors, and explains how the size and shape of NCs can alter the electronic structure of semiconductors.

2.2 From single atoms to molecules

The first step towards understanding the optical properties of semiconductors is to deduce their electronic structure.\textsuperscript{1,2} To achieve this, we have to start by looking at how electrons behave as single atoms. In the case of a single atom, electrons form an electron cloud that surrounds the nucleus (protons and neutrons). Due to the “wave–particle duality”, electrons in general can be described as a wave, which can be derived through the Schrödinger equation, as shown in equation (2.1). The shape of an electron cloud can be described in relation to its wave function ($\psi$):

\begin{equation}
H\psi = E\psi
\end{equation}

in which $H$ is the Hamiltonian (the quantum mechanical operator that describes the electron’s total energy) and $E$ is the electron’s overall energy. The Schrödinger equation also
be can be written in more detail by decomposing the Hamiltonian into the kinetic energy and potential energy operators, as is shown below in equation 2.2:

\[
(2.2) \left( -\frac{\hbar^2}{2m} \nabla^2 + V \right) \psi = E\psi
\]

in which \( \hbar \) is the reduced Planck constant, \( \nabla^2 \) is the Laplace operator, and \( V \) is the electrostatic potential containing both electron-nucleus and electron-electron coulombic interactions. By solving this equation, one can derive the wave function for specific electrons in different atoms. In the case of electrons that orbit nuclei, these wave functions are called atomic orbitals (AOs). Due to Heisenberg’s uncertainty principle, which states that we cannot predict both the exact position and the momentum of the electron, we cannot refer to an electron’s exact location, but rather to the region of space where one has a high probability (around 90%) of finding an electron, which is often depicted as shown in figure 2.1. This probability is proportional to \( \psi^2 \).

Atoms can contain a large number of electrons, but, based on Pauli’s Exclusion Principle, one AO can only be occupied by two electrons at maximum. Therefore, atoms (especially those with high atomic numbers) have many different AOs filled with electrons. The size and shape of these AOs, which are important for atoms to bond in order to form molecules and “solids”, vary, and they can be catalogued by their so-called ‘quantum numbers’. Although not formulated in this thesis, as it will mainly focuses on optical properties of semiconductors, these quantum numbers are naturally derived by solving the Schrödinger equation, as only certain solutions are allowed. These solutions contain quantum numbers can take on only discrete values of integers (0, 1, 2…), or half integers (\( \frac{1}{2}, \frac{3}{2}, \frac{5}{2}… \)) when also electron spin is considered.

The first quantum number, the \textit{principal quantum number} \( n \) (\( n = 1, 2, 3 \) etc.), specifies the energy of the electrons and determines the size of the AOs. All AOs with the same principal quantum number can be grouped together in so-called ‘shells’. The maximum amount of AOs per shell is \( n^2 \), therefore the amount of electrons per shell is \( 2n^2 \). The number of shells that are filled with electrons is directly related to the number of electrons in the atom, and thus to the place of the atom in the periodic table; one shell is gained as the atom goes down one place in the periodic table. An AO’s average distance from the nucleus increases in shells with higher principal numbers, and its occupying electrons have a higher energy. For instance, a Cl atom has \( n = 3 \) for and an I atom has and \( n = 5 \), resulting in the I atom being about 40% larger compared to a Cl atom.

The secondary quantum number, also known as the \textit{azimuthal quantum number} \( \ell \) (\( \ell = 0, 1, 2, \ldots, n \)) describes the orbital angular momentum and mainly influences the shape of the orbitals. This secondary quantum number divides the shells into subshells, and every subshell has a group of AOs with different shapes. The subshells that are formed from the secondary quantum number are called the \textit{s} (\( \ell = 0 \)), \textit{p} (\( \ell = 1 \)), \textit{d} (\( \ell = 2 \)) and \textit{f} (\( \ell = 3 \)) shells.* Some of these orbitals are shown in figure 2.1. Within one shell, the energies of the different types of orbitals’ slightly increase \( (s < p < d < f) \), but each shell has a lower energy than the next main shell. This means that the electrons in an atom first fill the subshells with the

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* The names the orbitals originate from their respective spectroscopic emission lines, which were classified as \textit{sharp}, \textit{principal}, \textit{diffuse} and \textit{fundamental}. 

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Chapter II

lowest available energy before occupying the next main shell. For instance, a Cl atom has 17 electrons, arranged in the 1s (2 electrons), 2s (2 electrons), 2p (6 electrons), 3s (2 electrons), 3p (5 remaining electrons) orbitals. When an atom participates in sharing electrons (bonding), it does so with the electrons in the AO with highest energy (electrons that are the weakest bond to the nucleus). These electrons are called valence electrons. In the case of a Cl atom, the valence electrons consist of those in the 3p orbitals. For this reason, the elements in the periodic table can divided into the s-block (column 1 and 2), p-block (columns 13-18), d-block (columns 3-12) and f-block (lanthanides and actinides).

When multiple atoms are combined into a molecule, the wave functions of the single AOs are combined (hybridization). The shape of the orbitals in the newly formed molecule can be determined using the “linear combination of atomic orbitals” (LCAO) approach, which combines the wave functions of the AOs, forming so-called ‘molecular orbitals’ (MOs). There are two possibilities to realize a linear combination of the two orbitals: either by taking the sum, or the difference of the two AOs, as is shown in equation 2.3.

\[(2.3)\ \text{constructive, } \psi = \psi_A + \psi_B. \ \text{Destructive } \psi = \psi_A - \psi_B\]

As is shown in figure 2.2a, when two simple s orbitals are summed, i.e. they have both the same sign in the linear combination, they constructively overlap, and the electron is more likely to be in between the two atoms. In this case, the electrons strongly interact with both atoms, resulting in MO bonding (depicted as \(\sigma\)). The constructive overlap, therefore, causes the electrons’ energy to decrease compared to that of the two starting s orbitals (figure 2.2a). However, when the atomic orbitals are taken with opposite signs in the linear combination, a destructive overlap of AOs occurs, especially in the region between the atoms, where a nodal plane is formed. In this case, there is a low chance of finding the electron between the two atoms. This MO is called the ‘antibonding orbital’ (which is depicted as \(\sigma^*\)), and it has a higher energy than the individual AOs (figure 2.2b). In the simple case of a H\(_2\) molecule, which only consists of a combination of two 1s orbitals with each one electron, this leads to a MO energy level diagram, as is shown in figure 2.2c. It is important to remember that number of electrons in a MO equals that of the total

![Figure 2.1. Overview of most basic AO. 1s, 2p and 3d molecular orbitals shown in x, y, z coordinates.](image-url)
The physics behind semiconductor nanocrystals

electrons in the original AOs. Therefore, in the case of H₂, the two electrons that occupied the two 1s AOs of each H atom both occupy the MO of H₂. As the bonding orbital has a lower energy, the two electrons will occupy the bonding MO, consequently forming a “bond”. Therefore, H₂ is more stable than the two separate H molecules. Of course, more complex molecules lead to more complex MOs, since differently shaped orbitals can form MOs (like s-p orbitals) as well as orbitals of different shells. In these complex cases, certain orbitals will hybridize and form bonding and anti-bonding orbitals, while others might remain unchanged depending on whether or not the differently shaped orbitals overlap. The formation of the bonding and antibonding orbitals often, but not always, results from the hybridization of the filled orbitals with the highest energy, or the nearest in energy available empty orbitals, as these are the furthest away from the atom’s core. For instance, in the case of a PbI₆⁴⁻ cluster, as is shown in figure 2.2d, this results in the hybridization of Pb 6s and 6p orbitals with the I 5s orbitals. After filling the MOs with the appropriate number of electrons, one can find the electrons with the highest energy in the so-called ‘Highest Occupied Molecular Orbital’ (HOMO), and the empty MO with the lowest energy in the Lowest Unoccupied Molecular Orbital (LUMO).

Figure 2.2. Formation of molecular orbitals from atomic orbitals. (a) constructive LCOA of two 1s AO, resulting in a bonding MO. (b) deconstructive LCOA of two 1s AO, resulting in an anti-bonding MO. (c) Example of a MO diagram of a H₂ molecule. (d) Example of a more complex MO diagram of a [PbI₆]⁴⁻ cluster with multiple s and p AOs.

2.3 Building semiconductors

In a similar way to the LCAO formation of MOs, one can combine multiple AOs in a large molecular framework.¹ As shown in figure 2.3a, the addition of more and more AOs to the framework results in the formation of more and more MOs. In the case of an array of many atoms, as in a crystal of a semiconductor, a large number of AO are combined together, forming a lower energy band and a higher energy band, respectively. It is important though to remember that each band still consists of individual, discrete MOs with their own specific discrete energy, but as the difference in energy between them is so small (significantly less than kT at room temperature), they become quasi-continuous. The most bonding and most antibonding MOs are in these bands called the “band edges”. The lower
energy band, which is completely filled with the valence electrons from the valence AOs of the individual atoms, is called a \textit{valence band} (VB). The higher energy band, which is instead empty, is called the \textit{conduction band} (CB), as the electrons promoted in this band can freely move throughout the crystal (practically hopping from one atom to a neighboring one), leading to electric conduction. In these bands, the highest and lowest MOs still consist of the most bonding (lowest energy) and most antibonding orbitals (highest in energy). The energy difference between the most antibonding MO in the valence band and the most bonding MO in the conduction band is called the \textit{bandgap} ($E_g$). When the valence band and conduction band overlap or the bandgap is below $kT$ at room temperature (about 25 meV), the material is called a metal, as its electrons can freely move from the full MOs in the valence band to the empty MOs in the conduction band by simply absorbing heat from the surroundings (i.e. through thermal excitation). For a bandgap that is roughly 25 meV – 3 eV, which corresponds to energies of light in the visible spectrum, the materials is called a semiconductor. Therefore, semiconductors are often black or brown materials, as they tend to only partially absorb visible light. Materials with a bandgap higher than 3 eV are called insulators, and they do not absorb visible light (they reflect it), resulting in colorless materials.

A more mathematical way of describing the VB and CB in materials is through the calculation of “the density of states” (DOS).\(^1\) The DOS describes the number of states per given energy. Although the DOS will not be derived here, the DOS for a simple three dimensional (3D) material, in which electrons can freely move in all dimensions (free electron model, which is not the case in reality) is square root dependent on the energy ($\sim E^{1/2}$) as shown in \textbf{figure 2.3b}. In reality, the DOS of semiconductors are highly complicated and are calculated computationally, as done for instance in Chapter 6.4.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_3}
\caption{\textbf{Figure 2.3. General band gap diagrams of semiconductor. (a) Formation of a semiconductor though the LCOA of multiple AOs. In the case of CdS, the OA forming the VB and CD mainly consist of empty Cd 5s orbitals and filled Se 4p orbitals. (b) Density of states for a semiconductor.}}
\end{figure}

\subsection*{2.4 Conductivity, light absorption and emission in semiconductors}

For electric conductivity, electrons need to be able to move around in a material.\(^4\) For this to happen, they need to be able to move through empty orbitals. In the case of a semiconductor, the bandgap separates the filled orbitals in the VB from the empty ones in the CB. As there are no empty MOs in the valence band, and no electrons in the conduction band, the electrons (presuming they do not experience any external bias that can provide them with the energy to jump from the VB to the CB) are immobilized in the VB without enough energy to reach the CB. One way an electron can reach the CB is through the
absorption of a photon (light), as is shown in **figure 2.4a**. Here, the photon needs to have an energy that is larger than the bandgap of the semiconductor. This process is called *photon excitation*, and it results in an excited electron in the CB, which then can freely move through the empty orbitals. The “empty orbital (or rather the lack of an orbital occupied with an electron)” in the VB, which contained the now excited electron, is called a *hole*. Like an air bubble moving in a liquid, this missing electron can be seen as positively charged particle moving in the crystal, but in the direction that is opposite to that of an electron. Similar to an excited electron that is free to move in the conduction band, a hole is free to move in the valence band. It must be noted though that the concomitant promotion of an electron in the valence band and the creation of a hole in the valence band by the absorption of a photon can occur only if such electron and hole, in the moment in which they are formed, have momenta that are equal in modulus (and are obviously opposite in sign). This requirement arises from a simple momentum conservation rule: as the massless photon has a very small, nearly-zero momentum compared to that of a massive particle, once it is annihilated and an electron-hole pair is formed, the sum of the individual momenta of the electron and the hole has to be close to zero. A semiconductor in which this “direct transition” is allowed has a so-called direct bandgap. This means that, in short, the electron in the band edge of the CB and VB needs to have the same momentum. If this is not the case, for instance in silicon (which has an indirect bandgap), the electron can only be excited though the combined interaction with a photon and a lattice vibration (phonon). As this three-body interaction in an indirect bandgap is significantly less likely to occur compared to the two-body interaction (electron + photon) in a direct bandgap material, it is significantly less probable to excite electrons through light absorption in an indirect bandgap material. For instance, the solar light absorption in silicon (indirect bandgap) is several orders of magnitude lower than that in for instance lead halide perovskites or CdTe (both direct bandgaps), even though silicon has a significantly smaller bandgap allowing it to absorb a larger range of energies from the solar spectrum. As a note to the reader, this thesis mainly focuses on lead halide perovskites (which exhibit a direct bandgap). Therefore, semiconductors throughout this thesis are generally considered direct.

As mentioned previously, the excitation of an electron in a direct semiconductor can occur through the absorption of any energy that is larger than the bandgap (even from high-energy electrons or X-rays). Electrons that are excited highly into the CB can lower their energy to a state near the band edge by dissipating their excess energy mainly as heat. This process is called *relaxation*, as is shown in **figure 2.4b**. To reverse the excitation process, the excited electron can recombine with the hole, releasing its gained energy as a photon. As this photon emits from the band edge of the conduction band to the band edge of the valence band, it emits the energy of the bandgap. This process, which is shown in **figure 2.4c**, is called ‘radiative recombination’, and it is the main form of *photoluminescence* (PL) in semiconductors. Again, it is important to note that this is only the case for a direct bandgap semiconductor, as excitons in direct bandgap semiconductors require the change of momentum through the interaction with an phonon, which drastically lowers the possibility of excitation. The rate at which excited electrons recombine with the holes is called the ‘radiative recombination decay rate’, $\nu_{rad}$, and it is strongly material dependent. However, not all excited electrons recombine with holes through the emission of a photon. Throughout the semiconductor, so-called ‘trap states’ can form. These trap states are often formed by lattice defects, i.e. by missing atoms, misplaced atoms, chemical impurities etc.
These trap states often result in less hybridized MOs, therefore they create states around their AOs, and thus in the bandgap, as is shown in figure 2.4d. Since these trap states lie below the CB or above the VB, electrons and holes will tend to move to the defect states and recombine there, often though heat dissipation. Therefore, trap states result in non-radiative recombination. Defects can quench the radiative recombination, and this can be detrimental to devices that require either radiative recombination (LEDs, lasers etc.) or that need to extract the electrons and holes (solar cells). Another type of trap state is a so-called ‘surface trap state’. These trap states originate from the under-coordinated atoms at the surface of a material, and, just as lattice defects, they mainly form states in the bandgap. Although this type of defect is less detrimental in bulk materials, which have a relatively small percentage of atoms at the surface, it is considerably more important in NCs which have a very large amount of their atoms at the surface, as will be further discussed in chapter 3.3.

![Figure 2.4. Interaction of semiconductors with photons. (a) Photon absorption, (b) electron relaxation, (c) photon emission through radiative recombination and (d) non-radiative recombination.](image)

As mentioned before, radiative recombination results in the emission of light, and it requires the material to be as trap free as possible. To quantify the radiative recombination, and thus derive a figure of merit for the emission’s efficiency, the rates of both the radiative recombination and the non-radiative recombination can be compared. The rate at which excited electrons radiatively recombine can be described as their decay rate $\gamma_{\text{rad}}$. Similarly, the non-radiative recombination can be described as $\gamma_{\text{nrad}}$. Therefore, the ration between $\gamma_{\text{rad}}$ and $\gamma_{\text{nrad}}$, as is shown in equation 2.4., describes the quantum efficiency ($\eta$), or photoluminescence quantum yield (PLQY) of a material.6

$$\frac{\gamma_{\text{rad}}}{\gamma_{\text{rad}} + \gamma_{\text{nrad}}}$$

The PLQY of a material is therefore not a material property but rather depends on the quality of the material and thus on the way it has been processed/synthesized. The PLQY is one of the most important figure of merits of luminescent semiconductor NCs, and it will be discussed in each experimental chapter in this thesis.
2.5 Nanocrystals as artificial atoms; quantum confinement

As described in chapter 1, semiconductive NCs exhibit different optical properties compared to their bulk counterpart. The most simple way of the changes in the optical properties, of a semiconductor going from bulk to a NC, is by considering NCs as a very large molecules, consisting of about 100 – 100000 atoms. NCs have the DOS of both bulk, with quasi-continuous (VB and CB) MOs, and of single molecules, with well-defined individual states at the band edges. This double behavior can also be rationalized through the LCAO, as is described in chapter 2.3. Going from a molecule (a few atoms) to a small NC (few hundred atoms), coupling of a large number of AO (s and p orbitals for most semiconductors) takes place, resulting in quasi-continuous bands formed by a multitude of MO (figure 2.5, from the rightmost cases, moving to the left). Yet, these small molecules still have single, discrete states for the most bonding and anti-bonding states, with the HOMO and LUMO being the most isolated states. When the size of the NCs is increased (from 100 – 100000 atoms, or about 2 – 20 nm), not only the energy separation between individual MOs with each band decreases, but also the energy separation between the bands decreases. Still, states that are closer to the band edges are discrete (figure 2.5, intermediate cases). In a bulk solid, all states within a band merge in a continuum (figure 2.5, leftmost case), and the energy separation between the bands is at its minimum for that specific material. One could also envision this description in reverse (figure 2.5 from the left to right), essentially going from a bulk crystal to a small NC and then to a cluster of only a few atoms: upon decreasing the NC size, the bandgap increases and there are more discrete energy levels at the band edges. The effect connected to the widening of the band gap is called the ‘quantum confinement effect’, and is what gives rise to the two most dominant changes in semiconductor NCs.

Figure 2.5. Quantum confinement effect. Comparison of bulk, NCs and molecules, indicating the size dependent bandgap of NCs and the formation of discrete states near the band edge.
A more physical way to look at the quantum confinement effect is by looking at the electron-hole pair, as is described in chapter 2.3. Due to Coulomb interactions, an excited electron in the CB is still bound to the corresponding hole in the VB. This electron-hole pair, called an exciton, occupies a certain ‘space’. This space, or rather its radius, can be described by the exciton Bohr radius \( (a_0) \), as is depicted in equation 2.5.

\[
(2.5) \text{Exciton Bohr radius } (a_0) = \frac{\hbar^2}{e^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right)
\]

The Exciton Bohr radius depends on the effective masses of the electron and the hole, which, in turn, depend on the material they are in. Therefore, the exciton Bohr radius is strongly material dependent with, for instance, CdSe, InAs, PbTe having an exciton Bohr radius of 5, 29 and 104 nm, respectively.\(^7\) When the semiconductor is significantly larger than the \( a_0 \), the exciton can freely move through the semiconductor. When the size of the semiconductor is about the same as that of \( a_0 \), the exciton will no longer be able to freely move through the NC and therefore will be spatially confined. When the NC size decreases even further, until it is smaller than \( a_0 \), the exciton will not only become confined, but will also increase in energy, similar to a particle in-a-box, which increase its energy when the ‘box’ decreases in size. The bandgap of a spherical NC, can be described by the Brus Equation, as shown in equation 2.6:

\[
(2.6) E_{QD} = E_{gap} + \frac{\hbar^2}{8r^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right)
\]

Here, the bandgap of the NC thus increases as the NC size decreases. As the exciton Bohr radius is dependent on the semiconductor composition, the extent of quantum confinement a certain sized NC exhibits is depended on its composition. For instance, a 20 nm CsPbBr\(_3\) NC \( (a_0 = 5 \text{ nm}) \) will not exhibit any quantum confinement effects, as its size is significantly larger than its exciton Bohr radius. On other hand, a 20 nm PbTe NC will \( (\text{with } a_0 = 104 \text{ nm}) \), will exhibit strong quantum confinement and will thus have optical properties very different from its bulk equivalent.\(^7\)\(^8\)

The aforementioned cases all describe the quantum confinement effects for NCs whose three dimensions are all confined (so-called quantum dots). In reality, NCs of different sizes and shapes can be synthesized, therefore each of their dimensions can be of a different size, as further discussed in chapter 3.6. The different shapes can generally be classified by their dimensionality. For instance, ‘three dimensional’ (3D) NCs, with none of their dimensions exhibit quantum confinement, have properties close to their bulk counterpart. Two-dimensional (2D) NCs exhibits quantum confinement in only one dimension, and can be described as nanosheets (NSs) or quantum wells. One-dimensions (1D) NCs are elongated NCs with two dimension exhibiting quantum confinement, such as nanowires or quantum wires. Finally, ‘zero dimensional’ (0D), such as QDs or clusters, have all three dimensions exhibiting quantum confinement, and in general exhibit the strongest quantum confinement effects.

As is shown in figure 2.6, changes in the dimensionality have a strong effect on the DOS.\(^6\) As described in chapter 2.2, the bands of a bulk semiconductor are square root dependent of their energy (\(\sim E^{1/2}\)). In the case of a 2D quantum well, excitons are free to move
in two dimensions, but they are confined in the lateral dimension. This results in a stepwise DOS with a constant dependency ($\sim E^0 = \text{constant}$) in which all energies are available, but only increase in quantified steps. In the case of a quantum wire, the exciton can only move along the wire. This results in a DOS with an inverse square energy dependence ($\sim E^{-1}$). Here, the DOS only increases in quantified amounts, but the DOS quickly decreases between every quantified step. Finally, 0D quantum dots exhibit a DOS with states only allowed at certain energies. This results in the same model as the one that is described in figure 2.6. It is important to note that NCs can have various sizes and shapes, and cannot always simply be described by the DOS of 2D, 1D or 0D models. For instance, CsPbBr$_3$ nanoplatelets (which have an exciton Bohr radius of 7 nm) can be synthesized with dimensions of 20 by 5 by 2 nm (see chapter 5). Therefore, these nanoplatelets have one dimension not exhibiting any quantum confinement (exhibiting bulk properties), one dimension with only a weak quantum confinement (weakly confined excitons the bandgap only exhibiting a small increase), and one dimension exhibits a very strong quantum confinement (strongly confined excitons with very discrete states and a large increase in bandgap). This thus results in a quasi-2.5D model.

Figure 2.6. Effect of dimensional confinement on the density of states. (a) bulk (3D) with continues DOS, (b) quantum wells with a step-like DOS, (c) quantum wire (1D) with a saw-tooth dependent DOS and (d) Quantum dots (0D) with only discrete sates available.

References
Chapter III

The chemistry behind colloidal nanocrystals
Chapter III: The chemistry behind colloidal nanocrystals

Abstract: The synthesis of colloidal nanocrystals is an interesting field that bridges the gap between organic, inorganic and physical chemistry. Understanding semiconductor nanocrystals therefore requires interdisciplinary knowledge across different fields of chemistry. This chapter will discuss the general chemical and physical aspects of colloidal nanocrystals including their surface chemistry, synthesis approaches and how to achieve size and shape control.

3.1 Introduction

Although semiconductor NCs are small, their respective chemistry can be rather complex. Thus, producing high quality NCs that are nearly monodisperse and have a high PLQY requires knowledge pertaining to the fields of organic, inorganic and physical chemistry. Furthermore, achieving control over the size and shape of these NCs requires an understanding of the relationship between all the components that are in the reaction, like ligands, precursors and solvents, as well an understanding of the atomic structure of the final NCs. This chapter will discuss the general synthetic and chemical aspects with regard to the synthesis of semiconductor NCs. A more in depth description of the synthesis of perovskite NCs is provided in chapter 4. First, chapter 3.2 and 3.3 will discuss the inorganic core and organic shell, as well as their interface, since this is important for obtaining high quality, defect free NCs. Chapter 3.4 will elaborate on general synthesis methods, and chapter 3.5 will address the nucleation theory, which can describe how single molecular precursors can form well-defined colloidal NCs. Finally, the last section will describe the general theory of how the size and shape control of colloidal semiconductor NCs can be achieved.

3.2 A chemical description of colloidal semiconductor nanocrystals

For the synthesis of colloidal semiconductor NCs, it is important to understand their physical structure. As is shown in figure 3.1a, colloidal NCs consist of two parts; a nano-sized inorganic semiconducting core, and an outer organic ligand shell. The outer organic ligand shell is not only needed for the colloidal stability of the NCs, but it also allows for surface passivation. Furthermore, it allows for control over the general size and shape of the NCs during their growth. Thus, it is important to understand the interactions between the ligands and the surface of the inorganic core, as well as the interaction between the ligands and the solvent that the NCs are dispersed in.

The inorganic core can consist of various materials. Some of the most common semiconductors used consist of binary compositions such as CdE, PbE, Cu$_{2+x}$E, and ZnE (in which E = S, Se or Te), ternary compositions like CuInS$_2$, CsPbX$_3$ (in which X = Cl, Br, I) and even quarterly compositions like Cu$_2$ZnSnSe$_4$. Further complexities in the core can also be introduced by combining multiple semiconductor domains in a single core. These NCs are called hetero-NCs, and can comprise; core/shells NCs, in which one semiconductor is
completely covered by a different semiconductor; Janus NCs*, in which the NC consists of two separate semiconductor domains; or gradient alloys, in which the NC composition gradually changes from the core to the surface or from one side to the other side. Although the inorganic core can be described by its semiconductor crystal structure, the NC’s structure is much more complex. Due to their small size, spherical NCs are not perfect “spheres”. In fact, they are rather truncated, and contain so-called “facets”, as is shown in figure 3.1b and further discussed in section 3.5. The truncation and faceting originates from the fact that the NC surface has to lower its energy by avoiding sharp edges and corners and simultaneously grow large low energy planes. Similarly, cubic shaped NCs are not perfect cubes; they are also rather truncated where the corners are cut.

* Named after the two-faced Roman god Janus

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**Figure 3.1. Overview of colloidal semiconductor nanocrystals.** (a) Schematic representation of semiconductor nanocrystal, consisting of an inorganic core and an outer organic ligand shell. (b) A realistic computational model of a PbS nanocrystal with a diameter of 5 nm, covered with oleate and hydroxyl ligands. Figure 3.1b is adapted from ref°

The outer organic shell of colloidal NCs is made up of ligands which generally comprise a hydrophobic head like amines, carbocyclic acids, phosphines or phosphine oxides, and a long hydrophilic alkane or alkene tail which is often around 8-18 carbons long, as is shown in figure 3.2a. Although these large ligands are the ligands that are mainly used during the synthesis (which will be described in chapter 3.4), they can be replaced with smaller inorganic ligands, such as SnS₄²⁻, or simple halide ions, like I⁻. The way that ligands bind to the surface of the NCs depends on the type of ligands, as well as on the NC surface. Overall, there are three classes of ligand binding: L-type, Z-type and X-type. L-type ligands are charge neutral Lewis bases, and they tend to coordinate with available metal atoms at the surface, as is the case when amines and phosphines bind to a surface Cd atom. X-type ligands are ionic species that often bind to the surface as ionic pairs, like, for instance, ammonium-carboxylates (RNH₃⁺RCOO⁻) or ammonium halides (RNH₃⁺Br⁻). Finally, Z-type ligands are charge neutral Lewis acids like such as a CdCl₂ or Pb(OOCR)₂, and bind to non-metal atoms. It should be noted that the L-type, Z-type, and X-type nomenclature used here reflects the chemical reactivity of the ligand shell (for instance, how ligands are replaced upon the addition of different ligands) and not the atomic structure at the surface itself. For instance, two carboxylates ligands that are bound to a surface Pb²⁺ atom in PbSe can both
be described as two X-type ligands, or one Z-type ligand, but, as it often dissociates from the NC surface as Pb(OOCR)$_2$, it is in fact, a Z-type ligand. It is crucial to understand the way in which ligands bind to the surface of the NC, as the ligands not only provide colloidal stability and prevent the NCs from merging, but also passivate any under coordinate atoms at the surface, as will be explained in the next section.

![Figure 3.2. Ligand chemistry of colloidal semiconductor nanocrystals. (a) Overview of commonly used ligands for the synthesis of colloidal NCs. (b) Overview of a ligand binding to the surface of NCs.](image)

### 3.3 A closer look at the surface of nanocrystals and the passivating role of ligands

The ligands at the NC surface are not only important for the colloidal stability and processability of NCs in apolar solvents, but also play an important role in passivating trap states. As mentioned in chapter 2.3, under-coordinated atoms can form trap states, consequently quenching the radiative recombination. The atoms at the surface of a NC act as under-coordinated atoms, forming trap states, which leads to non-radiative recombination. These surface trap states originate from non-bonding orbitals of atoms that protrude from the NC surface, and they are sometimes also called ‘dangling bonds’. Since NCs have a very high percentage of atoms at the surface (for instance, about a quarter of the atoms in a 5 nm CdSe NC lie at the surface), a careful passivation of surface atoms is required. In the case of an under coordinated metal atom (for example, Cd$^{2+}$ in CdSe), the metal atom can create an empty trap state below the conduction band, as is shown in figure 3.3a. To hybridize this MO, one has to introduce an electron donating ligand (L-type), which has a free lone pair, like alkyl amines or phosphines. Upon bonding, the passivated Cd-ligand MO has a HOMO that is lower in energy than the valence band edge. Therefore, the dangling bond from the Cd atom has now been passivated, preventing the formation of trap states. The same applies for non-metal atoms dangling bonds, such as Se in CdSe. Here, dangling bonds can form (filled) trap states above the valence band, and they require an electron accepting ligand (Z-type) like Cd-oleate$_2$ or CdCl$_2$ to passivate. However, a high quality, defect free NC surface is often not simply obtained by adding the right ligand, as the surface of a NC is often faceted, and deferred facets can have different atom terminations. For
instance, a small PbS NC (figure 3.1b) has a cuboctahedral shape and is terminated by the (111) and (100) facets. Here, the (111) facets are completely terminated with Pb atoms therefore they require X-type ligands, whereas the (001) facets are terminated with both Pb and S atoms and thus require both L-type and Z-type ligands. It is therefore essential to have detailed knowledge of the NC surface, and to be able to understand how ligands interact with the surface, in order to produce high quality NCs.

One other way to passivate the dangling bonds at the NC surface is by epitaxially overgrowing the NC with a shell made of a higher bandgap material. This technique is very similar to the surface passivation of silicon solar cells, whereby the surface is passivated by SiO₂, which binds to the dangling surface bonds at the silicon surface. By picking a semiconductor with a similar crystal structure and crystal lattice, but a (slightly) larger bandgap, one can completely passivate the surface of the NC, resulting in a defect free surface. All recombination should proceed through the original core of the NC, as it has a smaller bandgap, therefore the exciton should relax toward the core’s valence and conduction bands, as is shown in figure 3.3b. The larger bandgap shell can now comprise a large amount of surface traps, as the formed electrons and holes will immediately migrate away from the surface. These so-called core/shell NCs are among the brightest emitting NCs, and they also have the advantage of being chemically shielded, which, for instance, makes it less susceptible to being oxidized. One of the biggest downsides of these core shells is that using a shell with a larger bandgap makes it more difficult to both extract electrons and holes, as they tend to migrate quickly to the core, and to inject charges, as they often require high voltages to cross the shell. Also, their synthesis is rather complex, and obtaining high quality core/shell NCs that are also monodisperse can be difficult. Therefore, this type of core shell NCs is often limited to down-conversion applications.

Figure 3.3. The role and passivation of the surface. (a) A schematic representation of the effect of surface trap states on a semiconductor, and of how these trap states can be passivated with ligands. (b) A schematic representation of a CdSe|ZnS core|shell NC, and of how this allows for the passivation of CdSe surface traps.

Not all NCs have surfaces that are sensitive to dangling bonds which form trap states, as not all non-bonding orbitals at the surface fall within the bandgap of the semiconductor. In these cases, the material, or the NCs, can be called defect-tolerant. These defect-tolerant NCs often do not need a careful surface passivation. This defect-tolerance, which occurs in LHPs, such as CsPbBr₃, will be further discussed in chapter 4.4.
3.4 Commonly used synthesis methods for colloidal semiconductor nanocrystals

The synthesis of colloidal NCs is usually performed in a round bottom flask that is connected to a Schlenk line. Here, precursors can be purged from air and moisture by drying them under vacuum at 100 °C. The final reaction often is performed under a nitrogen flow (or argon). These steps are often necessary, as most NCs are air and moisture sensitive. For instance, lead and cadmium chalcogenide NCs are known to quickly oxidize in the presence of air and moisture, which drastically decreases their PLQY due to the formation of a metal oxide layer. It should be noted that the air and moisture free synthesis conditions are not actually needed for the formation of NCs, as most NCs can be synthesized in air on a simple hot plate (as will be further discussed in chapter 10). As is shown in figure 3.4, the synthesis of colloidal semiconductor NCs can be described in terms of the following general steps; precursor solution formation from metal and non-metal salts with ligands; precursor reaction leading to the formation of nuclei, the formation of NCs and finally the NC separation from the growth solution (i.e. purification).

![Figure 3.4. General overview for the synthesis of colloidal semiconductor nanocrystals. (a) Precursor formation. (b) Formation of nuclei upon a reaction with monomers. (c) Growth of nuclei and the formation of NCs. (d) Separation of NCs from the growth solution.](image)

The first step, namely the precursor formation, involves the preparation of metal and non-metal-ligand complexes, starting from off-the-shelf metal and nonmetal salts (figure 3.4a). Here, commonly used metal salts (such as metal acetates, halides or oxides) and common non-metal precursors (like sulfur, selenium, tellurium or iodides) are complexed with organic ligands (such as oleylamine (OLAM), oleic acid (OA) or trioctylphosphine (TOP) as shown in figure 2.3a) at elevated temperatures (100-200 °C)). It should be noted that the formed precursors in this case are not metal-organic precursors, as they consist of metal-S/O/P bonds, not metal carbon bonds. The formed complexes are sometimes also referred to as ‘monomers’. Although the examples of precursors that are mentioned above are the most common ones that are used in this process, other non-metal precursors, like dodecanethiol, do not require any complexation and can be used directly without any complexation. Several other highly reactive liquid precursors can also be used, including dimethyl-metals, trimethylsilyl chalcogenides/halides, or benzylhalides. However, this type of precursor always requires the use of a Schlenkline since they are highly sensitive to moisture and oxygen.

The second step is the nucleation step, in which the non-metal and metal monomers are combined and decomposed into clusters, followed by the formation of

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† This was developed by Wilhelm Schlenk in the early 1900’s, who used it to handle and synthesize the first, highly air-sensitive, organolithium compounds.
nuclei. Here, the clusters are small (often only a few monomers big), and the crystals and nuclei are defined as the smallest size cluster needed for the growth of NCs, as will be discussed later. The nucleation step is usually performed by using the hot-injection method, which was first described in 1993.\textsuperscript{14} In this hot-injection method, one precursor solution (often the non-metal precursor) is injected into a hot-solution (100-300 °C) that contains the second precursor (often the metal precursor). This method allows for the best size and shape control of the NCs, as well as the best method of obtaining (nearly) monodisperse NCs, but it often lacks in terms of reproducibility and scalability. Also, this method allows for the separation of metal (cation) and non-metal (anion) precursors, allowing for the synthesis of highly complex alloyed or hereto NCs.\textsuperscript{2} Alternatively, a quick and simple heating-up synthesis can be employed. In this method, all precursors, ligands and solvents are mixed in one solution and quickly heated up, followed by cooling down. This technique is often simply called the heating-up method, and results in having less control over the size of the NCs compared to the hot-injection method. Furthermore, the heating-up synthesis is limited with regard to composition tunability, as highly complex multinary systems often cause the nucleation of separate phases, since different precursors have different reaction temperatures. On the other hand, the heating-up method is more reproducible and is easier to scale up, making it a more robust synthesis approach for industrial syntheses of NCs.

In the third step, the nuclei, which are often only a few nm big, become vital, meaning that they cannot dissolve anymore, and they start to form small NCs. These nuclei are the building blocks for the growth of larger NCs. The formation of vital nuclei is one of the most important steps in the synthesis of NCs, and it strongly influences the size and monodispersity of the final NCs. A more physical description of this step will be described in section 3.5. The way in which the nuclei grow into larger NCs, reflexes in how size and shape of the final NCs can be obtained, and will be further discussed in section 3.6.

To stop the NCs from growing, the dispersion is cooled down to room temperature, sometimes quickly with an ice bath or by the addition of cold solvents, or sometimes slowly by simply removing the heating source. After cooling, the NCs still need to be removed from the growth solution, which is the final step of the synthesis (figure 3.4d). This has to be done as residual precursors or ligands can cause the NCs to keep growing or reshape over time. This process, called Oswald ripening (see section 3.5), results in an increase in the size-distribution of the NCs. Furthermore, the solvents used for the synthesis are polar solvents with a high boiling point, like 1-octadecene (ODE) or diphenyl ether (DPE), as is shown in figure 3.5a. Solvents with a high boiling point such as these are detrimental to the conductivity of NC films and therefore need to be removed. To remove the NCs from their growth solution, the NC dispersions are transferred to a centrifuge and precipitated by centrifugation (300-12000 rpm, 5-30 min). The precipitated NCs, which are still covered with an apolar ligand shell, are redispersed in an apolar solvent with a low boiling point. The use of solvents with a low boiling point (like toluene, hexane or chloroform, as is shown in figure 3.5b) allow for a quick evaporation of the solvent. This is desirable for the preparation of solvent free NC films/deposits, which can be made either by drop-casting or spin-coating the NC dispersions on a substrate. Depending on the required properties of the NC solutions (like type of solvent, percentage of allowed residual ligands), the NCs can be further washed by adding an ‘anti-solvent’. This anti-solvent (often isopropanol, methanol or methylacetate) results in the precipitation of the NCs, which allows them to be separated by centrifugations, before being redispersed in an apolar solvent. This extensive washing
step is often necessary for NC-based devices that require electron injection/extracting (LEDs, solar cells etc.), as any residual high boiling point ligands or solvents drastically lower the conductivity of NC films. Chapter 11 will focus more on the use of NC solutions for devices, and will give a more detailed description of the limitations of high boiling point solvents commonly used in the synthesis of colloidal LHP NCs.

![Figure 3.5. Overview of commonly used solvents for colloidal nanocrystals. (a) Solvents with a high boiling point for the synthesis. (b) Solvents with a low boiling point for storage and processing.](image)

A final synthesis aspect, which is often overlooked, is the scale at which colloidal NC are synthesized. Colloidal NC synthesis are often performed in small “lab scale” quantities, often on a mmol scale (around 100 mg of precursor salts), and often in relatively small volumes (5-25 ml). In terms of scalability, the hot injection works well at this scale, since precursors can be quickly and homogenously mixed in seconds in small quantities, which is often required for monodisperse NCs. On the other hand, as mentioned precisely, large quantities (like liters) cannot be quickly mixed within seconds, thus making the hot injection method only suitable for lab scale synthesis.

### 3.5 A physical description of the nucleation and growth of colloidal NCs

From a physical point of view, there are three stages to the formation of colloidal NCs from monomers in solution: induction (pre-nucleation), nucleation, and growth. Here, the induction phase (phase I) is the phase in which the monomers start to form small nuclei. The nucleation phase (phase II) is the period in which the nuclei form so-called critical nuclei and start to became large enough to not dissolve. Finally, the growth stage (phase III) marks the period in which the critical nuclei grow into larger NCs. This overall growth scheme is shown in figure 3.6a, and it is strongly correlated with the so-called saturation level of the monomers’ concentration.

The concentration of the monomers strongly correlates into how the monomers are being consumed for the formation of nuclei and NCs. The monomer concentration can be divided into three important categories. The critical saturation concentration ($S_{\text{crit}}$) is the minimum concentration that is needed for the formation of nuclei, and is the concentration when the solubility of the monomers reaches its limit. When a supersaturation concentration ($S_{\text{sup}}$) is obtained, the solution becomes thermodynamically unstable, and results in the rapid formation of nuclei. This occurs when the concentration of monomers becomes higher than their solubility limit. Finally, the lowest concentration needed for the consumption of monomers is called the minimal saturation ($S_{\text{min}}$). At this saturation level, the monomers’ concentration is too low for the formation of nuclei, as it is thermodynamically too costly, but does allow for the growth of existing nuclei or NCs.
For a narrow size distribution of the final NCs, it is important that the three phases are well separated; one does not want new nuclei to form during the growth of other nuclei. The phrases can be separated by quickly reaching a supersaturated solution, which allows for a rapid burst of nuclei, followed by a rapid drop in the monomer concentration, blocking the formation of new nuclei, but promoting the growth of nuclei that had already formed. To reach a fast supersaturation, one can quickly heat up a concentrated precursor solution (as with the heating-up synthesis described in the previous section) or suddenly increases the precursor concentration (by injecting one precursor into the other). Similarly, one can quickly lower the temperature, resulting in a rapid decrease in the solubility of the monomers. Both the rapid increases of the precursor concentration and the drop in temperature can be obtained by the hot-injection synthesis. The injection of a cold concentrated precursor solution at a high temperature results in an almost instant supersaturated solution, which is further promoted by the sudden drop in the reaction temperature. In other words, using the hot-injection method, the monomer consumption rate exceeds the monomer production rate, resulting in a rapid drop in the monomers’ saturation level, below the $S_{\text{crit}}$ but above the $S_{\text{min}}$. This promotes growth, resulting in monodisperse NCs.

The classic nucleation theory (CNT) can be used to describe the formation of nuclei and NCs from a physical point of view. This theory explains how the thermodynamics of the system tend to minimize the Gibbs\textsuperscript{1} free energy during the formation of “bulk” and interfaces, which lowers the overall entropy of the system.\textsuperscript{15} Although the CNT originally described the formation of liquid droplets from a vapor phase, it was adopted by La Mer for the formation of solid colloids that are formed from liquids.\textsuperscript{3} Here, the Gibbs free energy, $\Delta G$, consists of two terms: a term for the formation of bulk, the Gibbs free bulk energy ($\Delta G_v$); and a term for the loss of energy due to the formation of a surface (Gibbs free surface energy, $\Delta G_s$). In the case of a perfect spherical particle, these lead to an overall Gibbs free energy, as is depicted in equation 3.1 below:

$$(3.1) \text{Gibbs free energy, } \Delta G = \Delta G_v + \Delta G_s = \frac{4\pi}{3} r^3 \rho \Delta \mu + 4 \pi r^2 \gamma$$

Here, $r$ is the radius of the particle, $\rho$ is the density of the particle, $\Delta \mu$ is the chemical potential difference between the monomers and the nuclei, and $\gamma$ is the surface area energy. As is shown in figure 3.6b, the Gibbs free energy is positive with very small particle sizes, as it is mainly dominated by the high “cost” of the small nuclei’s very large surface areas. With increasing particle size, the gain in the Gibbs bulk free energy overcomes the Gibbs free surface energy and allows the system to lower its overall Gibbs free energy. The maximum Gibbs free energy (the activation energy) is reached at the critical radius $r_c$, and the corresponding activation energy, $\Delta G_c$. Thus, when a particle is smaller than $r_c$, it will lower its Gibbs free energy through dissolution, whereas particles with a radius larger than $r_c$ will favor growth into larger particles. The critical radius, as is depicted in equation 3.2, can be derived from the Gibbs free energy, and is given by:

\textsuperscript{1} Named after Willard Gibbs, who published his theory in A Method of Geometrical Representation of the Thermodynamic Properties of Substances by Means of Surfaces.\textsuperscript{15}
Here, $k_b$ is the Boltzmann constant, $T$ is the temperature, and $S$ is the entropy. Therefore, $r_c$ is the size of the nuclei when the chance of dissolution and the chance of further growth are equal. Thus, $r_c$ marks the separation between the nucleation and the growth stage. This further explains the success of the hot injection method; at high temperatures and supersaturation, the critical radius is very small, which rapidly promotes the formation of vital nuclei. A quick drop in both the temperature and the saturation results in an increase in the critical radius, consequently suppressing the formation of new nuclei and promoting the consumption of monomers for the nuclei to grow into NCs.

$$ (3.2) \text{critical radius, } r_c = -\frac{2\gamma}{\rho k_b T \ln S} $$

Figure 3.6. General formation of colloidal nanocrystals from dissolved monomers. (a) The formation of monomers, nuclei and NCs, depending on the saturation level of the monomers. (b) Gibbs free energy for the formation of solids from solutions (formation of NCs from monomers), indicating both the Gibbs surface energy and the Gibbs bulk free energy.

The critical radius also explains another important phenomenon that is often observed after prolonged reaction times: the so-called ‘Oswald ripening’. When NCs are left in their reaction solutions for a long time, resulting in a very low monomer saturation, or are kept at a low temperature, the $r_c$ will become very large. This large critical radius will promote the dissolution of the smallest NCs, which encourages the growth of larger ones, resulting in an increase in the size distribution. Thus, it is important to separate the NCs from their growth solutions before the saturation drops too low and the NCs start to ripen. Of course, the rate of Oswald ripping strongly depends on the rate of precursor consumption as well as the $r_c$, which both strongly depend on the reactivation of the precursors, as well as on the activation energy that is needed to form the NCs. For instance, CsPbBr$_3$ NCs are often formed within seconds therefore they require a quick separation to suppress Oswald ripening, whereas CdSe NCs often have a slower nucleation and don’t reach the Oswald ripening stage until half an hour after the nucleation has occurred.

All the above mentioned parameters (the Gibbs free energy, supersaturation, critical radius etc.) are strongly dependent on the chemical environment of the monomers. For instance, slightly changing the polarity of the reaction solvent (from ODE to DPE) can greatly affect the solubility of the monomers, and consequently the nucleation rate and

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5 Named after Wilhelm Ostwald, who first described the formation of larger crystals by the consumption of small particles, in 1896. He received a Nobel Prize in Chemistry in 1909.
overall formation dynamics. Similarly, the choice of precursors and ligands strongly influences the final reaction kinetics. For instance, highly reactive precursors (like trimethylsil or dimethyl compounds) have a very fast decomposition rate, resulting in a fast nucleation rate, whereas thioureas molecules decompose rather slowly, which can be used for a slow nucleation rate. Finally, the concentration of ligands can increase the solubility of the precursors and monomers, resulting in a higher monomer saturation concentration, thus increasing the $r_c$ and often suppressing the nucleation rate.

### 3.6 Obtaining shape control of colloidal nanocrystal

As was mentioned in *chapter 2.4*, it is not only the size of the NC that strongly alters its optical properties, but also the shape. Although the first syntheses of colloidal semiconductor NCs focused on size control, control over shape has also been extensively investigated over the past two decades. To understand the shape control of colloidal NCs, one has to understand the true shape of NCs. As previously mentioned, NCs do not have perfect spherical or cubical shapes, but are rather highly faceted structures. Each crystallographic facet has its own *free energy*, and the final shape of a NC depends on the individual free energies of the different facets. In general, the final shape of a NCs is such that it reduces the amount of high energy facets, like those formed at edges and corners. Due to the reduction of these high energy facets, NCs often do not resemble their unit cell. For instance, PbSe has a cubic rock salt unit cell, but PbS NCs often have a truncated octahedral shape. To obtain NCs with their equilibrium shape, the NCs have to be grown under *thermodynamic control*. This means slow growth rates and precursors with a low reactivity. To promote the growth of highly anisotropically shaped NCs, such as nanoplatelets (NPLs) or nanowires, one can: 1) grow NCs under kinetic shape control, 2) use NCs with an anisotropic or polar crystal structure, 3) alter the ligand chemistry, 4) use templated growth, 5) or grow NCs through oriented attachment.

In the case of *non-thermodynamic growth* control, NCs are grown under conditions which do not allow the NCs to reach their equilibrium shape. This can be achieved, for instance, by performing syntheses at a high growth rate (high temperature, high monomer concentration, highly reactive precursors, etc.). As the growth rate of a facet is exponentially dependent on its surface free energy, the faster high energy facets tend to grow at higher temperatures than the lower energy facets, causing anisotropic growth.

The second type of shape control can arise from the crystal lattice of the material. Several crystal lattice are *inherently polar*, like wurtzite CdSe, and often promote the growth of rods or multypods. Of course, this type of shape control is material dependent, and it cannot be applied to all semiconductors. For instance, the zinc blende crystal lattice is non-polar, and therefore zinc blende based NCs tend to grow more isotopically.

The third shape control method, and probably most common way of shape control, is through *ligand chemistry*. As mentioned in *chapter 3.3*, different facets tend to bind different ligands. To achieve anisotropic growth, one can use certain ligands that very strongly bind to certain facets (nearly blocking their growth) and ones that bind weakly to the others facets (thus promoting their growth). In this case, one can simply alter the ligand chemistry, and use a combination of several ligands to gain shape control. The use of ligand chemistry to gain shape control in CsPbBr$_3$ NCs will also be discussed in *chapter 5*.

The last two methods of shape control are less common, and they can only be used for the growth of large NSs (2D NCs). In the case of anisotropic growth *through a template*,
one requires the formation of a stable, lamellar template, which often consists of a layer of metal cations that is “sandwiched” between two layers of linear alkyl ligands. If these templates remain stable at the thermal decomposition temperature of the monomers, the templates can be converted into 2D NSs. This applies, for instance, to the synthesis of copper sulfide NSs, which use a copper-thiolate template. In the case of oriented attachment, one first synthesizes small NCs with a uniform size, and epitaxially grows them together during the synthesis. Through the precise tuning of the reaction conditions, this can result in the formation of large NSs. In this case, the small NCs spontaneously self-assemble, and this is driven by a minimization of their high surface energy facets. The oriented attachment growth method can be applied, for example, to PbSe NSs, which can grow up to several micrometers long in terms of their lateral dimensions, but only a few nanometers thick.

In reality, an anisotropic growth control of NCs is often accomplished by combining several of the above mentioned techniques. For instance, CdSe NSs can be synthesized by utilizing the ligand chemistry method, as well as using its polar crystal lattice, while working under kinetic shape control conditions. In this case, the same material can be synthesized in almost any shape like dots, platelets, wires, sheets, octapods, tetrapods rods etc.

Thus, it is obvious that, even though the synthesis of colloidal NCs might seem simple, almost every component (the ligands, precursor, type of semiconductor, solvent, reaction temperature, reaction time, rate of mixing, rate of heating up/cooling down etc.) strongly influences the outcome of the reaction. Therefore, if one wants to be able to tune the reaction, they must understand how all these different components work. Although this might seem overwhelming, it allows chemists to precisely alter the size shape and composition of many different type of NCs, sometimes even up to single atom precision.

References


Chapter IV

An introduction to lead halide perovskites
Chapter IV: An introduction to lead halide perovskites*

Abstract: The majority of this thesis focuses on the synthesis and properties of lead halide perovskite nanocrystals, mainly in the form of CsPbX$_3$ (X = Cl, Br, I). Since these lead halide perovskites are rather different to conventional semiconducting nanocrystals, both from a chemical and optical point of view, this chapter will provide an introduction to lead halide perovskites, their properties, and the current state of colloidal lead halide perovskite nanocrystal research.

4.1 Introduction

Mainly driven by the field of photovoltaics (PV), LHPs have attracted the attention of diverse materials scientists in the past two decades due to their unique optical versatility and facile syntheses. Following the success of LHP voltaic devices, the colloidal NC research community quickly started to investigate LHP NCs. These LHP NCs have a rather “soft” and predominantly ionic lattice, and their optical and electronic properties are highly tolerant to structural defects and surface states, making them significantly different from the conventional semiconductor NCs. Therefore, LHPs cannot be approached with the same experimental mindset and theoretical framework as conventional semiconductor NCs. In this chapter, the general properties of LHP will be discussed. Furthermore, this chapter will give a general historical overview of LHP research as well as current research pursuits and challenges in applications.

4.2 The soft ionic crystal lattice of lead halide perovskites

Traditional colloidal semiconductor NCs, which have been actively investigated since the discovery of the hot-injection, high-temperature synthesis of Cd chalcogenide NCs, primarily constitute binary compounds with rather simple crystal structure types: tetrahedrally-bonded compounds of zinc-blende (chalcogenides: ZnS, ZnSe, CdS, CdSe, HgTe; pnictides: InP, InAs) or wurtzite (ZnS, ZnSe, CdS, CdSe) structure, or face-centered rock-salt-type compounds (PbS, PbSe). These semiconductor NCs, which are spheres or cubes smaller than 20 nm and are therefore quantum-confined in all three dimensions, are also termed quantum dots (QDs). The anions and cations in the crystals of these traditional semiconductor NCs have crystallographically identical positions/sublattices. LHPs (figure 4.1a) instead crystallize in the cubic APbX$_3$-type perovskite lattice [where A is methylammonium (MA, CH$_3$NH$_3$$^+$), formamidinium (FA, CH(NH$_2$)$_2$$^+$) or cesium (Cs$^+$), X is one or more halides (Cl$^-$, Br$^-$ or I$^-$)] or its octahedrally tilted variants, isostructural to traditional oxide perovskites such as CaTiO$_3$. These structures are characterized by the 3D interconnection of their [PbX$_6$]$^{4-}$ octahedra, with the A-site cation residing in the large voids in between. The typically cubic or orthorhombic symmetries of these lattices are apparent in the commonplace observation of the cuboidal shapes of the LHP NCs (figure 4.1b). According to the Goldschmidt tolerance factor, which concerns the close-packing of ions,

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only MA, FA and Cs ions can stabilize the 3D PbX\textsubscript{6} framework due to their geometric fitness within a twelve-coordinate A-site. Larger or smaller cations favor the formation of polymorphs of a lower dimensionality (0D, 1D or 2D), with edge- or face-sharing of the octahedra, and as a consequence, larger and often indirect energy bandgaps.\textsuperscript{2}

The chemical bonding in LHPs is intrinsically much more ionic than in the more rigid, highly covalent lattices of metal chalcogenides and pnictides. This has broad implications for the synthesis, surface functionalization and processing of LHP NCs. Conventional QDs require elevated synthesis temperatures in order to promote crystallization. Existing hot-injection synthesis methods, typically at temperatures of 100-350 °C, are ideal for NCs of moderately ionic compounds such as Cd and Pb chalcogenides, and to a large extent also for InP QDs. However, it remains challenging to synthesize high-quality Si and GaAs QDs in the standard solution phase fashion, even at temperatures as high as 400 °C.\textsuperscript{3} Their synthesis also requires molecular precursors that are highly air-, moisture- or heat-sensitive or difficult to make. In contrast, due to their highly ionic bonding, LHP NCs form within seconds even at room-temperature (RT), from a vast selection of precursors.\textsuperscript{4-6} Initially, the synthesis and processing of CsPbX\textsubscript{3} NCs were primarily approached with the same methods as conventional QDs. For example, ligand-assisted hot-injection synthesis (RT-200 °C) was used to synthesize the first CsPbX\textsubscript{3} NCs.\textsuperscript{5} An alternative strategy is the ligand-assisted re-precipitation method, wherein an ionic solution of the respective ions (A\textsuperscript{+}, Pb\textsuperscript{2+} and X\textsuperscript{-}) in a polar solvent is rapidly destabilized by mixing with a non-solvent inducing a burst of nucleation, as originally proposed for MAPbBr\textsubscript{3} NCs.\textsuperscript{4} Both methods are applicable to the whole APbX\textsubscript{3} family and the reaction conditions can be adjusted to yield non-cuboidal shapes, such as nanoplatelets, NSs and nanowires.\textsuperscript{7-10} Other facile routes to colloidal LHPs include microwave-assisted synthesis, sonication of the precursors in a solvent/ligand mixture and ball-milling.\textsuperscript{11-13} Automated, high-throughput screening, such as using robotics\textsuperscript{14} or microfluidics equipped with on-line optical characterization,\textsuperscript{15} can also enable accelerated progress in the discovery of novel perovskite NCs.

Figure 4.1. Colloidal lead halide perovskite nanocrystals. (a) The APbX\textsubscript{3} perovskite structure with 3D-corner-sharing octahedra. Two typical structures are shown: cubic (MAPbX\textsubscript{3}, FAPbX\textsubscript{3}; two unit cells shown) on the left and orthorhombic (CsPbX\textsubscript{3}) on the right. (b) high-angle annular dark-field scanning transmission electron micrograph (HAADF-STEM) of a single, cube-shaped CsPbBr\textsubscript{2}Cl NC, with 15 nm edge length. (c) Photograph of highly luminescent colloidal LHP NCs.
4.3 A brief historical overview of lead halide perovskites

Although LHP and metal halide NCs in general may appear to be newcomers in materials science, this is rather a misconception. As stated in chapter I, the earliest reports of particulate semiconductor systems known to exhibit crystal size effects on the excitonic optical absorption and emission spectra were CuCl nanocrystallites in a NaCl matrix (in 1950s)\textsuperscript{16} and, a decade later, AgI colloids (1967).\textsuperscript{17} Decades later, glass- and NaCl-embedded copper halide QDs played a historic role in the theoretical rationalization of quantum-size effects.\textsuperscript{18-19} The history of bulk cesium LHP materials extends much further back in time. The existence of crystalline compounds with composition CsPbX\textsubscript{3}, as well as other related phases like CsPb\textsubscript{2}X\textsubscript{5} and Cs\textsubscript{4}PbX\textsubscript{6}, were first reported in the 1890s.\textsuperscript{20} In 1957-1958, CsPbX\textsubscript{3} were found to crystallize in a perovskite-type lattice and exhibit photoconductivity.\textsuperscript{21-22} High ionic conductivity, presently known as a reason for the electronic instability of perovskite materials as photovoltaics (PV) and a significant factor enabling fast ion-exchange in LHP NCs, was already reported for CsPbX\textsubscript{3} in the 1980s.\textsuperscript{23}

The line of research that would prove to be influential in the eventual discovery of colloidal CsPbX\textsubscript{3} NCs in 2015, began in the 1970s and concerned crystalline CsX materials doped with Pb\textsuperscript{2+} ions (typically at 0.01-1 at% doping levels). The interest in these materials stemmed from their potential as fast X-ray scintillators for the detection of ionizing radiation due to bright PL with short (ns- to sub-ns, or even tens of ps in chlorides) radiative lifetimes and high photon yield under high energy excitation. The RT-emission peak at ca. 2.45 eV (506 nm) of Pb-doped CsBr single crystals was discovered, at latest, in the 1970s\textsuperscript{24}, and its origin was attributed, until the mid-1990s, to the intra-atomic emission of Pb\textsuperscript{2+}-related centers under the effect of Jahn-Teller splitting of the ns\textsuperscript{2} cations. The more recent interpretation of the bright PL in the visible spectrum of Pb-doped CsX melt-grown single crystals and thermally evaporated thin-film materials arose in the mid-1990s. The existence of few-nm sized, fluorescent inclusions of CsPbX\textsubscript{3} is now proposed to account for this bright PL, and the fact that the observed emission is often shifted to higher energies than that of bulk CsPbX\textsubscript{3} is attributed to quantum-size effects. For example, the PL of Pb\textsuperscript{2+} doped CsCl single crystals at 400-420 nm was interpreted to be due to excitonic emission from CsPbCl\textsubscript{3} clusters in 1995, an then also in Pb-doped CsBr\textsuperscript{25-27} It is not surprising that CsPbX\textsubscript{3} nanoscale inclusions remained undetected for so long, owing to the combined effect of very low Pb-content, significant broadening of XRD reflections at sub-10 nm sizes and low electronic contrast between the CsX matrix and CsPbX\textsubscript{3} inclusions (i.e., similar X-ray scattering factors).

To induce the formation of nanosized CsPbX\textsubscript{3} inclusions in the CsX matrix on purpose and reproducibly, Pb-doped CsX single crystals grown by Bridgman or Stockbarger methods or as polycrystalline materials must be annealed for 10-100 hours at 150-300 °C to nucleate CsPbX\textsubscript{3}. These annealing temperatures are sufficiently high to induce the motion and aggregation of ions, yet still below the melting points of the CsX matrix. Interestingly, the different PL spectra observed for samples annealed at 210 and 240 °C suggest the possibility that non-spherical, platelet-like CsPbCl\textsubscript{3} NCs were formed.\textsuperscript{26} Multiple PL bands at shorter wavelengths (down to 390 nm) were quantitatively modelled as lattice-matched, atomically flat quantum wells of various thicknesses, with the thinnest being around 2.4 nm (corresponding to ca. 4 unit cells).

From the late 1990s on, considerable attention has also been devoted to thin CsPbX\textsubscript{3} films with reduced CsX excess, typically thermally evaporated and up to several µm in thickness.\textsuperscript{28-30} Very bright PL with quantum-size effects on excitonic emission was
reported for CsPbBr$_3$ films that had initially been deposited in an amorphous phase at 77 K and which were then heated to RT to induce crystallization into a nanocrystalline state. Such films even exhibited stimulated emission at room-temperature under ns-pulsed excitation (0.5 ns, at 0.5 kW cm$^{-2}$ average threshold). These early observations, as well as the widespread general attention for MAPbX$_3$ compounds as absorber materials for highly efficient PV in recent years and the notion that all-inorganic compositions of LHPs are generally superior for chemical stability, motivated the development of the hot-injection synthesis routes to CsPbX$_3$ NCs. These NCs were the first in the colloidal NC family to exhibit bright PL over the entire visible spectral range, without electronic surface passivation; they are characterized by high PLQYs (up to >90%) and a narrow full width at half maximum (FWHM) of <100 meV (12-42 nm).

In a similar way, the history of organic-inorganic hybrid LHPs can be traced back to later 1970s, when the synthesis and crystal structures of MAPbX$_3$ were introduced. The structure and properties of FAPbBr$_3$ and FAPbI$_3$ have been reported only in the last decade. Works on particulate toluene dispersions of MA-based and other alkylammonium lead halides can be found since 2012-2013. Much improved colloidal dispersibility of MAPbBr$_3$ nanoparticles was obtained with ligand-assisted re-precipitation method in the presence of long-chain ligands, first introduced by in 2014. Colloidal platelet-like and cuboidal FAPbBr$_3$ and FAPbI$_3$ NCs were reported since 2015.

4.4 Defect tolerance in lead halide perovskites

Conventional wisdom, developed over decades of research on Si, CdTe, GaAs and other conventional semiconductors, holds that PV-grade electronic quality requires ultralow concentrations of impurities and crystalline defects, typically at ppb-levels, that all act as dopants or electronic traps. LHPs are different, as highly efficient LHP PV devices can be easily fabricated based on polycrystalline films synthesized with technical-purity chemicals at low temperatures, deposited in an ambient atmosphere and, often, containing an ultra-high density of point defects such as vacancies (up to 1-2 atomic %). Likewise, LHP NCs are bright emitters without electronic surface passivation. It is clear that the electronic properties of LHPs are highly tolerant to the material’s defects and surfaces. This defect tolerance seems to be a fortunate coincidence of several factors. Firstly, out of a large variety of conceivable point defects, only vacancies (primarily A- and X-site vacancies, figure 4.2a) are characterized by sufficiently low formation energies and are therefore exclusively observed. Interstitial and anti-site defects, which would form deep trap states in the electronic structure, are almost absent since ions in the perovskite lattice are energetically difficult to misplace. Secondly, the shallow character of the vacancy-related states is due to unique specifics of the bonding in LHPs, namely the antibonding character of the valence band maxima (with mixed I 5p and Pb 6s character; figure 4.2b) and spin-orbit effects in the conduction band (which has a predominant Pb 6p character). NC surfaces can simply be imagined as a plane of vacancies and should therefore exhibit similarly benign behavior as vacancies. This intuition explains the observation of high PL QYs without surface passivation in LHP NCs. However, it should be also pointed that LHP NCs are not entirely defect-free, as PL QYs are normally reported in the range of 80-95% in the green-red region and down to 10-20% at the blue border region (close to 400 nm, i.e., CsPbCl$_3$). Yet, these values greatly exceed any other non-passivated QD material in the same range of wavelengths. There exist multiple reports of the beneficial effects of various post-synthetic
ligand treatments, such as with thiocyanates, PbBr\textsubscript{2} or trioctylphosphine-PbI\textsubscript{2}, raising the PL QY close to 100\%,\textsuperscript{41-42} presumably due to the improved passivation of under-coordinated Pb ions.

The defect tolerance of LHPs, emerging from the s and p contributions of the Pb atoms, is also pronounced in Pb chalcogenide NCs, which exhibit bright PL without surface modification except when oxidized. The far greater complexity of the defect formation in Pb chalcogenide NCs has been recently summarized,\textsuperscript{43} pointing out the importance of the dielectric constant, effective masses and defect-defect interactions in these mechanisms. Interestingly, the role of defect-defect interactions might be engineerable by external impurities. Overall, a unified understanding of the exceptional defect-tolerance in LHPs has not been achieved at the current time.

![Figure 4.2. Factors contributing to the defect-tolerant behavior of lead halide perovskites.](image)

(a) Typical point defects in LHPs, including vacancies, interstitial and anti-site atoms, in order of increasing formation energy (or decreasing probability of occurrence), and their depths in the bandgap. (b) Schematic representation of electronic band structure of typical defect-intolerant semiconductors and LHPs. In conventional semiconductors, such as cadmium chalcogenides, the bandgap is formed between bonding (σ) and antibonding (σ*) orbitals. Point defects or dangling bonds emerge as weak bonding or non-bonding states within the bandgap. In LHPs, the bandgap is formed between two antibonding orbitals. Defects states will thus form only shallow traps or will be enclosed in the conduction or valance band, and will thus not strongly influence the radiative recombination and other optical properties.

4.5 Structural lability of lead halide perovskite nanocrystals

Structural and optical stability will remain as the foremost challenge for LHP NCs in the research spotlight. An important paradigm about LHP NCs is that, as easy as it is to make them, it is just as easy to break them. Hence, the retention of their colloidal and structural integrity during isolation, purification and handling has been a problem of paramount importance. The ligand chemistries of conventional QDs have so far primarily relied on long-alkyl-chain ligands bound to the NC surface via a single anchoring group,\textsuperscript{44} or on carboxylate or phosphonate (X-type) ligands attached at surface metal adatoms.\textsuperscript{44-45} LHP NCs are terminated by oleylammonium bromide and/or oleylammonium carboxylate.\textsuperscript{45} Each of these coordinates to the surface as an ionic pair: ammonium groups displace a surface A-site cation, whereas carboxylates (bromides) act as surface anions. These ligands tend to quickly desorb (figure 4.3).\textsuperscript{45} The most dramatic consequence of such loose ligand binding
is the difficulty met in isolating and purifying colloids using standard methods for QDs, namely by a repetitive precipitation with a non-solvent followed by redispersion in a pure solvent.

\[
\text{LHP NCs} = \text{CsPbX}_3 \quad \text{NC} \quad \bullet = \text{NH}_3^+ \quad \bullet = \text{COO}^- \quad \bullet = \text{NH}_2 \quad \bullet = \text{COOH}
\]

**Figure 4.3. Structural lability of lead halide based perovskite nanocrystals** LHP NCs often lose their colloidal stability, or even structural integrity, due to the desorption of weakly bound ligands.

To obtain a more stable ligand shell, ligands containing several anchoring groups, such as zwitterionic molecules (figure 4.4a), containing quaternary ammonium and carboxylate groups (or sulfonate, phosphonate, or other groups) could be used. Oligomeric ligands with a larger number of these charged groups and long hydrocarbon chains per molecule can be envisaged as well. Due to the fairly ionic bonding character and low crystal lattice energy, LHPs are soluble in nearly all polar organic solvents; in practice, this eventually disintegrates LHP NCs upon exposure to such solvents. This problem will remain difficult to mitigate until a strategy for the full encapsulation of individual LHP NCs in an inert shell is identified (for instance, within silica, titania, alumina, salts with extremely low solubility products such as BaSO$_4$ or similar, see figure 4.4b). A classical approach to coating LHP NCs with SiO$_2$, however, would require adapting a sol-gel process such as the Stöber method. This has not been demonstrated yet, presumably due to the necessity of using alcohols or similar protic polar solvents. As a result of LHP NCs being so fragile, complex morphologies, such as core-shell NCs and other NC heterostructures, have not been demonstrated to this date.

A promising alternative path to stable LHP emitters is the melt-growth of glass-embedded LHP NCs (figure 4.4c), such as in recent reports employing typical phosphate or borosilicate glasses. Thus-obtained crystalline NCs, whose size is tunable by melt-quenching and by adjusting the subsequent thermal conditions, are surrounded by an amorphous, chemically stable, water- and oxygen-impermeable glass matrix. Such glass-embedded NCs, easily obtainable in powdered form by a grinding step after quenching the melt, can be easily integrated into any down-conversion-based application of LHP emitters – be it backlighting in displays or as a remote phosphor in lighting.
Chapter IV

4.6 Utilizing the lability of lead halide nanocrystals for post synthesis reactions

The high ionicity and structural instability of LHP NCs can also be exploited for post-synthetic transformations, either with the retention of the original crystal structure, or through reorganization into a new crystal structure. In well-controlled cases, such transformations take place while preserving the overall NC size and shape, or at least the initial size uniformity, as depicted in figure 4.5.37, 58-61 Perhaps the most striking example is that of anion exchange,58-59 whose fast rate can be attributed to the high concentration of halide vacancies and the high mobility of singly charged halide anions. The PL color of LHP
NCs can be adjusted by anion-exchange to any wavelength in the visible spectrum, starting from just one progenitor NC sample (Fig. 4a). It has further been established that mixed-halide compositions in NCs are more easily retained than in thin-films, which suffer from photo-induced halide-ion segregation. In metal chalcogenide NCs, only the cations have been manipulated in a similarly facile way. In LHPs, the high plasticity of the lattice enables the exchange of both cations and anions. The A-site cations can be partially or fully exchanged (Cs⁺ with FA⁺ or MA⁺, and in reverse), whereas Pb²⁺ can be partially exchanged with Sn²⁺, Cd²⁺ and Zn²⁺ cations (Fig. 4b,c). Similarly, doping CsPbCl₃ NCs with several at% of Mn²⁺ yields strongly orange-luminescent NCs (PL QY = 58%; emission from the dopant).

Extensive restructuring of LHP NCs is also possible, by either eliminating or adding ions (Fig. 4d-g). For instance, upon removing ¾ of the Pb atoms in the form of PbX₂, CsPbX₃ NCs can transform into Cs₄PbX₆ NCs, which are characterized by a structure in which all [PbX₆]⁴⁻ octahedra are disconnected from each other (0D-perovskite). Back conversion into CsPbX₃ NCs can be accomplished by re-inserting PbX₂ into Cs₄PbX₆ NCs or by extracting CsX by the action of suitable ligands. It is also possible to extract PbBr₂ from CsPbBr₃ NCs, forming CsBr NCs or, vice versa, to convert pre-synthesized CsBr NCs into CsPbX₃ NCs. These conversions are readily observable owing to a color change due to the large difference in bandgap energies (2.43 eV for CsPbBr₃, 3.95 eV for Cs₄PbBr₆ and 7.3 eV for CsBr). Such chemical transformations, using a presently unexplored variety of A- and B-site metals, will enable the discovery of new functional metal halide NCs, including those that cannot be obtained by direct synthesis.
Chapter IV

Figure 4.5. Structural and compositional post-synthetic engineering of lead halide perovskite nanocrystals. (a) Anion exchange enables bandgap tuning over the whole visible spectrum, as shown in the left inset. (b) “B” cation exchange allows the study of the optical properties of other divalent metals, such as Mn$^{2+}$ (whose photoluminescence at various concentrations is shown in the right inset) in an LHP environment. (c) “A” cation exchange allows the tuning of the thermodynamic stability (left inset) of the 3D-LHPs by mixing Cs$^+$ with, for instance, FA$^+$, which is key to the stability of iodides. (d) Phase-transformation from CsPbX$_3$ to Cs$_4$PbX$_6$ and CsX via reactions with Pb$^{2+}$ or PbX$_2$. (e-g) TEM images of NCs obtained by deliberate transformations between different Cs-Pb-Br compounds.

4.7 LHP NC consumer optoelectronic devices and their toxicity

The wide color gamut of the PL of LHP NCs meets the existing color standards for display applications. The small FWHM of this PL of ≤100 meV corresponds to just 18-20 nm in the green region around 520-530 nm (CsPbBr$_3$, FAPbBr$_3$ NCs), making such emitters valid contenders with traditional green phosphors. A promising near-future application for LHP NCs is therefore in LCD backlighting, for which color-pure green and red emitters with PL peaks centered at 530 nm and 630 nm are desired. Closely related prospective applications include remote phosphors for lighting and color-controlling and color-enhancing films in portable gadgets. The InP-based NCs currently used in Samsung SUHD TV displays have broader PL bands (FWHM ~ 40 nm at 530 nm), which are difficult to improve upon due to inherent compositional and morphological inhomogeneities in the few-nm-sized InP-based emissive cores. Towards display applications, the incorporation of LHP NCs into optically transparent polymers or into an inorganic matrix is an obvious strategy for thermal and
environmental stabilization. Encouraging results on the long-term stability of such emitters were indeed obtained by incorporating LHP NCs in water-nonpermeable polymers and into salt matrixes (potassium halides or Cs₄PbX₆). The fact that electronic surface passivation with wide-gap shell materials is not required for LHP NCs might be a decisive advantage for facile charge carrier injection in light-emitting diodes (LEDs). Thus far, LEDs based on CsPbBr₃ NCs are the most studied, with typical external quantum efficiencies (EQEs) of 6.3% and 8.7%. The former study reported a peak luminance of over 15,000 cd/m², while the latter reported a more modest value of 1.660 cd/m². Both studies highlight the importance of purifying LHP NCs from excess ligands. Red CsPbI₃ NC LEDs showed an EQE of 7.3% and a peak luminance of 435 cd/m² at 688 nm. It remains difficult to construct efficient blue LEDs with perovskite NCs, where the best example is that of MAPbBr₁.₅Cl₁.₅ NCs, which exhibit an EQE of 1.18% and a peak luminance of 2473 cd/m² at 445 nm. For the blue-most CsPbCl₃ NCs, the highest achieved EQE to date is only 0.61% and the corresponding luminance was 11 cd/m² (at 404 nm).

LHP NCs also show great promise as versatile solution-based precursors for the low-temperature fabrication of absorber layers for PV. Solar cells with efficiencies up to 10.8% were demonstrated using CsPbI₃ NC thin-films deposited by multiple rounds of sequential spin-coating and ligand-removal steps. Further progress in this direction can be expected, utilizing more complex compositions of LHP NCs. This is motivated by recent trends in thin-film LHP PV where power conversion efficiencies exceeding 20% have been reported, by employing mixed-cation and mixed-anion compositions such as (Cs/Rb/FA/MA)Pb(Br/I). NC-based synthesis routes to such complex thin-films might have certain inherent advantages. For example, although the deposition of such films requires the solubilization of all of the precursor salts in polar solvents, coating, annealing and recrystallization of the LHPs in a single step, the use of LHP NCs separates the mixing of ions, film-formation and crystallization into three different steps. The nonpolar solvents used for depositing NCs might also be advantageous, for example, in maintaining solvent orthogonality in the deposition from solution of consecutive layers of the device. LHP NCs are also unique in their ability to form bulk heterojunctions with other solution-processable materials such conductive polymers, fullerenes or other QDs.

The presence of lead in LHPs raises obvious concerns about the toxicity of these materials upon introduction into consumer electronics. One should note here that the industrialized world has been exposed to massive amounts of lead over the decades. A now infamous, volatile compound, tetraethyl lead, has been used since the 1920s as an additive to fuels, and although its phasing out from automotive applications began in the 1970s, it is still far from completion. In its non-volatile, metallic form, or as stable and insoluble solid compounds, Pb remains widely used in, for example, lead-acid batteries, solder in silicon solar cells, piezoelectrics and even as a white pigment (PbO₂). The European “Restriction of Hazardous Substances” (RoHS) directive limits the use of heavy-metal-based substances in electrical and electronic equipment. The current limit for lead is 1000 ppm by weight in any continuous solid component of the device, which is not as stringent as the current limit for cadmium (100 ppm by weight). Current Cd-based QD TV displays require only about 1.5 mg of Cd (for a 55 inch display). For LHPs, one could assume that roughly the same quantity of Pb would be needed based on nearly identical extinction coefficients in blue (450-470nm; GaN emission for excitation) and similarly high PL efficiencies at the same PL wavelengths (530 and 630 nm). This corresponds to sub-1000 ppm concentrations of Pb within the 50-
100 µm thick polymer film, hence not requiring an RoHS exemption. With regard to consumer electronics, the recycling policies for Pb are well detailed and are highly efficient. Efforts are underway to find environmentally benign and, at the same time, chemically robust alternatives to lead-based chemistries for optoelectronic applications. As discussed above, defect-tolerant semiconductors are those in which both the s and p electrons of a metal hybridize to form the valence and conduction bands. In accordance with this principle, Sn\(^{2+}\) and Ge\(^{2+}\) analogues of LHPs do exhibit bright emissions but, unfortunately, are highly unstable. Even trace oxygen quantities cause degenerative p-type doping in tin and germanium perovskites through oxidation. Furthermore, Sn-based analogues of LHPs are, from a toxicity point of view, not ideal alternatives.\(^{79}\) High stability and bright emission have been reported for 0D-perovskite-like structures \((C_4N_2H_14Br)_4SnX_6\) \((X = Br, I)\),\(^{80}\) but with a very large FWHM of above 100 nm at RT.

The solar cell community has contributed great effort in the search for lead-free, LHP-like semiconductors.\(^{81}\) In particular, the replacement of Pb\(^{2+}\) with oxidatively stable Bi\(^{3+}\) is an attractive option. However, such ternary halides are structurally very different from LHPs since they typically crystallize into OD or 2D networks of M-X polyhedra, usually with indirect band gaps, such as in \(Cs_3M_2X_9\) \((M = Sb, Bi, In)\).\(^{82}\) So far, these phases have not exhibited efficient PL at RT. To retain the 3D-interconnection of octahedra, double perovskite compositions of \(A_2M^{II}M^{III}X_6\) have been investigated, such as \(Cs_2AgBiCl_6\) and \(Cs_2AgInCl_6\).\(^{83-84}\) Such compounds have not yet shown photophysical characteristics on par with LHPs, and they exhibit indirect band gaps, making them unsuitable as emitters. Overall, despite the growing skepticism of the PV community about the near-term probability of finding a substitute for LHPs amongst its close structural and compositional analogues, the chances of developing bright, LHP-like nanoscale emitters are far greater. The reasons for this optimism are as follows. First, while PV materials must have bandgaps beyond 700 nm, LHP NCs as bright emitters are primarily needed to function with bandgaps of 450-700 nm. Hence, many materials discarded by the PV research community might be perfectly suited for constructing NC emitters. Second, the spatial confinement of carriers in NCs usually drastically enhances the PL QY. To this end, and in retrospect, the bright green PL from CsPbBr\(_3\) could have been discovered much earlier; this compound has been known for over 100 years, and all that was needed to be done was intense mechanical grinding of the bulk material. However, this idea would have been hard to conceive of since bulk CsPbBr\(_3\) is essentially non-luminescent. In conclusion, it seems to make quite some sense to revisit numerous compounds that were discarded as PV materials and to systematically synthesize them in nanoscale form in order to observe whether or not they become luminescent.

### 4.8 Conventional quantum dots vs. lead halide perovskite nanocrystals

A final comparison between the physical and electronic properties of conventional QDs and LHP NCs is shown in Table 4.1. For decades, the primary challenge facing semiconductor NCs was the suppression of the role of mid-gap surface traps that render practically all as-synthesized semiconductor NCs that emit in the visible range poorly luminescent. This has been conventionally mitigated by the elaborate synthesis of sophisticated, core-shell CdSe-CdZnS NCs, via decoupling of the excitonic recombination from surface states. These NCs feature high PL QYs of up to 95-100%, narrow emission lines and excellent long-term stability, and they are currently applied as down-converting materials in several brands of modern liquid-crystal television displays (LCD-TVs) with high...
An introduction into lead halide perovskites

color saturation. From the first reports on, unpassivated LHP NCs have exhibited high PL QYs even when the synthesis was performed under ambient conditions and/or without pre-purified chemicals. Small FWHM and high PL QYs are also repeatedly reported with more complex, mixed-cation Cs/FA and mixed halide (Cl/Br, Br/I) stoichiometries. Solution-based compositional engineering has shown to be possible on all three lattice sites within LHPs, such as in FA$_{0.75}$Cs$_{0.25}$Sn$_{0.5}$Pb$_{0.5}$I$_3$ or (Cs/Rb/FA/MA)Pb(Br/I)$_3$.$^{77, 85}$ However, it is difficult to achieve a combination of high optoelectronic quality and atomistic homogeneity in multinary metal chalcogenide NCs (CuInS$_2$, CuIn$_x$Ga$_{(1-x)}$Se$_2$ and Cu$_2$ZnSnS$_4$)$^{86}$ and it remains completely elusive for pnictide NCs. Typically, for the tetrahedrally-bonded compounds, site disorder (interstitial and anti-site atoms) and phase inhomogeneities are enhanced in NCs as compared to the bulk. In contrast, the LHP lattice, wherein ions cannot easily be misplaced due to their specific sizes, coordination numbers and ionic charges, is intrinsically immune to such defects. With regards to multinary LHP NCs such as (Cs/FA)Pb(Br/I)$_3$, a detailed structural analysis is still pending and will be crucial for further taming the presently unstable red and near-IR emitting LHP NCs.

Given the rate at which scientific results related to LHP NCs are published, it is not surprising that the literature is sometimes controversial; only through careful and less precipitous investigations can these ongoing issues be settled. For instance, CsPbBr$_3$ NCs were initially assigned as a cubic phase,$^5$ but deeper analysis revealed that this phase is actually orthorhombic and exhibits highly dynamic structural disorder.$^{87}$ Even more debated issues are related to the correct assignment of optical and electronic structures to specific phases and compositions of cesium lead halides. Cesium, lead and bromine, for example, can crystallize into CsPbBr$_3$ perovskite or into non-perovskite phases, CsPb$_2$Br$_5$ and Cs$_4$PbBr$_6$. The latter non-perovskite has been reported to be green-luminescent by several groups, but at the similar wavelengths at which the emission of CsPbBr$_3$ is usually observed (ca. 520 nm).$^{88}$ Contrarily, other groups report larger bandgaps for both Cs$_4$PbBr$_6$ and CsPb$_2$Br$_5$, with no luminescence at all.$^{60, 89}$ The compositional and structural complexity of LHP NCs is only starting to be fully recognized and rationalized.

It is clear that LHPs have enticed materials scientists, chemists and physicists to further development the, yet fundamental, research of LHP NCs, as well as finding ways the implement their applications. Efficient pure-color or white-light generation with LHPs will gain increasing scientific interest and, very likely, will turn into a great commercial opportunity in the near future (in displays, lighting and other applications). In this regard, it should be emphasized that colloidal APbX$_3$-type NCs are not the only promising forms of LHPs as versatile photonic sources. Quantum-confined LHPs can also be obtained in a stable bulk form. A notable case is that of the 2D Ruddlesden-Popper phases, in which 3D-like layers of [PbX$_6$] octahedra are electronically disconnected by the partial replacement of Cs/MA/FA cations with larger cations such as butylammonium. These can be obtained as polycrystalline materials or as thin-films.$^{90, 91}$ Such “2D” perovskites share many similarities with the aforementioned colloidal synthesized LHP nanoplates/NSs, due to their strong quantum-confinement in one dimension. Combining the essential properties of colloidal LHP NCs and bulk 2D perovskites to achieve “multidimensional 3D/2D” LHP NCs has proved to be an interesting avenue of research, wherein the dimensionality of the electronic structure is engineered on both the atomic scale and nanoscale.$^{92-94}$ This, and other research opportunities described in this thesis, will likely reveal their real potential in the following years.
Table 4.1. Comparison of the chemistry, durability and optical performance of lead halide perovskite nanocrystals with conventional nanocrystals. Only NCs emissive in the visible spectral range are included.

<table>
<thead>
<tr>
<th></th>
<th>Metal chalcogenide and pnictide core-only nanocrystals</th>
<th>Metal chalcogenide and pnictide core/shell nanocrystals</th>
<th>Lead halide perovskite nanocrystals</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Composition</strong></td>
<td>CdSe, ZnSe, InP</td>
<td>CdSe/CdS, CdSe/CdZnS, InP/ZnS</td>
<td>(Cs,FA)PbX₃ (X = Cl, Br, I)</td>
</tr>
<tr>
<td><strong>Used in</strong></td>
<td>no commercial use</td>
<td>LCD TV (Samsung, Sony, etc.), discontinued for Cd-based.</td>
<td>under development for LCD TV</td>
</tr>
<tr>
<td><strong>Spectral range and efficiency</strong></td>
<td>entire visible (400-700 nm) for II-VI</td>
<td>limited (510 - 650 nm)</td>
<td>entire visible (400-700 nm)</td>
</tr>
<tr>
<td><strong>PLQY</strong></td>
<td>low (0-10%)</td>
<td>high (up to 95%)</td>
<td>high (up to 99%)</td>
</tr>
<tr>
<td><strong>FWHM</strong></td>
<td>narrow for II-VI (&lt;25 nm; e.g. &lt;100 meV), but limited for InP-based (ca. 40 nm at 530 nm PL peak)</td>
<td>narrow over entire visible range (&lt;100 meV)</td>
<td></td>
</tr>
<tr>
<td><strong>Defectiveness</strong></td>
<td>low in binary compounds; high in multinary compositions (vacancies, antisites and interstitials)</td>
<td>intrinsically high (vacancies)</td>
<td></td>
</tr>
<tr>
<td><strong>Synthesis</strong></td>
<td>high-purity precursors, air-free synthesis; high-temperature</td>
<td>elaborate, lengthy synthesis; high-temperatures</td>
<td>facile synthesis; possible under ambient conditions</td>
</tr>
<tr>
<td><strong>Post-synthesis tunability</strong></td>
<td>only cation exchange</td>
<td></td>
<td>cation exchange (both A and B sites) and anion exchange</td>
</tr>
<tr>
<td><strong>Surface ligands</strong></td>
<td>highly versatile organic and inorganic surface functionalization</td>
<td>limited affinity to the surfaces</td>
<td></td>
</tr>
<tr>
<td><strong>Hetero-nanostructures</strong></td>
<td>yes (complex core shells/dumbbells/Janus etc.)</td>
<td>none to date</td>
<td></td>
</tr>
<tr>
<td><strong>Thermal stability</strong></td>
<td>stable</td>
<td>stable</td>
<td>limited to below 100 °C due to low melting points</td>
</tr>
<tr>
<td><strong>Oxidative and photostability</strong></td>
<td>low to moderate</td>
<td>high</td>
<td>high</td>
</tr>
<tr>
<td><strong>Solvent compatibility</strong></td>
<td>compatible with all solvents, including water</td>
<td>finite solubility in water and many polar solvents, insoluble in all others</td>
<td></td>
</tr>
<tr>
<td><strong>RoHS compliance</strong></td>
<td>limited for CdSe-based (100 ppm limit for Cd), unlimited for InP-based</td>
<td>limited but higher than for CdSe-based (1000 ppm limit for Pb)</td>
<td></td>
</tr>
</tbody>
</table>
References

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Chapter V

Shape control of CsPbBr$_3$ nanocrystals
Chapter V: Shape control of CsPbBr$_3$ nanocrystals*

Abstract: The quantum confinement effects on semiconducting nanocrystals are not only determined by the size of the nanocrystals, but also by their shape. In this chapter, the synthesis and optical properties of two dimensional CsPbBr$_3$ nanoplatelets will be discussed. The thickness of these nanoplatelets can be precisely tuned from 3 to 5 monolayers, resulting in nanoplatelets with a strong quantum confinement in one dimension and with an overall narrow photoluminescence. Furthermore, this chapter will discuss the reaction mechanism, which results in a strong anisotropic growth. In the case of CsPbBr$_3$ nanocrystals, the anisotropic growth is driven by the direct competition of large oleylammonium cations with Cs$^+$.

5.1 Introduction

Ultrathin semiconductor NSs and NPLs have recently come under intense scrutiny, in part due to the growing interest in 2D systems triggered by research on graphene and related materials.$^{1-4}$ In the time span of only a few years, a plethora of colloidal syntheses of 2D NCs of various materials, including PbS, SnSe, Cu$_{2-x}$S, ZrxS$_2$, MSE$_2$ (M = Mo, W)$^5-9$ and CdE (E= S, Se, Te)$^{10-14}$ have been reported. Especially the cadmium chalcogenide platelets/sheets have received much attention due to the tight control over size and shape that could be achieved, so that their well-defined optical properties could be directly compared to those of spherical/rod shaped CdE NCs that have been studied so intensively in the previous years.$^{15-16}$ Colloidal NCs of LHP represent the latest entries, with reliable synthesis approaches having appeared only in the last two years.$^{17-22}$ These NCs immediately gained huge interest due to their high quantum yields (up to 99%), their sharp emissions lines (0.12 eV linewidth) and the freshly discovered possibility to tune the halide composition, both during synthesis and by post-synthetic anion exchange reactions.$^{23-25}$ Furthermore, LHP NCs have already been shown capable of lasing and acting as quantum emitters.$^{26-28}$

In comparison to the more mature case of inorganic semiconductors NCs, the size and shape control of LHP NCs in the form of sheets/platelets is less advanced, with only a few papers dealing with this issue. Two works reported colloidal MAPbBr$_3$ NSs with control over the sheet thickness,$^{29-30}$ while in another work (C$_4$H$_9$NH$_3$)$_2$PbBr$_4$ NSs were directly grown on a substrate and then detached from it.$^{31}$ Yet, in order to directly correlate dimensionality with quantum confinement effects in sheets/platelets, colloidal synthesis approaches need to be refined in a way as to reach control of the thickness down to a discrete number of monolayers, with differences in thickness from sample to sample at the level of a single monolayer. Such control would allow for disentangling quantum

confinement from dielectric confinement effects. Also, colloidal free standing particles are clear from spurious behaviors which are often overwhelming in perovskites grown on a substrate, due to their inherently deformable structure.\textsuperscript{31-33}

This chapter discusses the synthesis and formation mechanism of CsPbBr\textsubscript{3} NPLs with precise thickness tunability in the range from 3 to 5 unit cells. This was made possible by devising a room temperature synthesis scheme in which a mixture of chemical precursors remained unreactive unless acetone was injected into it, which initiated the nucleation and the growth process (section 5.2 – 5.5). The low temperature at which the synthesis was carried out made shape control possible. At this small thickness, the CsPbBr\textsubscript{3} NPLs emitted in the blue region of the spectrum, a region that is notoriously not well covered by many colloidal nanocrystal systems. Such level of control in platelet thickness could then be extended to the corresponding CsPbCl\textsubscript{3} and CsPbl\textsubscript{3} materials by means of anion exchange, which preserved size and shape of the starting particles. The final part of this chapter focuses on two cases proving that the anisotropic growth is driven by the presence of oleyl ammonium cations. In section 5.5 it is discussed that mixtures of OA and OLAM in a non-polar medium lead to the protonation of OLAM by OA. Oleylammonium-rich synthetic conditions promoted anisotropic growth through a competition between oleylammonium and Cs\textsuperscript{+} ions. The concentration of oleylammonium (RNH\textsubscript{3}\textsuperscript{+}) could be increased not only by raising the concentration of OA but also by lowering the reaction temperature. This thus results in the anisotropic growth of CsPbBr\textsubscript{3} NPLs at either low temperature, or acid environment. Similarly, NPLs with controlled thicknesses, down to a single monolayer sheet with a (RNH\textsubscript{3})\textsubscript{2}PbBr\textsubscript{4} composition could be synthesized using this method. Finally, section 5.7 discusses the case were OLAM is replaced by various dialkyl ammines. These dialkylamines, in the form of dialkylammonium cations, are too bulky to replace the Cs\textsuperscript{+}, and therefore cannot drive the anisotropic growth. This thus results in nearly monodisperse nanocubes, even under conditions that normally results in highly anisotropic NPLs, when synthesized with OLAM.

### 5.2 Synthesis and characterization of CsPbBr\textsubscript{3} nanoplatelets

The synthesis of the CsPbBr\textsubscript{3} NPLs, differently from previous reports, was carried out at room temperature starting from a mixture of Cs oleate, OLAM, OA, PbBr\textsubscript{2} and HBr that remained stable unless an additional component was added to it. PL spectra of this “precursor” solution, taken in rapid succession (every two seconds, see appendix 5.1a), evidenced the steady presence of a broad peak centered at around 3.2 eV that originates from the surfactants present in the flask (see appendix 5.1b) and is not due to the formation of small CsPbBr\textsubscript{3} clusters. Then, as soon as acetone was added to the precursor mixture, a narrower peak appeared at around 2.95 eV. Within seconds, this peak further red-shifted and narrowed (indicating the nucleation and growth of CsPbBr\textsubscript{3} NPLs), and finally settled to an energy value that depended on the amount of HBr added (for example 2.83 eV, for a 7.5 µl addition of HBr, see appendix 5.1a). It is likely that acetone destabilizes the complexes of Cs\textsuperscript{+} and Pb\textsuperscript{2+} ions with the various molecules in solution and therefore sets the trigger for the nucleation of the particles. This was further confirmed by a set of experiments in which different time lags between injection of the Pb precursor and acetone were tested, but all yielded NPLs with the same morphological and optical features (appendix 5.2). Other polar solvents, for example protic solvents like isopropanol and methanol, were also tested, but were not as effective as acetone in shape control (appendix 5.3a). The addition of methanol,
for example, led to the quick formation of large particles (20-40 nm in size, see appendix 5.3b), most likely due to excessive destabilization of the initial metal complexes.

TEM and HRTEM images of a typical sample of CsPbBr$_3$ NPLs synthesized with this approach are reported in figure 5.1a-d. In grids prepared from diluted samples, the NPLs were lying flat with respect to the substrate (figure 5.1a and c), whereas samples deposited from concentrated solutions were characterized by stacks of face-to-face aligned NPLs, with the particles often oriented perpendicularly with respect to the carbon support film (see figure 5.1b and d). This latter arrangement enabled a precise estimation of the NPL thickness. In this specific sample obtained without HBr in the precursor solution, the NPLs had a thickness of 3.0 ± 0.4 nm (corresponding to 5 unit cells) and average lateral dimensions of 7.9 ± 1.2 nm by 40.9 ± 6.8 nm. During the exposure of the CsPbBr$_3$ NPLs to the electron beam, metallic lead particles were formed (figure 5.1a and appendix 5.4), as revealed by combined HRTEM and compositional analysis. This electron-beam induced transformation of the sample is consistent with what already reported for large MAPbBr$_3$ sheets. The platelet morphology is particularly evident from dark field TEM analysis (figure 5.1e), in which NPLs either lying flat or edge on with respect to the support film could be seen.

X-ray diffraction (XRD) diffraction analysis was carried out on the platelets. At low angles, a series of diffraction peaks originating from the stacked superstructure of the NPLs were observed (see appendix 5.5). The interplanar spacing of 5.1 nm corresponding to these peaks is in good agreement with the thickness of the NPLs (3.0 nm) plus two layers of passivating organic ligands (OLAM/OA, about 1.0 nm per layer). A conventional pattern collected on CsPbBr$_3$ NPLs is instead reported in figure 5.1f. Due to the anisotropic shape of the NPLs, the [0 0 l] (l = 1,2,3,4...) planes parallel to the lateral dimensions exhibited narrow peaks, with a high intensity (figure 5.1f, green line). The other peaks, which are related to families of planes that are actually reduced only to a few unit cells, were also present but were much broader and less intense (figure 5.1f, zoom in, purple line). Also, the peaks were shifted towards lower angles with respect to those of the reported diffraction pattern of cubic CsPbBr$_3$. Using the most intense [002] diffraction peak and considering a cubic cell, a unit cell size of 0.599 nm was calculated, which is larger than the bulk cubic CsPbBr$_3$ cell (0.587 nm) by 0.012 nm. A possible explanation from this deviation in cell size is due to passivation of top and bottom facets of the cell by protonated OLAM ligands, which locally would effectively mimic an alkyl ammonium lead halide type of cell. This is also in line with the Cs:Pb:Br ratios equal to 0.59:1.00:2.95 measured by elemental analysis (via STEM-EDS), which indicate a substantial cesium deficiency in the NPLs. Therefore, it is likely that Cs$^+$ ions of the top and bottom facets are mostly replaced by oleyl ammonium ions, and this can slightly expand the overall lattice, given the extremely small thickness of the platelets. XRD patterns collected on samples heated at increasing temperatures gave peak positions that were closer to that of the bulk pattern (already at 50 °C, with an almost perfect match at 150 °C, see appendix 5.6). As the intensity ratios too were closer to the bulk, it was concluded that annealing caused partial sintering of the NPLs, with consequent desorption of part of the ligands and overall reorganization of the lattice that gets more in line with that of bulk CsPbBr$_3$ than the initial NPLs. Also, it is interesting to note that the unit cell parameters estimated by HRTEM analysis (performed at 80 kV to minimize electron beam damage) were similar to those of the bulk, with an estimated lattice parameter around 0.58
± 0.02 nm (figure 5.1c and d). It is likely that the electron beam irradiation on these platelets has an effect similar to that observed by annealing films of NPLs.

![Figure 5.1. Structural analysis of CsPbBr₃ nanoplatelets emitting at 460 nm. TEM images of (a) CsPbBr₃ NPLs at low concentrations and (b) high concentrations. HRTEM images of NPLs (c) in top view and (d) in stacks as well as their respective electron diffraction patterns in the insets. (e) STEM-dark field image of NPLs. (f) XRD pattern of CsPbBr₃ NPLs. Reference pattern of cubic CsPbBr₃, ICSD 29073.](image)

### 5.3 Monolayer thickness control

The thickness of the NPLs was precisely controlled by dosing the amount of added HBr during the synthesis, from a minimum value of 3 monolayers (ML) when adding 7.5 µl of HBr, up to 5 ML in the absence of HBr. TEM analysis showed indeed that the NPLs thickness decreased from 3.0 nm for the 5 ML sample to 2.5 and 1.8 nm, respectively for the 4 ML and 3 ML samples, as shown in figure 5.2a, appendix 5.7 and 5.8. Furthermore, as shown in appendix 5.9, the example of the 3 ML sample, the thinner NPLs retained the crystallinity and the lattice parameters of the 5 ML sample. Such level of control may be explained considering that the increased acidity of the solution due to the addition of HBr aids in the protonation of OLAM, as also reported by Yuan et al. The protonated OLAM can compete with Cs⁺ ions on the surface of the growing platelets, essentially slowing down the growth in the vertical dimension. This will be further discussed in section 5.8 and 5.9.

The optical bandgap was remarkably sensitive to the number of layers in this 3-5 ML regime, as shown in figure 5.2a-c, with blue shift and strengthening of the excitonic transition for thinner sheets as a result of confinement effects. Although the PLQY of the 5 ML NPLs dropped to 31% from the 78% value of the cube-shaped CsPbBr₃ NCs, the yield was still comparable to that of CsPb(Br:Cl)₃ NCs prepared by anion exchange (as reported in previous works) and emitting at the same energy (PLQY at 2.75 eV = 37%). The stability of the NPLs was related to the number of layers: the 4 ML sample, emitting at 2.75 eV, was only stable for a day, and quickly formed a 2.70 eV 5 ML emitting sample, whereas the 3 and 5 ML samples were stable at least for one month, with only the appearance of a secondary emission peak at 2.36 eV, as well as a sedimentation of a green/yellow
precipitate, indicating the formation of larger non-quantum confined CsPbBr$_3$ aggregates (see appendix 5.10). Due to the instability of the 4 ML NPLs, as reported above, no reliable HRTEM and XRD data could be recorded for that sample.

As it was shown for cube-shaped CsPbBr$_3$ NCs,$^{23-24}$ also in the present case the Br$^-$ anions in the NPLs could be easily replaced with Cl$^-$ and I$^-$ anions, delivering NPLs that were progressively richer in Cl$^-$ or in I$^-$, as shown in figure 5.2d. Here, the absorption could be finely tuned by the addition of Cl$^-$ and I$^-$ complexes (appendix 5.11). As calculated by Protesescu et al.$^{18}$, the exciton Bohr radius is related to the halide composition, being 2.5 nm for CsPbCl$_3$, 3.5 nm for CsPbBr$_3$ and 6 nm for CsPbi$_3$. This can also be observed for the three different samples of NPLs with different halide compositions. While the emission of the 5 ML CsPbBr$_3$ NPLs had blue shifted by 0.34 eV relative to the bulk (2.36 eV), the CsPbi$_3$ NPLs prepared by anion exchange, and thus with the same thickness as the starting CsPbBr$_3$ NPLs (apart from a variation due to the changed lattice parameter), exhibited a more pronounced confinement effect: the emission was blue shifted by 0.36 eV compared to its bulk value of 1.77 eV. On the other hand, the emission from the CsPbCl$_3$ NPLs was blue shifted by only 0.08 eV from its bulk value (2.96 eV), which is in line with the smaller Bohr radius of the CsPbCl$_3$ perovskite.

![Figure 5.2](image.png)

**Figure 5.2.** Optical and structural properties of different thicknesses of CsPbBr$_3$ nanoplatelets and their anion exchanged nanoplatelets. (a) Three different thickness with 5 ML emitting at 2.70 eV, Stoke shift (Ss) = 0.11 eV and FWHM = 0.11 eV, 4 ML emitting at 2.76 eV, Ss = 0.12 eV and FWHM = 0.17 eV and 3 ML emitting at 2.83 eV, Ss = 0.11 eV and FWHM = 0.09 eV. (b) and (c) TEM and HRTEM image of 3 ML thick sample indicated a thickness of 1.8 nm. (d) Fine-tuning the PL of CsPbBr$_3$ NPLs with anion exchange reactions to CsPbCl$_3$ and CsPbi$_3$.

### 5.4 Quantum confinement effects in CsPbBr$_3$ nanoplatelets

In figure 5.3a the absorption and emission spectra of Br-based NPLs of different thicknesses are compared with those of colloidal cube-shaped CsPbBr$_3$ NCs (as reported in previous works, also see appendix 5.12)$^{23}$ and from polycrystalline thin film prepared by direct crystallization of the precursors on a glass substrate (see Experimental section). The thin film was made of crystallites of size ranging within hundreds of nanometers (see appendix 5.13), the cube-shaped NCs had a dimension of about 8.5 nm. The cubes and the polycrystalline thin film exhibited very similar optical edges. The absence of any remarkable differences in both the absorption and emission spectra of the two samples suggests that the 8.5 nm cube-shaped particles presented only weak quantum confinement effects. This is in agreement with the fact that the exciton Bohr radius of CsPbBr$_3$ is around 3.5 nm, as
discussed earlier. The NPLs on the other hand, with their thickness of 3 nm or below, did experience a blue shift of the optical edge.

To further investigate the electronic properties of the synthesized NPLs DFT calculations were performed on 2D periodic slabs of cubic CsPbBr$_3$ of increasing dimensions, up to ca. 11 nm along the non-periodic direction, see figure 5.3b. DFT calculations were performed by including relativistic effects at both the scalar relativistic (SR) and spin-orbit coupling (SOC) level. It was previously shown that SOC plays a central role in determining the electronic properties of organohalide lead perovskites. Though SOC-DFT it was found to considerably underestimate the band-gap of these semiconductors, with more elaborate SOC-GW calculations delivering an improved agreement, the two methods provide qualitatively similar band-gap trends. Here, the level of theory to SOC-DFT was limited since GW calculations are impracticable even on the smallest considered slab. The evolution of the experimental (from PL measurements) and calculated band-gap are reported in figure 5.3c SR- and SOC-DFT results have been scaled so that the bulk band-gap matches the experimental 2.36 eV value. Due to the use of a 2x2 unit cell, the cubic bulk CsPbBr$_3$ phase shows a direct band gap at the Γ point (instead than R) of the Brilluoin zone. As it can be noticed, the SOC-DFT calculations nicely reproduce the experimental band-gap evolution, showing a nonlinear (approximately square-root like) trend with 1/r$^2$ (r being the NPLs dimension along the aperiodic c direction). SR-DFT results deliver a significantly different picture, confirming the importance of SOC effects not only in determining the electronic and optical properties of bulk organohalide lead perovskites but also in defining their quantum confinement behavior. According to the effective mass model, by plotting the band-gap vs. 1/r$^2$ one should obtain a straight line. This was verified for CsPbBr$_3$ quantum dots by Protesescu et al. In practice, deviations from this ideal behavior are found in ultrasmall quantum wells, like the NPLs investigated here, due to tunneling of the electron/hole wavefunctions outside the well boundaries, i.e. due to the lack of effectively infinite potential barriers at the NPLs border. This is precisely the case of the NPLs synthesized here, for which an almost linear behavior is found for the larger systems (down to 5 ML, ca. 3 nm, corresponding to ca. 0.1 in the scale of figure 5.3c), with a significant deviation found for smaller dimensions, similar to what reported by Sichert et al. A variation of the dielectric properties of CsPbX$_3$ NPLs with quantum confinement was also recently reported by Sapori et al., indicating a decrease of the dielectric constant with reduced NPLs thickness.
5.5 A closer look at the photoluminescence of CsPbBr$_3$ nanoplatelets

Figure 5.4a reports the PL dynamics from the cubic-shaped 8.5 nm NCs and from the NPLs, at different excitation densities. The decays were purely mono-exponential and intensity independent. A monomolecular decay may be the result either of exciton decay or of carrier trapping at defects sites. The latter can be easily discarded by looking at the relative PLQY as a function of the excitation intensity, reported in figure 5.4b and appendix 5.14a. The PLQY is intensity independent, especially at low excitation densities (right side of the plot). This trend is not compatible with a trap limited process, which would instead exhibit an increase of PLQY with intensity due to trap filling (appendix 5.13b and appendix Note 5.1).\textsuperscript{32} Note that bulk films of CsPbBr$_3$, which should have a greater number of traps and thus more non-radiative losses than the ligand passivated NPLs, are characterized by shorter PL lifetimes at low excitation densities, which was ascribed to trap induced quenching. At higher excitation densities the traps are filled and thus their role in the excitation dynamics is reduced, and indeed the PL lifetimes increases. Therefore, it can be concluded that the CsPbBr$_3$ NPL’s intensity independent monomolecular lifetimes, along with high PLQY, are the fingerprint of a pure excitonic decay, with minimal non-radiative losses in the system. The PL dynamics is generally very sensitive to confinement effects. Greater overlap of electron and hole wavefunctions should lead to a larger recombination rate, thus to a reduction of the PL lifetimes.\textsuperscript{40-41} However, the behavior of NPLs did not differ much from that of cube-shaped NCs. As shown in figure 5.4a, in the NPLs (5 ML) a monomolecular decay with lifetime of about 3 ns (4 ns for the cube-shaped NCs) could be estimated, which is intensity independent within an excitation range between 1 and 100 nJ/cm$^2$. The 3 ML NPLs exhibited very similar lifetimes, as shown in appendix 5.14b.
Shape control of CsPbBr$_3$ nanocrystals

To qualitatively explain the observed trends in lifetimes, the effective electron and hole masses for the investigated series of NPLs and for the bulk CsPbBr$_3$ were calculated by SOC-DFT. This was done by parabolic band fitting along the $\Gamma \rightarrow M$ direction of cubic the Brilluoin zone. Notice that, due to the employed cubic symmetry, no Rashba/Dresselhaus $k$-dependent band splitting was observed in the SOC-DFT band structures. The calculated effective masses along with the corresponding exciton reduced masses ($m_h * m_0 / (m_e + m_h)$) are reported in Table 5.1. As expected, the calculated effective masses and the exciton reduced mass both increase with quantum confinement, with the carriers effective masses remaining very close to each other along the series, suggesting almost perfect ambipolar transport in CsPbBr$_3$. The calculated reduced mass for the bulk ($\sim 0.09$) is consistent with available experimental estimates (0.12-0.13), although this value is likely underestimated, as SOC-DFT tends to underestimate the band-gap. According to the Kane model, the interband oscillator strength is $f_0 \approx m_0 / m_e$, meaning the exciton oscillator strength, decreases by increasing $m_e$. The exciton lifetime is inversely proportional to the radiative rate constant ($\tau \sim 1 / k_r$), which is equal to the oscillator strength times the square of the emitted energy ($E_g$), $\tau \propto E_g^2 f_0$, thus $\tau \propto 1 / (E_g^2 f_0)$. Based on the SOC-DFT calculated quantities (with $E_g$ scaled to match the experimental bulk value) a comparable $k_r$ for the $n=1$ and $n=\infty$ systems was estimated, in line with the similar values of measured PL lifetimes values.

Table 5.1. Spin orbit coupling density functional theory calculated band-gap ($E_g$) electron/hole effective masses and reduced masses, in units of $m_0$, where $m_0$ is the electron mass. The calculated band-gap values were rescaled by 2.09 eV to match the measured PL band-gap for the bulk.

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</table>
5.6 Understanding the anisotropic growth of CsPbBr$_3$ nanoplatelets†

As mentioned in section 5.2, the thickness of the CsPbBr$_3$ NPLs could be tuned by increasing the amount of HBr. Such level of control may be explained considering that the increased acidity of the solution, which aids in the protonation of OLAM, as also reported by Yuan et al. The protonated OLAM, in the form of oleylammonium, can compete with Cs$^+$ ions on the surface of the growing platelets, essentially slowing down the growth in the vertical dimension. This view is also in line with what recently observed on MAPbBr$_3$ NPLs, where the thickness control was achieved by tuning the acidity of the reaction bath by changing the concentration of OA.

To further prove this hypothesis, the formation of NPLs in the reported synthesis method by Protesescu et al. was studied. With this synthesis, a range of nanocubes, NSs and NPLs were prepared at various temperatures or by increasing the concentration of OA in the reaction mixture (from 25 mM to 0.5 M) as well as in the injection solution (see figure 5.5a and appendix table 5.1 and 5.2). The thickness of the NPLs could be reduced by decreasing the amount of Cs$^+$ or by increasing the amount of OA, as is evidenced by the absorbance and PL spectra of the samples (see also appendix 5.15). Similar to findings in the previous sections, the NPLs exhibited narrow PL peaks (figure 5.5b) and their structural anisotropy was evidenced by strong (hk0) reflections in their XRD patterns (figure 5.5c). The thickness of the NPLs could be tuned from 2.4 to 1.8 nm (figure 5.5d). When Cs$^+$ ions were not included in the injection solution, a white precipitate formed upon cooling the mixture. This precipitate consisted of micron-sized NSs whose crystal phase could be assigned to that of a hybrid organic-inorganic two-dimensional perovskite slab with the formula (RNH$_3$)$_2$PbBr$_4$, in which RNH$_3$ denotes the oleylammonium ion (figure 5.5e). Its PL spectrum is characterized by a peak at 3.09 eV, with a long tail to lower energies, which is in agreement with previous reports for two-dimensional perovskites.$^{20,21}$

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Shape control of CsPbBr$_3$ nanocrystals

Figure 5.5. Size and shape control of CsPbBr$_3$ nanocubes and nanoplatelets. (a) Sizes and shapes CsPbBr$_3$ nanocubes and nanoplatelets synthesized using various concentrations of OLAM and OA and different reaction temperatures (size distributions are represented as vertical bars across each symbol). (b) Absorbance (black solid line) and photoluminescence (blue dashed line) spectra, (c) XRD patterns and (d) TEM images of the depicted samples. (e) Size control obtained for different samples though increasing the amount of oleylammonium (compared to Cs$^+$) or by removing Cs$^+$ altogether.

To understand the shape control of cesium lead bromide under these conditions, the acid-base chemistry of OLAM and OA mixtures in non-polar solvents, without the presence of Cs$^+$ or PbBr$_2$ were studied. It is known that, in aprotic solvents, partially substituted nitrogen bases and carboxylic acids can form hydrogen bonded ionic salts, as shown in equation 5.1 and figure 5.6a.$^{25}$

\[
B + H - A \leftrightarrow BH^+ ... A^-
\]

The first hint of the formation of ammonium carboxylate salts can be observed by simply mixing OLAM (base, B) and OA (AH) at a 1: 1 mol. ratio at room temperature. This generates heat and leads to the formation of a gel (figure 5.6b), indicating that the ions mainly associate in their salt form under these conditions. To confirm the formation of this ammonium carboxylate, nuclear magnetic resonance (NMR) analysis was performed on OLAM and OA mixtures in toluene-d$_8$ (figure 5.6c). In the presence of an excess of OA, the $\alpha$-CH$_2$ resonances of OLAM (1) exhibit a downfield shift in the $^1$H-NMR spectrum, which
occurs as a consequence of the nitrogen protonation, while the α-CH₂ resonances of OA (2) show a downfield shift with the de-protonation of the carboxylic acid.

As previously mentioned, the formation of the ammonium carboxylate is exothermic, which implies, based on Le Chatelier’s principle, that the equilibrium will shift towards the reactants when the temperature is increased. This was also confirmed by ¹H-NMR spectroscopy. Notably, the α-CH₂ ¹H-NMR resonances of the protonated OLAM (1) and those of OA (2) shifted upfield when the temperature was increased, which confirms the de-protonation of the oleylammonium ions and the protonation of the carboxylic acid (figure 5.6d). These facts have important implications in the colloidal synthesis and phase stability of CsPbBr₃ NCs, as will be outlined in the next section. It is well established that aliphatic ammonium (RNH₃⁺) ions can compete with Cs⁺ ions for lattice sites and promote the formation of hybrid layered structures with the general formula [RNH₃]₂[CsPbBr₃]n-₁PbBr₄ (in which n denotes the number of PbBr₆ octahedra along the thickness). Indeed, these results in terms of shape control showed that NPLs could be obtained by increasing the [RNH₃⁺]/[Cs⁺] ratio. Following this concept, and accounting the temperature dependence of [RNH₃⁺], pure NPL samples could be synthesized even at high temperatures (190 °C) by simply adjusting the [Cs⁺] accordingly (see appendix table 5.2 and appendix 5.16).

Figure 5.6. NMR data of oleic acid and oleylamine mixtures (a) Structure of OLAM (OLAM) and OA in their acid base equilibrium (b) Photographs illustrating the formation of the oleylammonium oleate salt. (c) Selected regions of the ¹H-NMR spectra of OLAM and OA solutions in toluene-d8. (d) ¹H-NMR spectra of a mixture of OLAM and OA in toluene-d8, recorded at different temperatures in the range of 27 to 80 °C (upfield shifts are observed for the α-CH₂ ¹H-NMR resonances 1 and 2. All resonances identified are in agreement with previous works.³¹,³²
5.7 Further studies of the role of oleylamine in the synthesis of CsPbBr$_3$ nanocrystals

To further support the claim that addition of OLAM to the synthesis of CsPbBr$_3$ can lead to the formation of anisotropic growth, several OLAM free synthesis of CsPbBr$_3$ NCs were performed. Here, a modified version of Imran et al.’s synthesis of CsPbX$_3$ NCs was used, were lead acetate trihydrate (PbAc$_2$·3H$_2$O) and a benzoyl halide are used separately as precursors for Pb and X (Cl, Br, I) respectively. In this case, benzoyl bromide is injected into a solution containing cesium and lead oleate either in the presence or absence of alkyl amines. A major finding is that no basic (amines/ammonium) ligands are actually needed for this type of synthesis, as Pb and Cs salts are perfectly soluble in a mixture of ODE and OA alone, as they form the corresponding metal oleates. Once the bromide precursor is injected, CsPbBr$_3$ NCs are immediately formed. These NCs have cubic shapes, as can be seen by TEM (appendix 5.17a). The absence of platelets under these synthesis conditions is most thus due to the fact that alkyl carboxylates are not known to be involved in the formation of layered halide perovskites. The NCs have an overall good optical quality, as is attested by UV-Vis optical absorption and photoluminescence (PL) spectra (appendix 5.17b). Their XRD pattern conforms to the orthorhombic phase (appendix 5.17c). These NCs though suffered from long term stability, presumably due to the lack of amine/ammonium ligands passivating the surface, and had a low size tunability.

To overcome these problems, secondary aliphatic amines were introduced to the synthesis, under similar reaction conditions. As shown in figure 5.7a, the use of didodecylamine (DDDA) resulted in nearly monodisperse CsPbBr$_3$ nanocubes, with no sign of anisotropic growth. Furthermore, the reaction temperature could be lowered to 50 °C still yielding monodisperse nanocubes of 6.2 nm with XRD analysis still indicating an orthorhombic perovskite phase (figure 5.7b). These NCs have an orthorhombic crystal structure (figure 5.7c). Their optical properties match the CsPbBr$_3$ NCs synthesized with OLAM, and, especially for the smaller NCs exhibit clear absorption transitions (figure 5.7d). Furthermore, a strong increase of the concentration of OA, even when the concentration of OA was increased fourfold (from 3 mmol to up 12.6 mmol), which strongly promotes the formation of NPLs in the case of primary amines, did not result in the formation of NPLs (appendix 5.186). This thus indicates that the dialkylamines does not seem to promote the anisotropic growth of CsPbBr$_3$.

To compare these secondary amines to primary amines, several control syntheses were carried out by using primary and secondary amines separately under fully protonated conditions. In two series of experiments, two pairs of amines: OLAM versus dioctadecylamine, and dodecylamine versus didodecylamine are compared. OA was used as the carboxylic acid in all the syntheses, and all other reaction conditions were kept the same. These reaction were performed at a temperature of 100 °C, which is known to promote the synthesis of NSs and NPLs in the case of primary amines. Indeed, when the primary amines were used, the formation of CsPbBr$_3$ NSs and NPLs were observed, as was evidenced by TEM, optical absorbance and PL spectroscopies (figures 5.8a and c). However, monodisperse nanocubes were formed in the case of secondary amines (figures 5.8b and c).

To further study the effect of the dialkylamine, and its inability to form 2D perovskites, the synthesis of NCs in the absence of a Cs$^+$ precursor was performed. These conditions, when using primary amines, are known to promote the synthesis of a 2D hybrid layered phase with formula L$_2$PbBr$_4$, (L denotes a primary alkylammonium ligand), and similar as those discussed in chapter 5.6. Indeed, a white precipitate immediately forms after the injection of benzoyl bromide in case of dodecylamine. TEM, XRD, UV-Vis
absorption and PL analyses confirmed that the white precipitate corresponds to the 2D (dodecylammonium)$_2$PbBr$_4$ phase (figure 5.9). Under the same reaction conditions, but working with didodecylamine, no precipitate was collected and the reaction mixture remained clear and colorless.

![Figure 5.9. Two-dimensional single layered perovskites nanosheets. (a) TEM image of layered lead bromide perovskite, (b) XRD pattern, and (c) absorbance and PL spectra.](image)

5.8 Conclusions

In summary, this chapter presented a fast and easy synthesis method that delivers CsPbBr$_3$ NPLs with the control over the thickness down to only 3 to 5 monolayers. While the optical bandgap of the 2D semiconductor was extremely sensitive to confinement effects, the emissive dynamics were not sensitive to confinement, suggesting that such excitonic system have exciting properties. Furthermore, the Br$^-$ anions were be replaced with Cl$^-$ or I$^-$ anions, resulting in shape control over CsPbCl$_3$ and CsPbI$_3$ NPLs. Finally, through a careful study of the OA and OLAM mixtures, as well as the synthesis in which the primary amine was replaced with a secondary amine, it was demonstrated that the OLAM, in the form of oleylammonium, strongly promotes the anisotropic growth of CsPbBr$_3$ NCs. This is a direct result of the replacement of Cs$^+$ atoms with oleylammonium atoms in the LHP lattice, which blocks the growth in one dimension, resulting in the growth of 2D NPLs or NSs.

5.9 Acknowledgements

The following people contributed to this chapter: **Silvia Genaro Motti, Ajay Ram Srimath Kandada, Valerio D’Innocenzo** and **Annamaria Petrozza** performed the PLQY and time resolved PL measurements on the NPLs as discussed in section 5.2-5.5. **Edoardo Mosconi and Filippo Di Angelis** contributed though the DFT calculations and **Brett A. Kamino and Laura Miranda** provided the measurement performed on CsPbBr$_3$ thin films, as presented in section 5.5. **Giovanni Bertoni**, provided HRTEM measurements as presented in section 5.2 and 5.3 and **Mirko Prato** performed XPS measurements presented in section 5.2. For section 5.6, **Guilherme Almeida** performed the synthesis of the NCs and **Luca Goldoni** performed the NMR experiments. In section 5.6, **Muhammad Imran** performed the synthesis of the NCs and **Palvasha Ijaz** performed the PLQY. Finally, **Liberato Manna** provided the final supervision on all presented work.

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5.10 Experimental section

Chemicals. Lead(II) bromide (PbBr₂, 99.999% trace metals basis), lead acetate trihydrate (PbAc₂·3H₂O, 99.99%), cesium carbonate (Cs₂CO₃, reagentPlus, 99%), benzyol bromide (C₆H₅COBr, 97%), cesium bromide (CsBr, 99.9%), tetrabutylammonium chloride (TBACL, ≥97.0%), iodine (I₂, 99.99%), hydrobromic acid (HBr, 48 wt.% in H₂O, ≥99.99%), 1-octadecene (ODE, technical grade, 90%), oleylamine (OLAM, 70%), oleic acid (OA, 90%), dioctdecylamine (DODAm, 99%), acetone (AcO, anhydrous, 99.8%), ethanol (EtOH, ≥99.8), 2-Propanol, (IsoP, anhydrous, 99.5%), dimethyl sulfoxide (DMSO, ACS reagent ≥99.9%) and N,N-dimethylformamide (DMF, anhydrous, 99.8%) were purchased from Sigma-Aldrich. Didodecylamine (DDDAm, 97%), was purchased from TCI. Toluene (TOL, anhydrous, 99.8%) was bought from Carlo Erba reagents. All chemicals were used without any further purification.

Synthesis and purification of CsPbBr₃ NPLs. The CsPbBr₃ NPLs were synthesized by an adaptation of the synthesis described by Schmidt et al. Here, the MA-Br precursor was replaced with a Cs-oleate precursor, as reported by Protesescu et al., and only OLAM and OA were used as ligands. All syntheses were performed in air, at room temperature and with unpurified/non-degassed chemicals (OA, ODE, OLAM, acetone, toluene). In a solution of 1.25 ml ODE, 0.125 ml OA, 0.125 ml OLAM, a variable amount of HBr (in the 0 – 7.5 µl range) and 0.1 ml of Cs-OA precursor (0.1 M, 0.35 g Cs₂CO₃ degassed in 20 ml ODE and 1.25 ml OA at 150 °C), 0.2 ml of PbBr₂ precursor (0.4 M, 735 mg PbBr₂ in 5 ml DMF) were swiftly injected. Within seconds, the solution turned turbid white and after 10 seconds, 5 ml of acetone were swiftly added to quench the reaction (the solution turned turbid and its color evolved slowly to green). The NPLs were precipitated by centrifugation at 3500 rpm for 5 minutes and then redispersed in toluene, resulting in a blue emitting solution. The thickness of the NPL solution were dispersed in 1 mL of TOL, and different quantities of OLAM precursor (0.1 M, 0.35 g Cs₂CO₃ degassed in 20 ml ODE and 1.25 ml OA at 150 °C), 0.2 ml of PbBr₂ precursor (0.4 M, 735 mg PbBr₂ in 5 ml DMF) were swiftly injected. Within seconds, the solution turned turbid white and after 10 seconds, 5 ml of acetone were swiftly added to quench the reaction (the solution turned turbid and its color evolved slowly to green). The NPLs were precipitated by centrifugation at 3500 rpm for 5 minutes and then redispersed in toluene, resulting in a blue emitting solution. The thickness of the NPLs could be controlled by tuning the amount of HBr in the mixture: the higher the amount the thinner the NPLs.

Anion exchange reactions. These were performed as described in a previous work of ours, with the only difference being that all exchanges in the present experiments were carried out in air: 0.25 ml of crude CsPbBr₃ NPL solution were dispersed in 1 mL of TOL, and different quantities of OLAM-I (0.5 mmol of I₂ reacted with 0.250 mL of OLAM overnight and dissolved in 5.75 mL of TOL) or 0.17 M TBACL in TOL were swiftly injected. Within seconds, the solution turned turbid white and after 10 seconds, 5 ml of acetone were swiftly added to quench the reaction (the solution turned turbid and its color evolved slowly to green). The NPLs were precipitated by centrifugation at 3500 rpm for 5 minutes and then redispersed in toluene, resulting in a blue emitting solution. The thickness of the NPLs could be controlled by tuning the amount of HBr in the mixture: the higher the amount the thinner the NPLs.

Preparation of CsPbBr₃ thin films. The solution for deposition was prepared by mixing 2.00 g PbBr₂ and 1.16 g CsBr to 17.23 mL anhydrous DMSO in an inert environment. The solution was heated at 100 °C for 16 hours, or until it became optically clear. It was then filtered through a glass fiber syringe filter with an average pore size of 2 µm. Films were prepared on O₂-plasma cleaned glass substrates (under inert atmosphere) and were spun at 1000 rpm for 300 seconds. This procedure yielded clear yellow films, which were cured at 100 °C for 5 minutes in a forced air convection oven under N₂.

Synthesis of cube-shaped CsPbBr₃ nanocrystals (via Kovalenko synthesis). All NCs were synthesized in 6.0 mL solutions containing 72 mg of PbBr₂ (0.2 mmol, 33 mM) and various amounts of OLAM, OA and 1-octadecene (see appendix table 5.1). Mixtures were degassed for 15 minutes at 100 °C in order to obtain colorless solutions. Thereafter, the temperature was ramped to the desired value under a dry nitrogen flow and 0.5 ml of a 0.15 M Cs-oleate solution in 1-octadecene (which had previously been heated for 10 minutes on a hot-plate set at 200 °C) was swiftly injected. Unless otherwise stated, the solutions were immediately cooled after injection with an ice bath and diluted with 5 mL of toluene. The dispersions were centrifuged at 2500 rpm (for 3 minutes) and the NCs were re-dispersed in 2.0 mL of hexane. 4.0 and 4.8 nm nanocubes could not be separated by centrifugation alone (even at 14 krpm). In both these cases, 1 mL of OA was added to the dispersion (to assist the precipitation process) and the particles were then precipitated by adding methyl acetate until the
solution became slightly turbid. The NCs were separated by the same centrifugation and re-dispersion steps.

**Synthesis of CsPbBr$_3$ nanocubelets (via Kovalenko synthesis).** The general procedure was similar to that of the nanocubes, except for the following points (see appendix table 5.2). All syntheses of NPLs were conducted with [OLAM] = 0.25 M and [OA] = 0.50 M. Furthermore, the injection solution consisted of 0.5 mL of a solution of Cs-oleate in OA. Note that the 1.7 nm thick NPLs tend to transform into 2.3 nm thick NPLs upon dilution, which did not allow us to investigate their photoluminescence quantum yields. In order to obtain (RNH$_3)_2$PbBr$_4$ NSs, the concentration of Cs in the injection solution was set to 0.

**Synthesis of CsPbBr$_3$ nanocubes (via benzylbromide method).** 76 mg of lead(II) acetate trihydrate, 16 mg of cesium carbonate and 10 mL of octadecene were combined in a 25 mL 3-neck flask. The reaction mixture was degassed for 5 minutes at room temperature then for one hour at 115 °C. The ligand mixture containing 1.5 mL of pre dried OA, 1.25 mmol of dialkylamine dissolved in 1 mL of anhydrous toluene was rapidly injected under nitrogen. After the complete dissolution of the metal precursors, the temperature of the reaction mixture was decreased to 80 °C. 50µL of a benzoyl bromide precursor diluted in 500 µL of dried ODE was then injected into the mixture. The mixture was cooled down after 15 seconds by using a water bath. Subsequently, 20 mL of an ethyl acetate and toluene mixture (with ratio of 6:1) was added into the crude solution to destabilize the colloids, and the NCs were collected by centrifugation at 9000 rpm for 10 minutes. Finally, the supernatant was discarded and the precipitate was redispersed in toluene.

**Transmission Electron Microscopy (TEM)** Conventional TEM images were acquired on a JEOL JEM-1011 microscope equipped with a thermionic gun at 100 kV accelerating voltage. High-resolution TEM (HRTEM) imaging was performed on a JEOL JEM-2200FS microscope equipped with a Schottky gun operated at an accelerating voltage of 80 kV, a CEOS spherical aberration corrector in objective lens enabling a spatial resolution of 0.9 Å, and an in column Ω-filter. The chemical composition was determined by energy dispersive X-ray spectroscopy (EDS) performed in high angle annular dark field scanning TEM (HAADF-STEM) mode with a 1.0 nm electron probe and a Bruker Quantax 400 system with a 60 mm$^2$ XFlash 6T silicon drift detector, and using the Cliff-Lorimer method for quantification of the elements. An analytical double tilt holder equipped with a low background beryllium tip was used in order to reduce spurious signal from the grid and holder. The samples were prepared by drop casting diluted NPLs colloidal suspensions onto 200 mesh carbon-coated copper grids for conventional TEM imaging, and 400 mesh ultrathin carbon-coated copper grids for HRTEM imaging, respectively.

**Powder X-ray Diffraction (XRD) analysis.** Accurate determination of the lattice parameter was carried out by measuring the samples on a Rigaku SmartLab X-ray diffractometer, equipped with a 9 kW Cu Kα rotating anode (operating at 40 kV and 150 mA) and DTeX Ultra 1D detector. The diffraction patterns were collected in Bragg-Brentano parafocusing geometry over a 2θ angular range of 10°- 100°, with a step size of 0.01°. XRD data analysis was performed using HighScore 4.1 software. The evolution of the NPLs sample after an annealing treatment at different temperatures was monitored using a PANalytical Empyrean X-ray diffractometer equipped with a 1.8 kW Cu Kα ceramic X-ray tube, PIXcel3D 2x2 area detector and operating at 45 kV and 40 mA. The diffraction patterns were collected in air at room temperature using Parallel-Beam (PB) geometry and symmetric reflection mode. All XRD samples were prepared by drop casting a concentrated solution on a zero diffraction silicon wafer. The annealing was performed on drop cast samples, heated on a hotplate in a glovebox.

**Optical Absorption Spectroscopy.** The spectra were taken on a Varian Cary 5000 UV–vis–NIR spectrophotometer. Samples were prepared by diluting the crude NPLs solutions in TOL (20 µL in 1 mL) in 1 cm path length quartz cuvettes.

**Time-resolved Photoluminescence (PL).** Time-resolved PL measurements were performed using a femtosecond laser source and a streak camera detection system (Hamamatsu C5680). The output of a tunable Ti: Sapphire laser (Coherent Chameleon Ultra II, temporal and spectral bandwidths
of ~140 fs and ~5 nm, respectively) was used to pump a second harmonic stage (based on BBO) to generate the pump pulses for the experiment. For the experiments with the thin films the pump wavelength was tuned to 400 nm, while for the colloidal suspensions of NPLs/NCs it was tuned to 480 nm. The thin film samples were mounted in a chamber under vacuum and the colloidal samples were measured in toluene solution in quartz cuvettes. The photoluminescence was collected and focused onto a spectrometer coupled to the detection system, and time-resolved with a linear voltage sweep module. The measurements were performed using either the original repetition rate of the laser output, 80 MHz, or at 4 MHz, obtained through the use of an acousto-optical modulating pulse picker (APE Pulse Select).

**PL Quantum Yield (PLQY).** A monochromatic laser diode centered at 405 nm was used as the pump and it was coupled into an integrating sphere (Labsphere) where a quartz cuvette containing the sample was placed. The emitted light was then collected from the sphere with an optical fiber coupled to a spectrometer (Ocean Optics MAYA Pro). PLQY was calculated according to the method described by de Mello Donegá et al. For evaluating the relative PLQY, the excitation was achieved using pulses of ~100 fs duration and central wavelength of 400 nm at 250 kHz. The pulses were provided by a Ti:Sapphire based regenerative amplifier (Coherent RegA 9000) operating at 250KHz seeded by a mode-locked Ti:Sapphire oscillator (Coherent Micra-18) operating at 80 MHz. The beam was focused onto a BBO crystal generating second harmonic at 400 nm and pulses of ~100 fs duration. The PL was collected perpendicular to the excitation line and focused into a fiber coupled to a spectrometer (Ocean Optics Maya Pro).

**Computational Details.** To simulate the CsPbBr$_3$ perovskite NPLs, a defined series of 2 × 2 periodic slabs cut from the optimized bulk cubic CsPbBr$_3$ crystal structure was used, which expose CsBr-terminated surfaces. The thickness of the slabs was varied from 1 inner layer to 17 inner layers, plus two symmetric capping layers on both NPLs sides. The employed periodic cell dimensions were $a = b = 11.802$ Å, corresponding to twice the experimental $a = b$ cell parameters. For all slabs a ~10 Å of vacuum was added along the non-periodic c direction. The choice of using periodic slabs is justified by the large lateral dimensions of the NPLs compared to their vertical size. To lift out the possible effects due to relaxation of the smaller slabs, all slabs were built using the geometry optimized for the bulk system. All the calculations were carried out with the PWscf code, as implemented in the Quantum Espresso package along with the GGA-PBE functional at Γ point of the Brillouin zone. For all calculations, electron-ion interactions were described by ultrasoft pseudopotentials with electrons from Cs 6s; Br 4s, 4p; Pb 6s, 6p, 5d shells explicitly included in the calculations. Both scalar relativistic and spin-orbit coupling calculations were performed. Plane-wave basis set cutoffs for the smooth part of the wave functions and the augmented density were 25 and 200 Ry, respectively.

**Nuclear magnetic resonance.** All spectra were acquired on a Bruker Avance III 400 MHz spectrometer, equipped with a Broad Band Inverse probe (BBI). Before each acquisition, automatic routines optimized the matching, tuning, resolution and 90 degree pulse calculation on $^1$H nucleus. $^1$H-NMR: 16 transients were accumulated, without steady state scans, at 300 K, over a spectral width of 20.55 ppm (offset at 6.175 ppm), at a fixed receiver gain (64), using 30 s of inter pulse delays. $^1$H-NMR at different temperatures (from 300 to 353 K): 16 transients were accumulated, with 4 steady state scans, over a spectral width of 20.55 ppm (offset at 6.175 ppm), at a fixed receiver gain (64), using 2.5 s of relaxation delay. $^{13}$C-NMR: 10240 transients were accumulated after a 30 degree pulse and 4 steady state scans, at 300 K, over a spectral width of 239 ppm (offset at 100 ppm), using 2.2 s of inter pulse delays. The receiver was automatically optimized. All NMR chemical shifts were referred to 7.09 ppm at $^1$H and 129.24 at $^{13}$C.

**References**


Appendices

Appendix note 5.1: For thin films, the excitation density represents average number of photo-generated carriers in unit volume and can be calculated as:

\[ n_p(P_{cw}) = \frac{P_{cw} \cdot \lambda_y}{RR \cdot h c \cdot A_p \cdot d(\lambda_y)} \]

Where \( P_{cw} \) is the pump power, \( \lambda_y \) is the pump wavelength, \( RR \) is the repetition rate, \( A_p \) is the spot size on sample and \( d(\lambda_y) \) is the penetration depth, which can be evaluated as \( d(\lambda_y) = d/\alpha(\lambda_y) \), where \( d \) is the sample thickness and \( \alpha(\lambda_y) \) is the absorbance of the sample at the pump wavelength. In the trPL data presented for CsPbBr\(_3\) thin films, the pump wavelength was 480 nm, \( RR=80\text{MHz} \), the spot size was around 50 \( \mu m \), and the sample optical density was around 0.5. The pump powers varied from 50 \( \mu W \) to 40 mW, covering a range of excitation densities from \( 10^{15} \) to \( 10^{18} \text{ cm}^{-3} \).

In the case of NC suspension, it is essential to estimate average number of excitations on each NC, rather than the excitations per unit volume. Since the NCs do not show any sign of strong confinement, one can assume that the value of absorptivity \( (\alpha \text{ cm}^{-1}) \) at 400 nm (corresponding to bulk carrier absorption) is similar to that of the film, which can be evaluated around \( 10^4 \text{ cm}^{-1} \). One can then estimate the average number of carriers on each nanocrystal as \( \sigma \Phi_{\text{photon}} \), where \( \sigma = \alpha V^3 \) \((V \text{ is the volume of the NC})\) is the cross-section and \( \Phi_{\text{photon}} \) is the photon flux. For the range of pump fluences used, it was evaluated that the average number of photo-excitations on each NC is much less than one (between 0.01 and 1), a regime that is comparable to the low-excitation regime of the thin films (> \( 10^{16} \text{ cm}^{-3} \)), where there are no strong multi-particle interactions.

Appendix table 5.1 Synthesis conditions used to prepare the CsPbBr\(_3\) nanocubes. Photoluminescence (PL) properties (\( \mu \) - mean size; \( \sigma \) – standard deviation; \( T \) – temperature; \( \lambda \) – photon energy at PL maximum; FWHM – PL full width at half maximum; - data not collected). All syntheses were immediately quenched upon injection of 0.5 mL of Cs-oleate (0.15 M, in 1-octadecene) except the > 100 sample where 2 mL of Cs-precursor was used and the growth time was increased to 60 s.

<table>
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Appendix table 5.2. Synthesis conditions used to prepare CsPbBr$_3$ nanoplatelets (NPLs) and (RNH$_3$)$_2$PbBr$_4$ nanosheets (NSs, 1 ML). Photoluminescence (PL) properties (T: synthesis temperature; [Cs]: concentration of Cs$^+$ in injection solution; hv: photon energy at PL maximum; FWHM: PL full width at half maximum; φ: PL quantum yield; τ: PL lifetime; “-”: data not collected). *formed during cooldown.

<table>
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<th>Photoluminescence</th>
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Appendix 5.1. Optical spectra of NPLs growth solution before and after injection of acetone. (a) PL measurement over time during the growth of NPLs. Before acetone injection, the precursor solution was characterized by a broad emission peak centered at approx. 3.2 - 3.3 eV. Immediately after acetone injection, a narrower peak appeared at around 2.95 eV. Within seconds, this peak further red-shifted and narrowed (indicating the nucleation and growth of CsPbBr$_3$ NPLs), and finally settled to an energy value that depended on the amount of HBr added. (b) PL spectra collected on different precursor mixtures, all characterized by a broad emission around 3.2 eV, and with no PL at the energy value seen for CsPbBr$_3$ NPLs.
Appendix 5.2. Optical spectra of NPLs growth (a) Absorption spectra of CsPbBr$_3$ NPLs obtained with different times between PbBr$_2$ and acetone injections, in the 5 seconds - 2 minutes range. (b) TEM image of NPLs obtained after 240s between the injection of PbBr$_2$ and acetone.

Appendix 5.3. Result of reaction with different solvents. (a) Comparison of PL spectra collected on CsPbBr$_3$ nanocrystals solutions obtained after using ethanol, isopropanol or acetone as triggers. (b) TEM image of CsPbBr$_3$ NCs obtained with EtOH instead of acetone.

Appendix 5.4. Analysis of lead NCs formed after e-beam irradiation. (a) Dark-STEM showing high density lead particles. (c) HRTEM of a lead particle, formed after electron irradiation in the TEM, with the lattice parameters compatible with metallic lead. (c) EDS analysis of the particle indicated only the presence of lead (the Cu peaks are from the copper support grid).
Chapter V

Appendix 5.5. Low angle XRD showing reflections of stacked NPLs.

Appendix 5.6. Evolution of XRD patterns of NPLs with annealing temperature. (a) When going from room temperature (RT) up to 150 °C, the diffraction peaks shifted towards higher angles, indicating a progressive shrinking of the unit cell. (b) Interestingly, the peak positions after the annealing at 150 °C closely matched the positions observed for cube-shaped CsPbBr$_3$ NCs. Annealing to higher temperatures induced a phase change in the material, as shown in the example of the annealing performed at 200 °C (orange pattern).

Appendix 5.7. More TEM images of CsPbBr$_3$ NPLs. 4 ML CsPbBr$_3$ NPLs from (a) top view and (b) side view.
Appendix 5.8. Thickness distribution of the 3 ML, 4 ML and 5 ML NPLs

Appendix 5.9. XRD patterns of 3 ML and 5 ML NPLs.

Appendix 5.10. Partial degradation of the 5 ML NPLs, and formation of bulk CsPbBr$_3$ after 1 week in air.
Appendix 5.11. PL and absorption spectra of the exchanged 5 ML NPLs with Cl$^-$ and I$^-$.

Appendix 5.12. TEM image of cubic CsPbBr$_3$ NCs. The scale bar corresponds to 50 nm.

Appendix 5.13. Supplementary data for CsPbBr$_3$ films. (a) SEM of CsPbBr$_3$ thin film and (b) intensity dependent PL dynamics.
Appendix 5.14. Additional PL data for CsPbBr$_3$ NPLs. (a) Relative PLQY of one sample of NPLs before and after a tenfold dilution. (b) Pump wavelength for both the experiments was at 400 nm with a fluence of about 100 nJ/cm$^2$.

Appendix 5.15. Effect of oleic acid concentration on the size and shape of CsPbBr$_3$ nanocrystals synthesized at 190 °C. (a) Size-distribution histograms and (b) optical spectra of nanocrystals synthesized with increasing concentrations of oleic acid ([OA] = 0.25, 0.50 and 1.00 M, [OLAM] = 0.25 M). (c) TEM image of nanocrystals synthesized with [OA] = 1.00M and [OLAM] = 0.25M. Note the presence of nanoplatelets.

Appendix 5.16. Absorbance and photoluminescence spectra of nanoplatelets synthesized at (a) 90 and (b) 190 °C.
Appendix 5.17. Amine free synthesis of CsPbBr$_3$ NCs. (a) TEM image (b) XRD pattern and (c) UV-Vis absorption and PL spectra. Bulk pattern for CsPbBr$_3$ in b) has Reference code 96-451-0746. Syntheses was carried out as follows: the amount of each precursor used was 0.2mmol of PbAc$_2$·3H$_2$O, 0.05mmol of Cs$_2$CO$_3$, 4.75mmol of OA; the reaction temperature was 80 °C; 50 µl of benzoyl bromide was diluted in 0.5ml of octadecene; the reaction time was 15 seconds.

App 5.18. TEM image of CsPbBr$_3$ NCs synthesized with different amount of OA. CsPbBr$_3$ NCs synthesized using 1.25 mmol of DDDAm and various concentrations of oleic acid, at an injection temperature of 80 °C.
Chapter IV

Alloying CsPbX₃ nanocrystals with Mn²⁺
Chapter VI: Alloying CsPbX₃ nanocrystals with Mn²⁺

Abstract: One of the most profound effects of a lead halide perovskite’s rather ionic lattice, is its ability to easily form complex alloys. In this chapter, the compositional tuning of lead halide perovskite nanocrystals will be discussed. One specific type of alloying involves introducing Mn²⁺ to the lead halide perovskite lattice. In the case of CsPbCl₃, this results in a strongly down-converted Mn²⁺ emission. Moreover, the introduction of Mn²⁺ to CsPbI₃ nanocrystals, which are still limited in terms of their potential use due to their phase instability, increases their phase stability, while maintaining essentially the same optical features and crystal structure as the parent α-CsPbI₃ system. This chapter will examine this type of alloying and how it can result in more stable red emitting lead halide perovskite nanocrystals.

6.1 Introduction

Among the LHP NCs, the CsPbBr₃ NCs are the most studied and understood, having PLQYs close to 100%¹ and a wide range of applications.²⁻⁵ On the other hand, CsPbI₃ NCs, which have a band gap of around 1.8 eV and a larger exitonic Bohr radius (6 nm for CsPbI₃ compared to 3.5 nm for CsPbBr₃) are, in principle, more appealing than CsPbBr₃ NCs for tunable LEDs, lasers, and solar cells, but they are significantly less stable.⁶⁻⁷ In the cubic CsPbI₃ phase (α-CsPbI₃), the Cs⁺ ions are not large enough to stabilize the cubic framework of corner sharing PbI₆⁻ octahedra, and a transition to the orthorhombic phase (δ-CsPbI₃) is seen below 315 °C.⁷ The band gap of δ-CsPbI₃ is larger than that of α-CsPbI₃ (2.25 vs. 1.73 eV) and is indirect, which makes it less suitable for many optoelectronic applications. Various methods have been reported on how to stabilize the α phase both in NCs and in thin films, for instance by partially replacing I⁻ with Br⁻ or Cl⁻, by incorporating large organic cations, or by surface treatments with different organic molecules.⁶,⁸⁻¹¹ Although Mn²⁺ has mainly been studied for its Stokes shifted emission in CsPbCl₃ NCs, leading to strongly red emissive CsPbCl₃:Mn²⁺ NCs,¹²⁻¹⁶ recent work has shown that Mn²⁺ alloying in CsPbX₃ NCs can help to stabilize their cubic phase.¹⁷

In this chapter, the alloying of CsPbX₃ NCs with Mn²⁺ is presented. In the case of CsPbCl₃ NCs, as discussed in section 6.2, this results in strongly down-converted, broad PL. In the case of the unstable α-CsPbI₃ phase, as presented in sections 5.3 and 5.4, the alloying it with Mn²⁺ does not result in any major changes in optical properties which is also confirmed by hybrid DFT) calculations. On the other hand, the alloyed CsPbₓMn₁₋ₓI₃ NCs remain stable and brightly luminescent for up to over a month, both in solution and as films stored in air, which is significantly longer compared to the non-alloyed CsPbI₃ NCs. Similar to the replacement of I⁻ ions with Br⁻, the stabilization through the replacement of Pb²⁺ with Mn²⁺ stems from a small decrease in the lattice parameters, combined with an increase in the cohesive energy.

6.2 Synthesis and optical properties of Mn-doped CsPbCl₃ nanocrystals †

Monodisperse Mn²⁺ doped CsPbCl₃ NCs were synthesized as described by Protesescu et al.,¹⁸ with addition of MnCl₂ (see experimental section). Briefly, 0.1 mmol of PbCl₂ and 0.1 mmol of MnCl₂, 5 mL octadecene, 0.5 mL OA and 0.5 mL OLAM were loaded in a 25 mL 3-neck flask and dried under vacuum for 1 h at 120 °C. After degassing, the temperature was raised to 180 °C and 0.4 mL of previously synthesized Cs-oleate (0.4 g Cs₂CO₃ degassed in 15 mL octadecene and 1.75 mL OA at 150 °C) was swiftly injected. 30 seconds after the injection, the NC solution was quickly cooled down to room temperature with an ice bath (see experimental section 6.6). The NCs were purified via centrifugation (at 3000 rpm for 30 minutes) twice, followed by redispersion in toluene.

A schematic depiction of crystal structure of a CsPbX₃ perovskite doped with 5% Mn not considering local changes in crystal structure, is reported in the inset of figure 6.1a, showing a Mn²⁺ ion in a substitutional Pb site with essentially identical octahedral coordination with six halide atoms. As shown in figure 6.1b, the Mn²⁺ alloyed CsPbCl₃ NCs are monodisperse and have an average size of size of 8.6 ± 0.6 nm. ICP on washed NCs indicated a 3.9% Mn doping. The XRD pattern reported in figure 6.1c indicates a match with cubic CsPbCl₃, in agreement with previous studies on Mn-doped CsPbCl₃ NCs.¹⁴,¹⁹ Figure 6.1d shows the optical absorption and PL spectrum of the NCs with the characteristic sharp absorption edge at ~395 nm and the respective narrow-line BE-PL peaked at ~405 nm accounting for ~20% of the total emission. The remaining 80% of emitted photons are due to the ¹⁴T₁→⁶A₁ optical transition of the Mn²⁺ dopants, giving rise to the characteristic broad peak at ~590 nm (hereafter indicated as Mn²⁺-PL), resulting in a very large ~200 nm (~1 eV) Stokes shift from the absorption edge of the CsPbCl₃ host NC.¹⁴,¹⁹⁻²⁰ The PL quantum yield, as measured with an integrating sphere is Φ_{PL,BE}= 5±1% for the BE emission and Φ_{PL,Mn}= 10±2% for the Mn²⁺-PL, in agreement with previous reports.¹⁹ Importantly, the Mn²⁺-PL is nearly completely unaffected by absorption by the NC host, as emphasized in the inset of figure 1f, where the enlargement of the absorption spectrum for absorption coefficient between 0 cm⁻¹ and 5×10⁻² cm⁻¹ is reported. On this expanded scale, it becomes clear that, in agreement with what observed for Mn-doped ZnSe NCs,²¹ the absorption tail on the high energy portion of the Mn²⁺-PL peak and the small band at ~630 nm, respectively due to the NC host and to intracenter Mn²⁺ transitions, are significantly lower than the absorption contribution due to the vibrational modes of the C–H bonds of OA and OLAM ligands²² between 650 nm and 900 nm, which, at this NC concentration (0.08 wt%) are still below 3×10⁻² cm⁻¹.

Figure. 6.1 Structural and optical properties of Mn\(^{2+}\)-alloyed CsPbCl\(_3\) nanocrystals. (a) Cubic perovskite CsPbCl\(_3\) crystal structure with Mn\(^{2+}\) partially replacing Pb\(^{2+}\). (b) TEM image, with an average side length of 8.6 ± 0.6 nm. (c) X-ray diffraction pattern of Mn:CsPbBr\(_3\) perovskite NCs at room temperature compared to the XRD pattern of bulk cubic CsPbCl\(_3\) perovskite (reference pattern 98-020-1251). (d) Optical absorption (in grey) and photoluminescence (PL) spectra of Mn:CsPbCl\(_3\) NCs (4% doping level) under 390 nm excitation in toluene solution. Schematic representation shows the three-level manganese-doped CsPbCl\(_3\) NC with the band edge (BE) and Mn\(^{2+}\) photoluminescence (PL) following UV excitation (purple arrow). The band edge (BE) and Mn-related PL bands are highlighted by blue and red shading respectively. A photograph of the solution under 365 nm excitation highlights the dominant yellow color due to Mn\(^{2+}\) emission with respect to BE-PL.

6.3 Synthesis of alloyed CsPb\(_x\)Mn\(_{1-x}\)I\(_3\) perovskite Nanocrystals

CsPb\(_x\)Mn\(_{1-x}\)I\(_3\) NCs (figure 6.2a) were synthesized similarly to previous works,\(^{18}\) with some minor changes (the addition of MnI\(_2\) to introduce Mn\(^{2+}\), see the experimental chapter 6.7). As depicted in figure 6.2a, these NCs are about 12 ± 1.7 nm in size. Although the Mn to Pb ratio was initially determined to be 0.44:0.56 (based on ICP-EOP), energy-dispersive X-ray spectroscopy (EDX) indicated a lower ratio of 0.09:0.91, matching previous reports stating that excess Mn\(^{2+}\) precursor complexes are difficult to remove from NC solutions.\(^{14}\) These relatively low levels of incorporation of Mn\(^{2+}\) compared to the high feed ratios match those previously reported for CsPbCl\(_3\), and presumably stem from the fast nucleation of CsPbX\(_3\),\(^{23}\) thus reducing the incorporation of Mn\(^{2+}\). Nonetheless, this high ratio of Mn:Pb indicates the formation of an alloy rather than Mn doping, as doping in NCs normally refers only to a few dopants per NCs, with doping percentages up till about 1%.\(^{24}\) It must be noted that higher feed ratios of Mn lead to the precipitation of PbI\(_2\), as has been reported by others, thus precluding the preparation of alloy NCs with higher Mn:Pb ratios with the current synthesis method. Neither the absorption nor the photoluminescence (PL) of the CsPb\(_x\)Mn\(_{1-x}\)I\(_3\) NCs differed much from those of the pure CsPbI\(_3\) NCs (figure 6.2c), in analogy with previous reports by others on CsPbBr\(_3\).\(^{12-13,17}\) Here, both the CsPbI\(_3\) and the CsPb\(_x\)Mn\(_{1-x}\)I\(_3\) NCs were emitting at 680 nm with a PL FWHM of about 40 nm, similar to previous
Alloying CsPbX$_3$ nanocrystals with Mn$^{2+}$

reports. Furthermore, as shown in figure 6.2d, both the PLQY and the PL lifetime in the CsPbI$_3$ sample and in the alloy one were similar (74% for CsPbI$_3$ and 82% for CsPb$_x$Mn$_{1-x}$I$_3$), and matched those previously reported for CsPbI$_3$ NCs.

![Figure 6.2](image.png)

**Figure 6.2.** Overview of optical and structural properties of CsPb$_x$Mn$_{1-x}$I$_3$ NCs. (a) Crystal structure of cubic perovskite CsPbI$_3$ with 1 out 8 Pb$^{2+}$ replaced with Mn$^{2+}$. (b) TEM and HRTEM image of CsPb$_x$Mn$_{1-x}$I$_3$ NCs. (c) absorption and photo luminescence compared with pure CsPbI$_3$ NCs. (d) Lifetimes and PLQYs of CsPbI$_3$ and CsPb$_x$Mn$_{1-x}$I$_3$ NCs.

According to the XRD patterns of figure 6.3a and b, the CsPb$_x$Mn$_{1-x}$I$_3$ NCs only have a slightly smaller unit cell than the pure CsPbI$_3$ NCs, with no other structural differences. This is in accordance with previous reports on CsPb$_x$Mn$_{1-x}$Cl$_3$, where relatively high incorporations only exhibit a small change on the lattice parameters. The long term-stability of CsPb$_x$Mn$_{1-x}$I$_3$ NCs is reported in figure 6.3c and d: drop-cast films of CsPbI$_3$ and CsPb$_x$Mn$_{1-x}$I$_3$ NCs were stored under ambient conditions (in a drawer, at about 25-30 degrees), and their XRD patterns were measured over the course of a month. The CsPbI$_3$ film started to degrade to δ-CsPbI$_3$ within a day, with a complete transition within 5 days. However, the CsPb$_x$Mn$_{1-x}$I$_3$ film did not show any visible degradation during the first two weeks and it was still mainly in the α-phase after one month. Similarly, a solution of CsPbI$_3$ NCs in toluene, stored in a nitrogen glovebox, completely degraded over 1 month, as it turned white/yellow and did not show any PL (appendix 6.2). A solution of CsPb$_x$Mn$_{1-x}$I$_3$ NCs, stored under the same conditions, was still red and strongly fluorescent. Notably interesting, CsPb$_x$Mn$_{1-x}$I$_3$ NCs also were highly luminescent and stable without separation from the reaction solvent, as unwashed CsPb$_x$Mn$_{1-x}$I$_3$ NCs after 3 days still were brightly luminescent with a PLQY of 60 ± 5%.
Figure 6.3. XRD data from CsPbI$_3$ and CsPb$_x$Mn$_{1-x}$I$_3$ nanocrystals. (a) XRD patterns of CsPbI$_3$ and CsPb$_x$Mn$_{1-x}$I$_3$ NCs. matching the perovskite phase of CsPbI$_3$ (b) Small decrease of lattice parameters from the CsPb$_x$Mn$_{1-x}$I$_3$ NCs. Time stability of (c) CsPbI$_3$ and (d) CsPb$_x$Mn$_{1-x}$I$_3$ NCs showing large increase of stability for the CsPb$_x$Mn$_{1-x}$I$_3$ NCs. XRD reference patterns correspond to 98-018-1288 (α-CsPbI) and 98-016-1480 (δ-CsPbI$_3$) respectively.

6.4 DFT calculations on the optical properties and stability of CsPb$_x$Mn$_{1-x}$I$_3$ nanocrystals

To corroborate the stabilizing effect of Mn$^{2+}$ and the unaltered optical properties of CsPb$_x$Mn$_{1-x}$I$_3$, DFT calculations were performed. Starting from the α-cubic phase of CsPbI$_3$, a 2x2x2 supercell was built by fixing the cell parameter to the experimental value, i.e. 6.289 Å. For CsPb$_x$Mn$_{1-x}$I$_3$, two configurations with a Pb:Mn ratio of 7:1 and 1:1 were obtained by replacing one Pb or four Pb atoms respectively with Mn atoms (see experimental section and figure 6.4). Such configurations correspond to Mn-doping of 12% and 50% respectively. Two geometry optimizations were performed: i) the relaxation of the ion positions by fixing the cell parameter to the experimental value; and ii) the relaxation of both the ion positions and the cubic cell parameter. All relaxations were performed by using the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional. The equilibrium lattice parameters, volume, cohesive energies and band gaps of the three systems are shown in appendix table 6.1 for both ions and total relaxations. Upon variable cell relaxations, the cell parameter of the CsPbI$_3$ supercell increased from 12.58 Å (twice the cubic lattice size) to 12.79 Å, while that of the alloyed CsPb$_x$Mn$_{1-x}$I$_3$ supercells decreased to 12.67 and 12.22 Å the system with one and 4 Mn replacing Pb atoms, respectively. Hence, the calculations predict a 1% lattice contraction going from CsPbI$_3$ to CsPb$_{0.88}$Mn$_{0.12}$I$_3$, which corresponds with the observed lattice contracting with XRD (1% contraction for CsPb$_{0.91}$Mn$_{0.09}$I$_3$). The cell contraction in the Pb/Mn alloy systems is due to the shortening of the metal-I bonds (from 3.14 Å for Pb-I to 2.97 Å for Mn-I). Most importantly, the ion relaxation preserves the octahedral coordination...
Alloying CsPbX$_3$ nanocrystals with Mn$^{2+}$

of the Mn ions in the Pb sites. The calculated cohesive energy shows a progressive stabilization of the CsPbI$_3$ perovskite upon Mn-alloying toward a value of 0.13 eV/formula unit (f.u.) (0.09 eV/f.u.) in CsPb$_{0.5}$Mn$_{0.5}$I$_3$ for the relaxed cell (fixed cell) optimizations. It should be noted that, besides the stabilization reported by the analysis of the cohesive energies, the configurational entropy further stabilizes the Pb/Mn alloy phase, while compensation effects by native defects on the other sub lattices are expected to play only a marginal role due to the isovalent substitutional doping.

In order to investigate the effects of the partial replacement of Pb with Mn on the electronic structure, the projected density of states (PDOS) on the atomic orbitals of the pristine CsPbI$_3$ and CsPb$_{0.88}$Mn$_{0.12}$I$_3$ systems were calculated at the HSE-06 level by including spin-orbit corrections (SOC). In figure 6.4, the PDOS of α-CsPbI$_3$ and CsPb$_{0.88}$Mn$_{0.12}$I$_3$ supercells are compared (see appendix 6.3 for calculation at PBE level without SOC, and appendix 6.4 for Cs$_2$PbMnI$_6$ with SOC). The calculated band gap of CsPbI$_3$ is 1.01 eV. The underestimation of the experimental band gap (~1.70 eV), is possibly due to neglect of thermal fluctuations which were shown to raise the band gap of cubic MAPbI$_3$ by ca. 0.5 eV.$^{29}$ In α-CsPbI$_3$, the valence and conduction bands are dominated by the p and s orbitals of I and Pb, respectively. The replacement of Pb$^{2+}$ with Mn$^{2+}$ introduces localized electronic states at ~6.5 eV below the VBM and between 4-6 eV above the VBM. The PDOS projected on the atomic orbitals (see appendix 6.5) shows that such states arise from the d orbitals of Mn, while negligible contributions of the Mn orbitals to the band edges are reported. The limited variation of the electronic structures at the band edges is in good agreement with experiments, which report no changes in the PL of the alloy system compared to the pristine perovskite.

![Figure 6.4 DFT calculations on CsPbI$_3$ and CsPb$_{0.88}$Mn$_{0.12}$I$_3$. Models of relaxed α-CsPbI$_3$ (top panel) and CsPb$_{0.88}$Mn$_{0.12}$I$_3$, and respective DFT projected densities of states (bottom panel) indicating no influential changes due to the incorporation of Mn$^{2+}$.](image)
6.5 Conclusions

This chapter has discussed alloying CsPbCl\textsubscript{3} and CsPbI\textsubscript{3} NCs with Mn\textsuperscript{2+}. It was shown that, in the case of CsPbCl\textsubscript{3}, the Mn\textsuperscript{2+} 4T\textsubscript{1}→6A\textsubscript{1} optical transition gives rise to the characteristic broad emission peak at ~590 nm. Alloying CsPbI\textsubscript{3} NCs with Mn\textsuperscript{2+} resulted in no changes in the optical features, but the alloyed NCs are much more stable than pure CsPbI\textsubscript{3} NCs. These preliminary results require further investigation, but calculations indicate that significantly higher Mn:Pb ratios, almost up to 1:1 (which is the same as that of Cs\textsubscript{2}PbMnI\textsubscript{6}) should be obtainable; they should have a strongly stabilized cubic perovskite phase, yet their properties should be similar to those of pure CsPbI\textsubscript{3}. Moreover, the replacement of Pb with Mn\textsuperscript{2+} can be seen as a way to partially mitigate the toxicity of these materials. Finally, novel synthesis approaches should be explored, like cation exchange or by insertion reactions with MnI\textsubscript{2} into Cs\textsubscript{4}PbI\textsubscript{6} NCs, so as to avoid the fast nucleation of CsPbI\textsubscript{3} when it is alloyed with Mn\textsuperscript{2+}.\textsuperscript{31-32}

6.6 Acknowledgements

The following people contributed to this chapter: Sungwook Park helped with the synthesis of CsPbCl\textsubscript{3}:Mn\textsuperscript{2+} NCs. Francesco Meinardi, Francesco, Michele Mauri and Sergio Brovelli conducted the optical analysis on the CsPbCl\textsubscript{3}:Mn\textsuperscript{2+} NCs. Daniele Meggiolaro and Filippo Di Angelis contributed though the DFT calculations as presented in section 6.4. Zhiya Dang, provided HRTEM measurements and elemental analysis as presented in section 6.2 and 6.3. Finally, Liberato Manna provided the final supervision on all presented work.

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6.7 Experimental section

Chemicals. Lead(II) iodide (PbI\textsubscript{2}, 99.999% trace metals basis), lead(II) chloride (PbCl\textsubscript{2}, 99.999% trace metals basis), manganese (II) iodide (MnI\textsubscript{2}, 99.99% trace metals basis),* manganese(II) chloride (MnCl\textsubscript{2}, 99.99% trace metals basis), cesium carbonate (Cs\textsubscript{2}CO\textsubscript{3}, reagentPlus, 99%), octadecene (ODE, technical grade, 90%), oleylamine (OLAM, 70%) and oleic acid (OA, 90%) were purchased from Sigma-Aldrich. Toluene (TOL, anhydrous, 99.8%) was purchased from Carlo Erba reagents. All chemicals were used without any further purification.

CsPb\textsubscript{3} and CsPb\textsubscript{3}Mn\textsubscript{x}I\textsubscript{3} NC synthesis and purification. CsPb\textsubscript{3}Mn\textsubscript{x}I\textsubscript{3} and CsPb\textsubscript{3} NCs were synthesized based on the synthesis method as described by Protesescu \textit{et al.},\textsuperscript{18} with some minor changes and the addition of MnI\textsubscript{2}. In a typical synthesis, 96 mg of PbI\textsubscript{2} (0.2 mmol), 30 mg MnI\textsubscript{2} (0.1 mmol), 5 mL ODE, 0.5 mL OA and 0.5 mL OLAM** were loaded in a 25 mL 3-neck flask and dried under a vacuum for 2 h at 100 °C. After degassing, the temperature was raised to 150 °C and 0.5 mL Cs-oleate (0.4 g of Cs\textsubscript{2}CO\textsubscript{3} degassed in 13 mL of ODE and 3 mL of OA at 150 °C) was swiftly injected. Immediately after the injection, the NC solution was quickly cooled down to room temperature with
Manganese doped CsPbCl₃ NCs synthesis and purification. CsPbCl₃ NCs were synthesized as described by Protesescu et al., 19 with addition of MnCl₂. In a typical synthesis, 0.1 mmol of PbCl₂ and 0.1 mmol of MnCl₂, 5 mL ODE, 0.5 mL OA and 0.5 mL OLAM were loaded in a 25 mL 3-neck flask and dried under vacuum for 1 h at 120 °C. After degassing, the temperature was raised to 180 °C and 0.4 mL of previously synthesized Cs-oleate (0.4 g Cs₂CO₃ degassed in 15 mL ODE and 1.75 mL OA at 150 °C) was swiftly injected. 30 seconds after the injection, the NC solution was quickly cooled down to room temperature with an ice bath. The NCs were purified via centrifugation (at 3000 rpm for 30 minutes) twice, followed by redispersion in TOL.

Transmission Electron Microscopy (TEM). Conventional TEM images were acquired on a JEOL JEM-1011 microscope equipped with a thermionic gun at 100 kV accelerating voltage. The samples were prepared by drop casting diluted NC suspensions onto 200 mesh carbon-coated copper.

Powder X-ray Diffraction (XRD) Analysis. XRD patterns were obtained using a PANalytical Empyrean X-ray diffractometer equipped with a 1.8 kW Cu Kα ceramic X-ray tube, PIXcel3D 2x2 area detector and operating at 45 kV and 40 mA. The diffraction patterns were collected in air at room temperature using Parallel-Beam (PB) geometry and symmetric reflection mode. All XRD samples were prepared by drop casting a concentrated solution on a zero diffraction quartz wafer.

Elemental analysis. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis performed on an iCAP 6000 spectrometer (ThermoScientific) was used to quantify the Mn to Pb ratio. Prior to measurements, the samples were decomposed in aqua regia (HCl/HNO₃ = 3/1 (v/v)) overnight. The elemental composition with TEM (STEM)-energy dispersive spectroscopy (EDS) was performed using a JEOL Silicon Drift Detector (SDD), equipped on a 120kV JEM-1400Plus TEM.

Optical Absorption Spectroscopy. The spectra were taken on a Varian Cary 5000 UV–vis–NIR spectrophotometer. Samples were prepared by diluting the NC solutions in toluene in 1 cm path length quartz cuvettes.

Photoluminescence (PL), Photoluminescence Quantum Yield (PLQY) and lifetime (LT) measurements. PL, PLQY and LTs were recorded on a Horiba Jobin Yvon Fluorolog-3 spectrometer. Samples were diluted in toluene and measured in cylindrical quartz cuvettes. For the PL and PLQY, a Xenon lamp was used set at an excitation of 440 nm. The absolute quantum yield (QY) of each sample was determined according to 'QY = (I_{em,sample} - I_{em,blank})/(I_{ex,blank} - I_{ex,sample})', where Iₚ is the integrated intensity of the emission (em) or scattering (ex) spectrum for the sample or blank and was measured between 656 and 765 nm. PLQYs were estimated as averages of 4 measurements. For the LTs, the samples were excited with a Horiba Jobin Yvon 637 nm NanoLED laser with a pulsewidth of 200 ps and a repetition rate of 1MHz. LT were recorded at 680 nm.

Computational details: Spin polarized DFT calculations have been performed on the cubic phase of the CsPbI₃ perovskite. Starting from the experimental lattice parameters of the high temperature cubic phase a = 6.289 Å,27 the structures of the pristine and Mn-alloyed perovskites have been calculated in the 2x2x2 supercell (8 formula units) i) by relaxing only the ions keeping fixed the cell to the experimental parameter and ii) relaxing both the ions positions and the cell. The singly alloyed supercell has been modelled by replacing one Pb ion with a Mn ion in its ferromagnetic configuration (total magnetization 5 Bohr magn/cell). For the 0.5:0.5 Mn:Pb system 4 Pb ions were replaced by 4 Mn and six inequivalent substitutional alloys have been modelled. The analysis of the relative cohesive energies highlights that among these configuration, the more stable configuration which preserve the cubic symmetry was the first configuration reported in, where Mn ions are placed in...
in alternate positions with lead ions in the lattice (see inset in Figure 3c). All six 0.5:0.5 Mn:Pb supercells have been modelled in their antiferromagnetic configurations (total magnetization 0 Bohr magn/cell). Further calculations on the ferromagnetic configuration of the most stable cubic 0.5:0.5 Mn:Pb system have also been performed, by showing negligible deviations in the total energies compared to the antiferromagnetic case. Calculations have been carried out by using Ultrasoft pseudopotentials, plane waves basis set and the Perdew Burke Ernzerhoff exchange correlation functional. Pseudopotentials with 14, 7, 15 and 9 electrons in the valence have been used for Pb, I, Mn and Cs, respectively. A cutoff on the wavefunctions of 40 Ryd (320 Ryd on the charge density) and 2x2x2 k points grids have been used throughout the calculations. The ions positions have been relaxed until forces on atoms was less than 0.001 Ryd/Å.

In order to accurately investigate the Mn-doping effects on the electronic structure of the pristine perovskite, hybrid calculations have been performed on the CsMn$_{0.12}$Pb$_{0.88}$I$_3$ and the most stable cubic Cs$_2$PbMnI$_6$ (0.5:0.5 Mn:Pb) alloyed systems system by using the HSE-06 exchange correlation functional and including spin-orbit corrections. The fraction of exchange has been tuned to the value of $\alpha=0.43$, which allows to reproduce the experimental band gap in the prototype tetragonal MAPbI$_3$ perovskite. Norm-conserving pseudopotentials were used in hybrid calculations with the same number of electrons employed in PBE calculations, except for Pb for which a 22 electrons pseudopotentials has been used, generated by including the 5s and 5p states into the valence by using the ONCV package. A cutoff on the wavefunctions of 70 Ryd and 2x2x2 k point grids have been used, by performing calculations on the PBE relaxed geometries found by keeping fixed the cell parameter to the experimental value. All calculations have been carried out by using the Quantum Espresso simulation package.

References
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Appendices
### Appendix Table 6.1

Calculated cell parameters $a$, cell volumes, cohesive energies (per formula unit) and band gaps for the pristine and Mn-alloyed systems calculated at the PBE level. In parenthesis the value calculated by relaxing both ions positions and the cell parameters have been reported. For the CsMn$_{0.5}$Pb$_{0.5}$I$_3$ system results refers to the most stable cubic configuration.

<table>
<thead>
<tr>
<th>System</th>
<th>$a$ (Å), volume (Å$^3$)</th>
<th>Cohesive energy (eV/f.u.)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsPbI$_3$</td>
<td>12.578 (12.791), 1990 (2093)</td>
<td>12.67 (12.71)</td>
<td>1.28 (1.44)</td>
</tr>
<tr>
<td>CsMn$<em>{0.12}$Pb$</em>{0.88}$I$_3$</td>
<td>12.578 (12.665), 1990 (2032)</td>
<td>12.70 (12.71)</td>
<td>1.24 (1.32)</td>
</tr>
<tr>
<td>CsMn$<em>{0.5}$Pb$</em>{0.5}$I$_3$</td>
<td>12.578 (12.221), 1990 (1825)</td>
<td>12.76 (12.84)</td>
<td>1.16 (1.12)</td>
</tr>
</tbody>
</table>

### Appendix 6.1

More TEM images of CsPbI$_3$ and CsPbI$_x$Mn$_{1-x}$I$_3$ NCs. (left) TEM image of CsPbI$_3$ NCs and (right) large area TEM image of alloyed CsPbI$_x$Mn$_{1-x}$I$_3$ NCs.

### Appendix 6.2

Stability photos of CsPbI$_3$ and CsPbI$_x$Mn$_{1-x}$I$_3$ NCs. (a) photo of CsPbI$_3$ and Mn-alloyed NCs after 1 month and (b) same samples under UV excitation.
Appendix 6.3. More details of DFT calculations. Sum of the spin-up and spin-down projected density of states calculated at the PBE level for (a) the pristine CsPbI$_3$ and (b-c) Mn-alloyed CsMn$_{0.12}$Pb$_{0.88}$I$_3$ and the most stable cubic CsMn$_{0.5}$Pb$_{0.5}$I$_3$ perovskites.

Appendix 6.4 PDOS calculated at the HSE06 level by including spin orbit corrections of the most stable cubic Cs$_2$PbMnI$_6$ system.
Appendix 6.5. Details of the pdos calculated at the HSE06 level by including spin orbit corrections of the CsMn$_{0.12}$Pb$_{0.88}$I$_3$ alloyed system. The contributions of the s and d states of Mn are compared with the overall density of states of the lead ions.
Chapter VII

Ruddlesden Popper Cl-I and Cl-Br-I lead halide perovskite nanocrystals
Chapter VII: Ruddlesden Popper Cl-I and Cl-Br-I lead halide perovskite nanocrystals*

Abstract: The vast majority of lead halide perovskite nanocrystals are currently based on either a single halide composition (CsPbCl$_3$, CsPbBr$_3$, CsPbI$_3$) or an alloyed mixture of bromide with either Cl$^-$ or I$^-$ (i.e. CsPb(Br:Cl)$_3$ or CsPb(Br:I)$_3$). In this chapter, a detailed optical and structural study of two halide alloying cases that have not previously been reported for lead halide perovskite nanocrystals is presented: Cs$_2$PbI$_2$Cl$_2$ nanoplatelets and triple halide CsPb(Cl:Br:I)$_3$ nanocrystals. In the case of Cs$_2$PbI$_2$Cl$_2$ NPLs, Ruddlesden Popper phase crystal structures are formed, and the nanoplatelets exhibit a strong excitonic absorption and a very weak photoluminescence. In the case of triple halide CsPb(Cl:Br:I)$_3$, the nanocrystals comprise a CsPbBr$_2$Cl crystal lattice and a small amount of iodide, which segregates at the Ruddlesden Popper planes’ interface in a similar way to Cs$_2$PbI$_2$Cl$_2$ nanocrystals. The iodide segregation is most likely linked to a strong photoluminescence quenching. Thus, this work demonstrates the limits of halide alloying in lead halide perovskite nanocrystals, since a mixture that contains halide ions of very different sizes leads to a severe quenching of a lead halide perovskite nanocrystal’s optical properties.

7.1 Introduction
Over the past decade, LHPs have gained much interest in the materials science community owing to their outstanding optoelectronic properties. More recently, research has also expanded to include studies on colloidal LHP NCs, especially cesium based ones (CsPbX$_3$, with X = Cl, Br, I). This has resulted in the successful synthesis of NC samples with tunable compositions, great control over their size and shape, and the fabrication of several different types of LHP NC based devices. One striking feature of LHP NCs is that they are easy to alloy and dope with other elements, which either improves their optical properties or causes a down converted emission. For instance, several groups have extended the synthesis of LHP NCs to quaternary compositions, such as [Cs:FA]PbI$_3$, CsPb[Br:X]$_3$ or Cs[Pb:M]X$_3$ (in which M = Sr$^{2+}$, Sn$^{2+}$, Mn$^{2+}$, Ni$^{2+}$ etc.), and even quinary compositions such as [Cs:FA]Pb[Br:I]$_3$. Of all these alloyed compositions, the most investigated ones are those in which two different types of halide are present (namely Br/Cl or Br/I). These halides can be mixed in the structure at any possible Br:Cl or Br:I ratio, which allows the bandgap to be precisely tuned from about 400 nm to 700 nm. As is the case in bulk LHPs, mixing Br$^-$ with either Cl$^-$ or I$^-$ anions results in homogenous alloys with a well-defined band gap and narrow PL peak. The formation of homogenous alloys is made possible by small variations in the length of the ionic radius, which only decreases by 8% going from Br$^-$ to Cl$^-$, and increased by 12% from Br$^-$ to I$^-$. On the other hand, the difference in the length of the ionic radii between Cl$^-$ and I$^-$ is apparently too big (19%) to permit homogenous mixing.

case of CsPbI \(_2\) NCs, the alloying with Cl\(^-\) is limited to only a few percent\(^{12,16-17}\). Interestingly, the incorporation of a small amount of Cl\(^-\) into MAPbI\(_3\) thin films or CsPbI\(_3\) NCs has been found to be beneficial in terms of increasing long-term stability and improving the optical properties\(^{16,18}\). There have not been any studies on mixing all three halides in LHP NCs, and there have only been few works on the bulk\(^{19}\).

In this chapter, two types of halide mixing that have not previously been reported for NCs are studied; Cs\(_2\)PbI\(_2\)Cl\(_2\) NCs with a Cl:\(I\) feed ratio of 1:1, and CsPb(Cl:Br:I)\(_3\) NCs with a Cl:Br:I feed ratio 1:1:1. In both these cases, the synthesized NCs are nanoplatelet-shaped. In the case of Cs\(_2\)PbI\(_2\)Cl\(_2\), the NCs crystallize into a Ruddlesden-Popper phase (RPP), matching that of previously investigated bulk CsPbI\(_2\)Cl\(_2\).\(^{20}\) Even though these NCs are relatively big (5 nm thick by 40 nm in the lateral dimensions), they exhibit an extremely confined excitonic absorption as a result of the individually separated Pb-Cl layers within the RPP. When the Cl:Br:I halides are mixed in a 1:1:1 ratio, perovskite NCs with an optical absorption and crystal lattice similar to those of CsPbBr\(_2\)Cl NCs are obtained, and only a small amount of I\(^-\) is incorporated into the NCs, as was confirmed by elemental analysis. These triple halide NCs, however, have a very poor PLQY (well below 1%), which is significantly lower than that of the CsPbBr\(_2\)Cl NCs. By means of high resolution high-angle annular scanning transmission electron microscopy (HAADF-STEM) analysis, it was found that the CsPb(Cl:Br:I)\(_3\) NCs predominantly crystallize in a perovskite crystal structure, but they contain several planar defects which could be identified as RPP planes. By combining a quantitative high resolution HAADF-STEM analysis with DFT calculations, it was confirmed that the iodide anions are segregated from the pure lead halide perovskite structure. Subsequently, they migrate to the RPP interface, forming RPP planes.

### 7.2 Synthesis and characterization of Cs\(_2\)PbI\(_2\)Cl\(_2\) nanocrystals

The Cs\(_2\)PbI\(_2\)Cl\(_2\) and CsPb(Cl:Br:I)\(_3\) NCs were synthesized based on the previously reported synthesis of CsPbBr\(_3\) NC\(^{21}\). Here, a Cs-oleate solution was injected into a solution of ODE, OLAM and OA containing either 1:1 PbCl\(_2\):PbI\(_2\) or 1:1:1 PbCl\(_2\):PbBr\(_2\):PbI\(_2\) (see experimental section 7.7). In the case of a 1:1 ratio of PbCl\(_2\):PbI\(_2\), NCs that were about 4.2 ± 0.6 nm thick and 21 ± 3 nm wide were produced, as is shown in figure 7.1a. As depicted on figure 7.1b These NCs crystallized in the RPP Cs\(_2\)PbI\(_2\)Cl\(_2\) phase (K\(_2\)NiF\(_4\)-type phase), which consists of corner-sharing [PbI\(_2\)Cl\(_4\)]\(^{4-}\) octahedra layers. In the Cs\(_2\)PbI\(_2\)Cl\(_2\) phase, the Cl\(^-\) occupy the equatorial halide sites and the I\(^-\) ions occupy the axial halide sites, as is depicted in figure 7.1c.\(^{20}\) Although the Cs\(_2\)PbI\(_2\)Cl\(_2\) crystal lattice shares similar diffraction peaks with the CsPbI\(_3\) crystal lattice, it has several additional peaks, as is demonstrated in appendix 7.1a. Furthermore, due to the breaking of symmetry in the z direction of the lattice, the diffraction from the [112] family of planes normally observed in CsPbCl\(_3\) cannot be observed in the Cs\(_2\)PbI\(_2\)Cl\(_2\) XRD pattern. As will be further discussed later on, the XRD pattern also confirmed that the NCs grow anisotropically, as several peaks, notably those of the [xy0] plane family are significantly sharper than the other diffraction peaks. This further indicates that the NCs are essentially formed by stacked layers of corner-sharing [PbI\(_2\)Cl\(_4\)]\(^{4-}\) octahedra which are charge balanced by Cs\(^+\) counter ions. The strong confinement of carriers inside these single layers of lead chloride perovskites is also evident from the optical absorption spectrum, which is presented in figure 7.1d. Here, the Cs\(_2\)PbI\(_2\)Cl\(_2\) NCs exhibit a narrow excitonic absorption around 400 nm (3.1 eV), which matches the bandgap of 3.04 eV that was reported by Kanatizdis’ group.\(^{20}\) This is a sharper absorption than that of CsPbCl\(_3\)
NCs appendix 7.1b). However, the PL of the Cs$_2$PbI$_2$Cl$_2$ NCs is significantly broader than that of CsPbCl$_3$ NCs, and it exhibits a broad tail that is similar to what has been reported previously (figure 7.1d). This broad PL was too weak to determine a PLQY, but the PL excitation (PLE), which is shown in figure 7.1d and appendix 7.2, matches the absorption, indicating that the broad asymmetric PL indeed originates from the Cs$_2$PbI$_2$Cl$_2$ NCs.

It is important to stress that, from the structural point of view, these “all-inorganic” RPP Cs$_2$PbI$_2$Cl$_2$ NCs are very different from the previously reported organic-inorganic RPPs (including organic-inorganic RPP NCs), in which bulky organic ligands act as spacers between the stacked lead-halide layers (like (BA)$_2$(MA)$_{n-1}$Pbn$_{3n+1}$, with BA = butylammonium). In our RPP Cs$_2$PbI$_2$Cl$_2$ NCs, the individual layers are not separated by bulky ligands (acting as cations), but rather by the large size difference of the Cl$^-$ and I$^-$ anions. Therefore, their periodicity along the stacking direction is much smaller than that of organic-inorganic RPP phase. As a consequence, no low angle XRD diffractions originating from large periodicities along the stacking direction were observed (figure 7.1b). The reported all-inorganic RPP Cs$_2$PbI$_2$Cl$_2$ NCs in this work are also different from the ligand-passivated ultrathin two-dimensional LHP NCs (nanosheets and nanoplatelets), which can have thickness down to a few unit cells and thus can exhibit superstructure effects at low diffraction angles which arise from the staking of the ligand-coated nanosheets on top of each other. The Cs$_2$PbI$_2$Cl$_2$ NCs, even though they are coated with organic ligands, are too thick for such periodicities to be appreciated by low angle XRD diffraction (see again figure 7.1b). Finally, because the individual layers in these Cs$_2$PbI$_2$Cl$_2$ NCs are not separated by bulky ligands, the NCs are expected to have electronic structure and optical properties that are significantly different from those of the organic-inorganic RPPs and of the ligand-coated ultrathin LHP nanosheets.
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Figure 7.1. Optical and structural data from Cs$_2$PbI$_2$Cl$_2$ NPLs. (a) TEM image of monodisperse Cs$_2$PbI$_2$Cl$_2$ NCs. (b) XRD pattern of Cs$_2$PbI$_2$Cl$_2$ NPLs matching that bulk Cs$_2$PbI$_2$Cl$_2$. (c) Crystal structure of a Cs$_2$PbI$_2$Cl$_2$ NC RPP phase. (d) Strong excitonic absorption from Cs$_2$PbI$_2$Cl$_2$, and broad PL of Cs$_2$PbI$_2$Cl$_2$ NPLs. PLE spectra of Cs$_2$PbCl$_3$I$_2$ nanocrystals (red line, recorded at 411 nm) overlap with the absorption, indicating that the PL originates from Cs$_2$PbI$_2$Cl$_2$. The asterisks mark the instrumental artifact. XRD reference patterns correspond to ref. 20

The crystal structure of the Cs$_2$PbI$_2$Cl$_2$ NCs was further studied via high-resolution HAADF-STEM imagining. The Cs$_2$PbI$_2$Cl$_2$ NCs were observed while they were lying parallel to the substrate, as can be seen in figure 7.2a. Here, only slight differences in the intensities were found throughout the nanostructure, which is similar to previous findings in HRTEM studies on RPP domains in CsPbBr$_3$. These intensities can be understood by observing such a NC from the side, as is depicted in figure 7.2b, since it consists of alternating RPP layers. Such alternating RPP domains result in atomic rows that contain both Cs and Pb, which is not the case for perovskite structures. Due to Cs and Pb mixing in one atomic row, which can be observed in figure 7.2b, no distinct intensity differences are present in the atomic columns in figure 7.2a. Although no clear proof of the coexistence of CsPbCl$_3$ was found in the XRD patterns of the Cs$_2$PbI$_2$Cl$_2$ NCs, the NCs did not solely consist of single layers of Cs$_2$PbI$_2$Cl$_2$. Indeed, they also displayed several bilayers of Cs$_3$Pb$_2$I$_5$ (see the bottom part of figure 7.2d as well as appendix 7.3a-c).

To further prove that the I$^-$ ions occupy the axial halide sites, and that the Cl$^-$ ions occupy the equatorial (perovskite) halide sites (see figure 7.1c), a quantitative high-resolution HAADF-STEM analysis was performed. Using StatSTEM, the intensities of the halide atomic columns were calculated by fitting a Gaussian function to each individual atomic column consisting of only halides. In figure 7.2c and appendix 7.4, the intensity values, i.e. the volume of each fitted Gaussian peak, are plotted, and the results indicate that the columns at the planar defect have a higher intensity than the columns in the NC bulk. Since the intensity in an HAADF-STEM image scales with the thickness of the sample
and the atomic number of the present elements, and since the NCs have a constant thickness, this could certainly indicate that more iodine is present in the columns that are located at the RPP. The halide columns between the Pb columns, on the other hand, clearly have a lower intensity value (figure 7.2c), which suggests the presence of Cl in these columns, since Cl has a lower atomic number than I (Z Cl = 17 and Z I = 53). Due to this low atomic number, the atomic columns are not visible in the HAADF-STEM images (figure 7.2b and d). Figure 2d shows a Cs2PbI2Cl2 NC that is overlayed with a model of alternating RPP layers, which is based on the quantitative HAADF-STEM results (purple: Cs+, black: Pb2+, blue: Cl− and red: I−). Usually, EDS can be used to retrieve compositional information. However, due to the high sensitivity of the NCs to the electron beam in this case, an atomic resolution EDS map with a sufficient signal-to-noise ratio cannot be acquired before any damage has occurred.

Figure 7.2. HAADF-STEM analysis of Cs2PbI2Cl2 NPLs. (a) Top view of a Cs2PbI2Cl2 NPL that is parallel to the substrate, with in the inset highlighting the atomic arrangement. (b) Side view of a Cs2PbI2Cl2 NPL, which clearly matches the alternating layers of the RPP. (c) The volume of the fitted Gaussian peaks of the halide columns of the NPL. The significant increase in the intensity values measured at the axial positions matches the excepted iodide positions (d) Cs2PbI2Cl2 NPL observed perpendicular to substrate overlaid with the crystal structure of Cs2PbCl2I2. For additional HAADF-STEM data, see appendix 7.3 and 7.4.

7.3 Synthesis and characterization CsPb(Cl:Br:I)3 nanocrystals

For the second type of halide alloying that, all three halides (Cl, Br and I) were used in the synthesis of LHP NCs. As is shown in figure 7.3a, this combination resulted in NCs with lateral dimensions of approximately 13 nm and thicknesses of about 5 nm. Different to the Cs2PbI2Cl2 NCs, the CsPb(Cl:Br:I)3 NCs crystalized in the perovskite crystal lattice, with a lattice spacing of about 5.8 Å, which matches that of CsPbBr2Cl NCs (see figure 7.3b and appendix 7.5). Furthermore, the CsPb(Cl:Br:I)3 NCs have an absorption edge (around 460 nm) and PL peak (around 470 nm) that are similar to those of CsPbBr2Cl NCs (figure 7.3c). Interestingly, the mixed CsPb(Cl:Br:I)3 NCs hardly exhibited any visible PL, which is in stark contrast to the CsPbBr2Cl NCs’ bright emission (figure 7.3d). Indeed, the CsPb(Cl:Br:I)3 NCs exhibited a measurable PLQY of about 0.1% (see appendix 7.6), which is about 50 times lower than that of the CsPbBr2Cl, which have a PLQY of 5.5%. These findings are in agreement with those that have been previously reported for untreated CsPb(Br:Cl)3 NCs.32 Contrary to the 1:1:1 Cl:Br:I feed ratio that is used in during the synthesis of the NCs, the final elemental Cl:Br:I ratio, which was measured with EDS, was found to be 1:1.7:0.3. This
again matches the optical absorption, as well as the crystal lattice, which is closer to that of 2:1 Br:Cl than that of the larger CsPbI₃ unit cell.

**Figure 7.3. Overview of CsPb(Cl:Br:I)₃ nanocrystals.** (a) TEM image of CsPb(Cl:Br:I)₃ NCs. (b) XRD pattern of CsPb(Cl:Br:I)₃ NCs, showing only a single crystal lattice that matches that of CsPbBr₂Cl NCs. (c) Optical properties of CsPb(Cl:Br:I)₃ NCs, evidencing an absorption edge at around 460 nm and a weak but narrow emission around 470 nm, matching the same bandgap of CsPbBr₂Cl NCs. (d) Absorption corrected PL of CsPb(Cl:Br:I)₃ NCs compared to brightly emitting CsPbBr₂Cl NCs, with a photo of CsPbBr₂Cl and CsPb(Cl:Br:I)₃ NCs under UV excitation, showing no visible PL for the CsPb(Cl:Br:I)₃ NCs. CsPbCl₃ (cubic) and CsPbBr₃ (orthorhombic) XRD reference patterns correspond to 98-002-9076 and 96-451-0746.

To further study the crystal lattice of these CsPb(Cl:Br:I)₃ NCs, and to further understand why their PLQY is so low, a high resolution HAADF-STEM analysis was performed. As is reported in **figure 7.4a**, the CsPb(Cl:Br:I)₃ NCs consist predominantly of a perovskite crystal structure with a lattice spacing of (5.9 ± 0.1) Å, which is in agreement with the XRD measurements. Large grain boundaries were observed in many of the CsPb(Cl:Br:I)₃ NCs, as is shown in **figures 7.4b** and **appendix 7.7**. These grain boundaries are made of shifted lattices over half of the unit cell along the [100] planes. These types of lattice shifts are similar to those of the Cs₂PbI₂Cl₂ RPP NCs, but consist of only a single shifted plane between two layers of 3D perovskites.²⁴⁻²⁵, ³⁰, ³³ Interestingly, many of the NCs contained multiple RPP planes, resulting in corners, zig-zags, single layers of RPPs, and double layers of RPPs (see **figures 7.4b** and **appendix 7.7**). These RPP planes are mostly present in only one part of the NC, and not throughout the whole NC, which explains why the overall crystal lattice is still observed as a perovskite lattice (**figure 7.3c**). These types of RPP plane shifts have been observed in pure CsPbBr₃ NCs before, but they originated from a post synthesis chemical fusion of the NCs.³⁴⁻³⁵

In some cases, the formation of RPP planes can also be observed from the [001] direction, as can be seen in **appendix 7.8**. If the lattice shift is located in the middle of the NCs, half of the crystal is shifted, which leads to mixed Pb and Cs atomic columns with equal
amounts of Pb and Cs throughout the atomic columns. Thus, the RPP shift results in averaging of the Pb- and Cs- intensities in the Pb- and Cs-containing columns, which leads to comparable intensity values, since no all-Cs or all-Pb atomic columns are present. This was observed for several NCs, which exhibited regions which did not show separate different intensities for Pb-X and Cs columns, but rather only columns with a comparable intensity. This is not caused by the alternating layers of a RPP, as is shown in figure 7.2b and d, but by a single RPP plane shift. The same was observed in large CsPbBr3 nanosheets, which sometimes contained RPP domains. Since the iodide ions tend to occupy the axial halide positions in the RPP Cs2PbI2Cl2 phase, it is likely that the small amount of incorporated iodine species in the CsPb(Cl:Br:I)3 NCs are segregated at the RPP halide positions. To confirm that the iodide halides segregate at the RPP, a quantitative high resolution HAADF-STEM analysis was performed to investigate the intensities of the halide columns. Using StatSTEM, it was found that all the halide columns that are directly positioned in the RPP exhibit significantly higher intensities compared to those outside the RPP planes (see figures 7.4c, 7.4d and appendix 7.9). This indicates that the iodide halides do tend to segregate into the RPP planes. This is in accordance with the small amount of iodide that was observed in the elemental analysis, but the NCs generally have the same properties as CsPbBr2Cl NCs.

Figure 7.4. Structural data of CsPb(Cl:Br:I)3 nanocrystals. HAADF-STEM images of Cs(Cl:Br:I)3 NCs, showing (a) the perovskite lattice and (b,c) NPLs with several plane shifts. (d) The volume of the fitted Gaussian peaks of the halide columns of the NPL as shown in (c), indicate increased intensity values of the halide columns around the RPP planes, confirming an increased concentration of iodide halides these positions. (e) RPP plane shift model overlapping an HAADF-STEM image of a CsPb(Cl:Br:I)3 NPL. For additional HAADF-STEM data, see appendix 7.7-7.9.

7.4 A closer look at the iodide segregation in CsPb(Cl:Br:I)3 nanocrystal

To identify whether the PL quenching originates from the presence of RPP planes in the inorganic cores of the CsPb(Cl:Br:I)3 NCs, or is mainly related to surface trapping effects, the NCs were subjected to a series of surface treatments that are generally known to increase the PL by passivating surface traps. The addition of ammonium thiocyanate increased the PLQY of the CsPbBr2Cl NCs by almost a factor of 6, from 5.5% to 33.1%, as is shown in appendix 7.6 and appendix 7.11. The PL lifetime of thiocyanate-treated CsPbBr2Cl NCs was characterized by a slower decay at early times (~0-30 ns) and a faster decay at longer times (~30-200 ns) compared to untreated NCs, similar to the prior reports (appendix 7.12). The same treatment on the CsPb(Cl:Br:I)3 NCs resulted in an overall faster PL decay of the treated NCs compared to untreated NCs (appendix 7.11 and appendix 7.13),
However with no significant enhancement of the PLQY (see appendix 7.11). Overall, these experiments indicate that the low PLQY cannot stem solely from surface trapping effects, and therefore must also be due to the presence of RPP planes in the core of the NCs that are not accessible by post-synthesis surface treatments.

To understand better this point, DFT calculations were carried out by reproducing the grain boundaries between the perovskite structure and the RPP. First, a CsPbBr₂Cl NC composed of a 4x4x7 cubic unit cell (which corresponds to 2.6 x 2.6 x 4.3 nm) was built. In this structure, each lead halide octahedron is formed equatorially by four bromide ions and axially by two chlorine atoms, which is in line with a 2:1 stoichiometric Br:Cl ratio (the actual ratio in the finite model system is about 1.5:1). From this structure, the RPP interface was formed by removing one layer of PbX₂ along the (100) direction, as is depicted in figure 7.5a. All halide atoms at the RPP boundary were then replaced by iodine, while the CsI units at this interface were shifted half a unit cell in the x and y directions to resemble the RPP planes. The final elemental ratio for the RPP model system is 1.7:1.0:0.5, which is qualitatively in alignment with the EDS measurements.

We relaxed both of the structures and calculated the density of states (figure 7.5b and c). It was found that the bandgap of each system is free of localized (trap) states, but there is a significant difference in the electronic structure near the valence band edge in the triple halide system. Here, the molecular orbitals (states) are predominantly composed of the np orbitals of the halides, however the contribution of the iodine 5p orbitals at the RPP planes is not at the band edge but few hundredths meV below. This behavior is surprising because the iodine orbitals are expected to contribute at higher energies compared to the other halides. This effect however can be explained by the lack of the PbX₂ layer at the RPP interface that breaks the connection between the corner edge octahedra lifting their electronic connection. This tells us that the interface resembles rather a wide bandgap CsI structure, with the iodine orbitals pushed below the valence band edge. This configuration, however, discards the idea that the segregation of iodine at the RPP interface alone localizes the hole carrier at the RPP interface, reducing the electron-hole overlap, and thus the emission efficiency. A most likely explanation to the loss of PLQY is that the RPP interface itself is defective, presumably due to some halide vacancies, which could form deep traps in the core region of the NCs that cannot be directly accessed post-synthetically via a surface treatment.

We also computed the optical spectrum of the CsPbBr₂Cl and CsPb(Cl:Br:I)₃ NCs at a time-dependent DFT level of theory, analyzing the lowest 700 electronically excited states (figure 7.5c). This revealed that the triple halide system maintains excitonic features in the bandgap region, which is in agreement with our experiments.
Figure 7.5. Computational data from CsPb(Cl:Br:I)\textsubscript{3} nanocrystals. (a) Relaxed CsPbBr\textsubscript{2}Cl structures (left) and CsPb(Cl:Br:I)\textsubscript{3} structures (right) shown from different directions and computed at the DFT/PBE levels of theory. (b) Electronic structure near the conduction and valence band regions. Each molecular orbital is decomposed in terms of atomic type contributions and is highlighted in a different color. (c) Absorption spectrum of each system, computed using the simplified time dependent (TDDFT/PBE) methodology.

To understand how the presence of the three types of halide atoms at different locations in the perovskite lattice can lead to iodine segregation at the RPP interface several isomeric CsPb(Cl:Br:I)\textsubscript{3} NC structures were studied with equal amounts of the three halogen atoms with DFT. First, a symmetric NC was designed which was built from a CsPb(Cl:Br:I)\textsubscript{3} unit cell that was replicated evenly along the three axes by 2 unit cells (the size of the NC was about 3 nm). Using this configuration as a point of reference, halides were swapped, for example, chloride ions at the surface with the iodide ions that are present in the core, so as to provide a qualitative picture of the diffusion of this latter ion type to the surface. The difference in the total energy of this structure compared to the one used as a point of reference provides us with a rough estimate of the likelihood that segregation will occur. An inspection of the DFT data shows that the segregation of iodide ions into the surface leads to an overall stabilization with respect to the symmetrical system by about 232 kcal/mol. This corresponds to about 3.7 kcal/mol for each Cl-I ion that has been swapped (in total, 62 were swapped). The inverse process, i.e. the diffusion of Cl ions to the surface, is energetically disfavored by about 121 kcal/mol, i.e. 1.95 kcal/mol per swapped halide.

We also analyzed the segregation of Br with I and I with Cl, as is illustrated in appendix 7.14. The overall trend is that smaller ions prefer to be located at the core of the NC, while heavier ions prefer the surface. Although this result is only qualitative, it provides some insight as to how halide ions might be distributed in mixed lead halide NCs, especially in those that contain ions of very different sizes. In particular, these results show that iodine...
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and chlorine have the lowest miscibility and that iodine prefers to move towards the surface of RPP interface rather than remain in the core of the NC. This analysis, together with the conclusion from the Kanatzidis group that Cs$_2$PbI$_2$Cl$_2$ is thermodynamically more favorable to form over CsPbCl$_3$ + Cs$_4$PbI$_6$ (as well as CsPbI$_3$ + Cs$_4$PbI$_6$) or CsCl + PbBr$_2$ (as well as CsBr + PbCl$_2$), confirms that iodide segregation in the triple halide mixed NCs towards RPP planes is indeed a thermodynamically driven process.

7.5 Conclusions
To summarize, this chapter presented the results of LHP NCs with two new halide compositions: Cs$_2$PbI$_2$Cl$_2$ and CsPb(Cl:Br:I)$_3$. The Cs$_2$PbI$_2$Cl$_2$ NCs crystalize in a pure RPP phase, and this is the first work to report such lead halide RPP NCs. The CsPb(Cl:Br:I)$_3$ NCs crystalize in a cubic LHP crystal structure, but each NC contains several RPP plane shifts. The presence of I in these NCs systematically produces the RPP type shifts due to its size difference with respect to the other halides in the structure. Thus, these ions migrate outwards and fill the halide positions at the plane interfaces.

7.6 Acknowledgments
The following people contributed to this chapter: Eva Bladt and Sara Bals performed and interpreted the HRTEM measurements. Urko Petralanda and Ivan Infante performed the DFT calculations and Zhiya Dang performed the EDS measurements. Emanuela Sartori, helped with the synthesis of the CsPb(Cl:Br:I)$_3$ NCs and Dmitry Baranov performed all the PLQY measurements. Ahmed L. Abdelhady helped with the design of the experiments and, Liberato Manna provided the final supervision on all presented work.

The research leading to these results has received funding from the seventh European Community Framework Programme under Grant Agreement No. 614897 (ERC Consolidator Grant “TRANS-NANO”), the framework programme for research and Innovation Horizon 2020 (2014-2020) under the Marie Sklodowska-Curie Grant Agreement COMPASS No. 691185 and the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2014R1A1A2009367). Part of the synthetic work was performed at the Molecular Foundry and was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

7.7 Experimental section
Chemicals. Cesium carbonate (Cs$_2$CO$_3$, 99%), lead(II) chloride (PbCl$_2$, 98 % trace metals basis), lead(II) bromide (PbBr$_2$, 99.999% trace metals basis), lead(II) iodide (PbI$_2$, 99.999% trace metals basis), ammonium thiocyanate (ATCN, 97.5%), oleylamine (OLAM, 98%), oleic acid (OA, 90%), 1-octadecene (ODE, 90%) and toluene (TOL, anhydrous, 99.8%) were purchased from Sigma-Aldrich. All chemicals were used as received, without any further purification.

Synthesis of Cs$_2$PbI$_2$Cl$_2$, CsPb(Cl:Br:I)$_3$, CsPbBr$_2$Cl and CsPbCl$_3$ NCs. The Cs$_2$PbI$_2$Cl$_2$, CsPb(Cl:Br:I)$_3$, CsPbBr$_2$Cl and CsPbCl$_3$ NCs were synthesized based on a hotplate synthesis that had previously been used to prepare Cs$_4$PbX$_6$ and CsPbBr$_3$ NCs. All syntheses were performed in air and without any pre-dried chemicals or solvents. In a typical synthesis, PbX$_2$ salts (in total 0.2 mmol, with 1:1 PbCl$_2$:PbI$_2$ for Cs$_2$PbI$_2$Cl$_2$, 1:1:1 PbCl$_2$:PbBr$_2$:PbI$_2$ for CsPb(Cl:Br:I)$_3$ and 1:2 PbCl$_2$:PbBr$_2$ for CsPbBr$_2$Cl) were dissolved in 5 mL ODE, 0.125 mL OA and 0.5 mL OLAM in a 20 mL vial on a hotplate set at 250 °C. When the temperature reached the 185 °C (for CsPb(Cl:Br:I)$_3$ and CsPbBr$_2$Cl) or 165 °C
(for Cs$_2$PbI$_5$Cl$_3$), 0.5 mL of Cs-OA (0.4 g Cs$_2$CO$_3$ dissolved in 15 ml ODE and 1.75 ml OA at 150 °C) was swiftly injected and the reaction was quickly cooled down with a cold water bath. The NCs were directly washed via centrifugation (at 6000 rpm for 10 minutes), followed by redispersion in 5 ml TOL. For HRTEM and XRD, the NCs were rinsed several times with TOL, as previously reported.\textsuperscript{42}

**Transmission Electron Microscopy (TEM).** Conventional TEM images were acquired on a JEOL JEM-1011 microscope equipped with a thermionic gun at an accelerating voltage of 100 kV. The samples were prepared by drop casting diluted NC solutions onto 200 mesh carbon-coated copper grids.

**Energy dispersive spectroscopy (EDS).** STEM-EDS was performed on a JEOL JEM-2200FS microscope equipped with a Schottky emitter operating at 200 kV, a CEOS spherical aberration corrector for the objective lens, an in-column energy filter (Omega-type), and a Bruker Quantax 400 EDS system with an XFlash 5060 detector.

**High-resolution high-angle annular dark-field imaging scanning transmission electron microscopy (HAADF-STEM).** High-resolution HAADF-STEM images were acquired using a cubed FEI Titan microscope operating at 300 kV. A probe semiconvergence angle of ~20 mrad was used. The quantitative HAADF-STEM analysis was performed using StatSTEM.\textsuperscript{31} The intensity values of the halide-containing atomic columns are calculated by fitting a Gaussian function to each individual area detector operating at 45 kV and 40 mA. The diffraction patterns were collected in air at room temperature using Parallel-Beam (PB) geometry and symmetric reflection mode. All XRD samples were prepared by drop casting a concentrated solution on a zero diffraction quartz wafer.

**Powder X-ray Diffraction (XRD) Analysis.** XRD patterns were obtained using a PANalytical Empyrean X-ray diffractometer equipped with a 1.8 kW Cu Ka ceramic X-ray tube and a PIXcel3D 2x2 area detector operating at 45 kV and 40 mA. The diffraction patterns were collected in air at room temperature using Parallel-Beam (PB) geometry and symmetric reflection mode. All XRD samples were prepared by drop casting a concentrated solution on a zero diffraction quartz wafer.

**Steady-state Absorbance, Photoluminescence and Photoluminescence Excitation Spectra.** Absorbance spectra from solutions of NCs were recorded using a Cary-300 spectrophotometer. The photoluminescence and photoluminescence excitation spectra were recorded using a FLS920 Edinburgh Instruments spectrofluorimeter. Concentrated NC solutions were diluted with TOL in 4 mm x 10 mm quartz cuvettes, as described below.

**Photoluminescence Quantum Yield (PLQY) measurements.** The PLQYS of as-synthesized and thiocyanate-treated CsPbBr$_3$Cl and CsPb(Cl:Br:I)$_3$ NCs were measured on freshly-made samples using FLS920 Edinburgh Instruments spectrofluorimeter equipped with integrating sphere. The samples for PLQY were prepared in the air by diluting 13-25 microliters of the concentrated NC solutions with 1 ml of anhydrous TOL in 4 mm x 10 mm quartz cuvettes capped with white PTFE stoppers (Hellma-Analytics, part number 114F-10-40). Dilutions were performed shortly before the measurements. The samples were excited at 350 nm using the xenon lamp (Xe900) with an excitation slit width set at 10 nm. The emission slit width was set at 0.40 nm. The cuvettes were oriented inside the sphere such that the excitation was through the 4 mm path length. The photon number spectra for the samples and TOL solvent reference were collected over 325-550 nm spectral range with a step size of 1 nm, and a dwell time of 0.2 seconds per step. Five consecutive scans were added together to obtain the data for PLQY calculations. Corrections for the background, PMT detector sensitivity, and the lamp reference detector were applied automatically during the data collection by the software. For PLQY calculations, the photon number spectra were integrated in the range of 335-365 nm in order to determine the total number of scattered photons (sc photons), and in the ranges 435-550 nm [CsPbBr$_2$Cl$_2$] or 435-500 nm [CsPb(Cl:Br:I)$_3$] to determine the total number of emitted photons (em photons). The values of PLQY were calculated using the following formula: $PLQY, \% = 100 \times \left(\frac{N_{sample}^{em \ photons} - N_{reference}^{em \ photons}}{N_{sample}^{sc \ photons} - N_{sample}^{sc \ photons}}\right)$, and reported without correction for self-absorption. It was attempted to measure PLQY of CS$_2$PbI$_5$Cl$_3$ NCs using 385 nm excitation, but the sample emission was too low, indicating that PLQY of the sample was much smaller than 0.1%. The PLQY results are summarized in Table S1.

**Photoluminescence lifetime measurements.** Time-dependent PL intensity decays were measured after the PLQY measurements on the same samples using the time-correlated single photon
Density functional theory (DFT) calculations. All DFT calculations were performed using the CP2K quantum chemistry code,\textsuperscript{43} employing the PBE exchange-correlation functional and a double $\zeta$ basis set plus polarization functions.\textsuperscript{44,45} Scalar relativistic effects have been incorporated with an effective core potential, while spin-orbit coupling effects were not added in the calculations. Charge-balanced nanocrystal models were built according to previous receipt from some of us.\textsuperscript{38,46-47} Time-dependent calculations were carried out using the simplified Tamm–Dancoff (sTDA) approach that allows the simultaneous computation of hundredths of excited states.\textsuperscript{48} This methodology has been implemented within the QMflows-namd software package and is suitable to compute the optical absorption spectrum of the mixed lead halide model systems until approximately 4.0 eV.\textsuperscript{49}

References


**Appendices**

**Appendix table 7.1.** Optical densities (pathlength 4 mm) and measured PLQYs of the as-synthesized and thiocyanate-treated (+TCN) CsPbBr\textsubscript{2}Cl and CsPb(Cl:Br:I)\textsubscript{3} nanocrystal samples.

<table>
<thead>
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<th>Nanocrystal samples in toluene</th>
<th>(\lambda_{\text{exc}}) nm</th>
<th>OD at (\lambda_{\text{exc}})</th>
<th>PLQY\textsubscript{obs}, %</th>
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</thead>
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<td>CsPbBr\textsubscript{2}Cl</td>
<td>350</td>
<td>0.18</td>
<td>5.5</td>
</tr>
<tr>
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<td>0.16</td>
<td>~0.1</td>
</tr>
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<td>0.23</td>
<td>33</td>
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<tr>
<td>CsPb(Cl:Br:I)\textsubscript{3} + TCN</td>
<td>350</td>
<td>0.22</td>
<td>~0.2</td>
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</tbody>
</table>
Appendix 7.1. Additional data for Cs$_2$PbCl$_2$I$_2$ and CsPbCl$_3$ NCs. (a) XRD patterns of Cs$_2$PbCl$_2$I$_2$ and CsPbCl$_3$ NCs, indicating several differences between the two phases, as well as the strong anisotropic growth indicated by the sharp $[xy0]$ diffractions. (b) Absorption and PL of Cs$_2$PbCl$_2$I$_2$ and CsPbCl$_3$ NCs, as well as their respective TEM images.

Appendix 7.2. PLE data from Cs$_2$PbI$_2$Cl$_2$ NPLs. (left) Steady-state absorption and photoluminescence spectra of Cs$_2$PbI$_2$Cl$_2$ nanocrystals in toluene. Excitation 390 nm. Arrows mark positions on the photoluminescence spectrum at which excitation spectra were recorded. (right) Steady-state absorption and photoluminescence excitation (PLE, recorded at 411 nm, 420 nm, and 440 nm, as indicated in the legend) spectra of Cs$_2$PbCl$_2$I$_2$ nanocrystals in toluene. Asterisks mark instrumental artifacts.
Appendix 7.3. Additional HAADF-STEM images of Cs$_2$PbCl$_2$Cl$_2$ NPLs. (a-c) NPLs observed from the side, laying perpendicular to the substrate. (d) NPLs observed from the top, laying parallel to the substrate.

Appendix 7.4. Additional StatTEM image of Cs$_2$PbI$_2$Cl$_2$ NPL laying perpendicular to substrate, indicating that the halide columns at the RPP interface consist of heavier halides, proving that these positions are indeed occupied by iodide halides.

Appendix 7.5. TEM image of monodisperse CsPbBr$_2$Cl nanocrystals with an average size of 13 nm.
Appendix 7.6. Photon number spectra of (left) CsPb(Cl:Br:I)$_3$ (PLQY ~0.1%) and (right) CsPbBr$_2$Cl$_2$ (PLQY ~5.5%) nanocrystals in toluene recorded in the integrating sphere under 350 nm excitation.

Appendix 7.7. Several different observed RPP planes in Cs(PbCl:Br:I)$_3$ NPLs.

Appendix 7.8. RPP observed from the z-axis resulting in the homogenization of the Pb-X and Cs columns.
Appendix 7.9. Additional StatSTEM image of CsPb(Cl:Br:I)₃ NPL confirming the agglomeration of iodide ions towards the RPP planes.

Appendix 7.10. Steady-state absorption and photoluminescence spectra of (left) CsPb(Cl:Br:I)₃ and CsPb(Cl:Br:I)₃+TCN nanocrystals in toluene with excitation at 350 nm [CsPb(Cl:Br:I)₃] and 400 nm [CsPb(Cl:Br:I)₃+TCN] and (right) CsPbBr₂Cl and CsPbBr₂Cl + TCN nanocrystals in toluene with excitation at 350 nm.

Appendix 7.11. Photon number spectra of (left) CsPb(Cl:Br:I)₃ (PLQY ~ 0.1%) and CsPb(Cl:Br:I)₃ + TCN (PLQY ~ 0.2%) and (right) CsPbBr₂Cl (PLQY = 5.5%) and CsPbBr₂Cl + TCN (PLQY = 33.1%) nanocrystals in toluene recorded in the integrating sphere under 350 nm excitation.
Appendix 7.12. Relaxed structures used to study the diffusion of halogens in mixed lead halide perovskite nanocrystals. In the central structure all three halogens are distributed uniformly through the NC. The energies per swapped halogen of the other six structures are calculated with respect to the central structure. In each of the latter six structures 62 halogens of one type are swapped by halogens of a second type, while the third type of halogen is left in the same positions as in the central structure. The swaps are carried out so that one type of halogen covers now 4 surface facet halide positions and the other type is maximally confined at the core halogen positions. The structures are ordered energetically, from left to right and from top to bottom, from the most to least stable.
Chapter VIII

Zero dimensional

$\text{Cs}_4\text{PbX}_6$ nanocrystals
Chapter VIII: Zero dimensional \( \text{Cs}_4\text{PbX}_6 \) nanocrystals

**Abstract:** This chapter focuses on the synthesis and characterization of cesium lead halide nanocrystals that do not conform to the perovskite crystal structure. The properties of these nanocrystals, which have a \( \text{Cs}_4\text{PbX}_6 \) composition, differ greatly from those of lead halide perovskites; they exhibit a disconnected octahedral network, and they have large bandgaps up to 4 eV. Therefore, a \( \text{Cs}_4\text{PbX}_6 \) phase is referred to as a “zero-dimensional phase”. Interestingly, these nanocrystals can be converted into lead halide nanocrystals through an insertion reaction with \( \text{PbX}_2 \).

8.1 Introduction

LHP NCs can be synthesized in a wide range of compositions, sizes and shapes.\(^1\)-\(^6\) Initially, the research focused on the LHP, whose structure is characterized by corner sharing \( \text{PbX}_6^{4-} \) octahedra, with the \( \text{A}^+ \) cations filling the voids created by four neighboring \( \text{PbX}_6^{4-} \) octahedra (Figure 8.1a).\(^7\)-\(^8\) Compared to the large gaps of individual \( \text{PbX}_6^{4-} \) octahedra (<< 400 nm),\(^9\)-\(^10\) originating from the splitting of the bonding and antibonding states, the coupling of the octahedra in LHPs leads to materials with much smaller band gaps, spanning the visible region of the spectrum up to the infrared. Recently, layered perovskites too have come into intense scrutiny.\(^11\)-\(^15\) As an example, the 2D “Ruddlesden–Popper” \( \text{A}_2\text{PbX}_4 \) phase is made of layers of corner-sharing \( \text{PbX}_6^{4-} \) octahedra alternating with layers of bulky cations. This is often realized by using a mixture of smaller and larger (for example butyl ammonium) monovalent cations.\(^11\)-\(^13\) In these 2D structures, like the one mentioned above, the exciton can no longer propagate in all dimensions, and instead it is confined in the two-dimensional \( \text{PbX}_6^{4-} \) layers, resulting in larger band gaps compared to the \( \text{ABX}_3 \) phase. As an example, (ODA)\( \text{PbBr}_4 \) (with ODA = octadecylammonium) has a 3.1 eV (400 nm) band gap, whereas \( \text{CsPbBr}_3 \) has a 2.36 eV (525 nm) band gap.\(^16\) Finally, in the \( \text{A}_4\text{PbX}_6 \) structure (\( \text{A} = \text{Rb}^+, \text{Cs}^+ \)), the \( \text{PbX}_6^{4-} \) octahedra are completely decoupled in all dimensions (Figure 1b), \(^17\)-\(^21\) and the optical properties of such crystals closely resemble those of individual \( \text{[PbX}_6^{4-} \) clusters which have been observed experimentally in halide salts doped with \( \text{Pb}^{2+} \) ions.\(^9\)-\(^10\) This results in insulator band gaps (\( \text{Cs}_4\text{PbCl}_6 = 4.37 \text{ eV}, \text{Cs}_4\text{PbBr}_6 = 3.95 \text{ eV} \) and \( \text{Cs}_4\text{PbI}_6 = 3.38 \text{ eV} \)),\(^18\)-\(^22\) and the \( \text{A}_4\text{PbX}_6 \) phase is thus often referred to as a 0-dimensional (0D) perovskite. While the 3D and 2D phases of LHPs are widely studied and well understood, 0D perovskites are comparatively less explored, with only very recent works revisiting the optical properties of \( \text{Cs}_4\text{PbBr}_6 \) powders and single crystals.\(^23\)-\(^25\)

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*Based on: Nearly Monodisperse Insulator \( \text{Cs}_4\text{PbX}_6 \) (\( \text{X} = \text{Cl}, \text{Br}, \text{I} \)) Nanocrystals, Their Mixed Halide Compositions, and Their Transformation into \( \text{CsPbX}_3 \) Nanocrystals. Quinten A. Akkerman, Sungwook Park, Eros Radicchi, Francesca Nunzi, Edoardo Mosconi, Filippo De Angelis, Rosaria Brescia, Prachi Rastogi, Mirko Prato and Liberato Manna. *Nano Letters*, 17, 1924–1930 (2017). Copyright © 2017 American Chemical Society.
This chapter focuses on the fast and simple ambient synthesis method for Cs$_4$PbX$_6$ (X = Cl, Br, I) NCs, by working under Cs$^+$ rich reaction conditions compared to the traditional CsPbX$_3$ NC synthesis. As described in section 8.2, the Cs$_4$PbX$_6$ NCs are nearly monodisperse and their size can be tuned from 9 to 37 nm and have large band with their optical absorption spectra are characterized by strong and narrow bands, independent of the size of the NCs. Furthermore, NCs with mixed halide composition (either Cl/Br or Br/I) can be prepared either by direct synthesis or by mixing pre-synthesized NCs with different halide compositions, via inter-particle anion exchange, as discussed in section 8.3. The mixed halide NCs have optical absorption bands that are at intermediate spectral positions compared to their pure halide counterparts and are much broader than in the pure halides, indicating that they contain various populations of [PbX$_6$]$^{4-}$ octahedra with different combinations of halide ions, as also supported by density functional theory (DFT) calculations. Finally, section 8.4 will depict the transformation reaction of the Cs$_4$PbBr$_6$ NCs into strongly fluorescent CsPbBr$_3$ NCs, which can be triggered via an insertion reaction with additional PbBr$_2$. Not only does this allow for the synthesis of large CsPbBr$_3$ NCs with high level of control over the size (from 9 up to 37 nm), but it also opens up a reliable post-synthesis method for the fabrication of novel NC compositions.

8.2 Synthesis and characterization of Cs$_4$PbX$_6$ nanocrystal

The Cs$_4$PbBr$_6$ NCs were prepared by modifying the traditional synthesis approach for CsPbBr$_3$ NCs, in practice by using an excess of Cs-oleate and lowering the reaction temperature, as detailed section 8.2. As seen from the (TEM) images of figure 8.2a-d and appendix 8.1, this resulted in nearly monodisperse Cs$_4$PbBr$_6$ NCs ranging from 9 nm to 37 nm. The monodispersity of the Cs$_4$PbBr$_6$ NCs was such that it resulted in large areas of monolayer self-assemblies and 3D supercrystals (see also appendix 8.2). The size of the NCs could be controlled by tuning the reaction temperature and the time. HRTEM, as shown in figure 8.1e and XRD, see figures 8.2f and appendix 8.3a) indicated that all the NCs have the hexagonal Cs$_4$PbBr$_6$ phase and no CsPbBr$_3$ phase was present. All the Cs$_4$PbBr$_6$ NC dispersions were colorless, with the smaller NC dispersions being completely transparent and the larger ones (from 17 nm and bigger) being turbid. The samples had a strong and
narrow optical absorption band at 314 nm, regardless of NC size (figures 8.2g and appendix 8.3b), and matching previous reports on bulk Cs₄PbBr₆ powders and films. This supports the fact that the [PbX₆]⁴⁻ octahedra in the Cs₄PbBr₆ NCs are completely decoupled, and thus the size of the NCs does not have any remarkable effect on the band structure. In comparison, CsPbBr₃ NCs still exhibit quantum confinement effects for sizes around 8-9 nm and beyond (this point is further discussed in later sections of this work). No strong PL was observed from any of the Cs₄PbBr₆ NCs. This matches previous reports on Cs₄PbBr₆ films and crystals, in which the excitonic PL decayed significantly at temperatures above 100 K. All samples of Cs₄PbBr₆ NCs, as well as the corresponding Cl and Br compositions (discussed later), prepared by us did exhibit a weak PL band around 380 nm, but this was independent of the halide composition, and was therefore assigned to ligands emission, since a similar emission was observed from a mixture of the surfactants used for their syntheses.

To confirm the wide band gap of Cs₄PbBr₆, DFT calculations were carried out within periodic boundary conditions on the experimentally reported structure of Cs₄PbBr₆. The calculated density of states is displayed in figure 8.3a (see also appendix 8.4) that compares the density of states of Cs₄PbBr₆ with that of CsPbBr₃). The Br-based valence band and the Pb-based conduction bands are separated by a band gap of 3.99 eV, in close agreement with the band gap value of 3.95 eV by Nikl et al. for Cs₄PbBr₆ films (the same value of 3.95 eV was found also by us on the Cs₄PbBr₆ NCs of this work). Interestingly, DFT calculations evidenced almost no band dispersion, within 30 meV or less across different k-points, suggesting closely to uncoupled PbBr₆ octahedra.
Figure 8.2. Overview of Cs$_4$PbBr$_6$ nanocrystal. TEM images of (a) 9.2 nm, (b) 14.7 nm, (c) 27.7 nm and (d) 37.0 nm Cs$_4$PbBr$_6$ NCs. (e) HRTEM of Cs$_4$PbBr$_6$ NC. (f) XRD patterns of different sized Cs$_4$PbBr$_6$ NCs matching the Cs$_4$PbBr$_6$ reference pattern (98-002-5124). (g) Optical absorption spectra of different sized Cs$_4$PbBr$_6$ NCs, characterized by a strong absorption band at 314 nm, independent of the NC size. (h) DFT calculation confirming the large band gap of 3.99 eV, as well as the strongly localized DOS.

Next to the Cs$_4$PbBr$_6$ NCs, nearly monodisperse Cs$_4$PbCl$_6$ (17 ± 1.4 nm) and Cs$_4$PbI$_6$ NCs (10 ± 0.8 nm) could be synthesized, by simply replacing the PbBr$_2$ precursor with PbCl$_2$ or PbI$_2$, respectively (figure 8.3a and b and appendix 8.5). HRTEM, as shown in inset figure 8.3c and d respectively. As in the case of Cs$_4$PbBr$_6$, the Cs$_4$PbCl$_6$ and Cs$_4$PbI$_6$ have wide band gaps (respectively 284 nm and 367 nm as shown in figure 8.3e). Furthermore, XRD (figure 8.3f and appendix 8.6) indicate that the Cs$_4$PbCl$_6$ and Cs$_4$PbI$_6$ NCs match their reported pure Cs$_4$PbX$_6$ phases. All Cs$_4$PbX$_6$ NCs, including the Cs$_4$PbI$_6$ NCs, remained stable under ambient conditions over the course of at least one month, without any sign of degradation (appendix 8.7). Although all Cs$_4$PbX$_6$ NCs could simply be separated by centrifugation, due to the lower solubility of the Cs$_4$PbX$_6$ phase compared to the CsPbX$_3$. 
phase,\textsuperscript{26} they could be washed several times with polar solvents like acetonitrile and isopropanol without being dissolved (appendix 8.8). The Cs\textsubscript{4}PbI\textsubscript{6} NCs still remained susceptible towards polar solvents, and were readily dissolved in isopropanol and acetonitrile, as NC dispersions quickly turned dark red/brown due to the formation of solvated I\textsuperscript{-} ions.

![Figure 8.3. Overview of Cs\textsubscript{4}PbCl\textsubscript{6} and Cs\textsubscript{4}PbI\textsubscript{6} NCs. TEM images of (a) Cs\textsubscript{4}PbCl\textsubscript{6} and (b) Cs\textsubscript{4}PbI\textsubscript{6} NCs, with HRTEM images in their respective insets (c and d). (e) XRD patterns of pure Cs\textsubscript{4}PbX\textsubscript{6} NCs, showing evident shifts towards larger unit cells when going from Cl to Br and then to I. (f) Absorption spectra of pure Cs\textsubscript{4}PbX\textsubscript{6} NCs.]

8.3 The case of mixed Cs\textsubscript{4}Pb(Br:Cl)\textsubscript{6} and Cs\textsubscript{4}Pb(Br:I)\textsubscript{6} nanocrystal

Similarly to the amply reported cases of CsPbX\textsubscript{3},\textsuperscript{1,27-28} Cs\textsubscript{4}PbX\textsubscript{6} NCs as well can form stable mixed halide compositions, as shown in figure 8.4. For example, both Cs\textsubscript{4}Pb(Br:Cl)\textsubscript{6} (16.5 +3.0 nm) or Cs\textsubscript{4}Pb(Br:I)\textsubscript{6} (13.6 + 3.4nm) NCs were prepared by mixing 14.7 nm Cs\textsubscript{4}PbBr\textsubscript{6} NCs with 10.0 nm Cs\textsubscript{4}PbCl\textsubscript{6} NCs or 17.0 nm Cs\textsubscript{4}PbI\textsubscript{6} NCs (figure 8.4a and b respectively). With preservation of size distributions, the NCs underwent interparticle halide exchange, resulting in the mixed Cs\textsubscript{4}Pb(Br:X)\textsubscript{6} phase.\textsuperscript{28} The formation of the mixed phases could be inferred from the XRD patterns, as shown in figure 8.4c. After the exchange, the NCs had lattice parameters that were intermediate between the starting pure halide NCs, and no diffraction peaks could be observed for the pure starting phases. In the optical absorption spectra, intermediate band gaps of 305 nm for the Cs\textsubscript{4}Pb(Br:Cl)\textsubscript{6} NCs and 343 nm (for the Cs\textsubscript{4}Pb(Br:I)\textsubscript{6} NCs were observed (figure 8.4d). Mixed Cs\textsubscript{4}Pb(Br:Cl)\textsubscript{6} and Cs\textsubscript{4}Pb(Br:I)\textsubscript{6} NCs could also be obtained by directly starting with mixed PbX\textsubscript{2} precursors (by partially replacing PbBr\textsubscript{2} with PbCl\textsubscript{2} or PbI\textsubscript{2} prior to the synthesis), as shown in appendix 8.9. The directly obtained mixed Cs\textsubscript{4}PbX\textsubscript{6} NCs also exhibited properties intermediate to their respective pure phases.

The Cs\textsubscript{4}PbX\textsubscript{6} NCs with mixed halide composition exhibited a significantly broader absorption band compared to the pure Cs\textsubscript{4}PbX\textsubscript{6} NCs (figure 8.4d and appendix 8.9d). This is markedly different from the case of CsPbX\textsubscript{3} NCs with mixed halide composition reported in previous works (which could be prepared by partial anion exchange as well), for which the absorption spectrum (and the PL spectrum) remained narrow.\textsuperscript{27-28} Focusing for example on the Br:I mixed composition, it can be stated that in the CsPbX\textsubscript{3} 3D perovskite structure, all the [PbBr\textsubscript{6-x}I\textsubscript{x}]\textsuperscript{4-} octahedra are electronically coupled and such coupling dictates the overall band structure. In the Cs\textsubscript{4}PbX\textsubscript{6} case, as already stated, the octahedra are no longer electronically coupled and the absorption is due to a collection of electronic transitions within the single [PbX\textsubscript{6}]\textsuperscript{4-} clusters. Therefore, the overall optical absorption from Cs\textsubscript{4}Pb(Br:I)\textsubscript{6} can be considered as a summation of the independent, weighted contributions from the
different populations of octahedra present in the sample. Note that each population differs by the others by the distinct numbers of I and Br ions (totaling 6) coordinating the Pb$^{2+}$ ion, i.e. [PbBr$_{6-x}$I$_x$]$^{4-}$ with $x = 0, 1, 2$ up to 6, and by the specific arrangement of the anions at the six corners of the complex with Pb$^{2+}$. Consequently, each population will be characterized by its own electronic transitions. The broadening in the absorption is thus explained by the different spectral positions, detailed features and relative contributions of each of these populations within a single NC.

The optical properties of the pure and mixed-halide NCs were also investigated by means of hybrid time-dependent DFT (TDDFT) calculations including spin-orbit coupling (SOC), see section 4.2 for further details. The TDDFT calculations were carried out on a simplified model made by a single PbX$_{6-x}$Y$_x$ cluster (X, Y= I, Br or Br, Cl) in cubic symmetry (total charge -4), where the Cs cations are replaced by 8 point charges, each of +0.5e, placed at the corner cubic sites, equivalent to an overall neutralizing charge of +4, see Figure 4e. The accuracy of the model has been validated through comparative calculations on both the [Cs$_8$PbBr$_6$]$^{4+}$ cluster extracted from the XRD structure and the charge-compensated PbBr$_6^{4-}$ anion, delivering a HOMO-LUMO gap difference within 0.2 eV; this simplified model is also justified in light of the vanishingly small band dispersion found by periodic DFT calculations. The employed model allowed us to effectively capture the optical transition features of individual NCs, beyond a simple single particle approximation. Notably, the effect of SOC, established in 3D and 2D lead-halide perovskites, is found to be relevant also in the case of 0D NCs, as it introduces a decrease of the HOMO-LUMO gap and a red-shift of the calculated absorption spectra by as much as 0.5 eV. This is due to both the stabilization of the unoccupied Pb 6$p$ states (~0.3 eV) and the destabilization of the occupied halide $p$ states (~0.2 eV for the X=I case). The calculated absorption spectra for charge compensated PbI$_6$, PbBr$_6$ and for a range of I-Br intermediate compositions are reported in figure 8.4f. The calculations almost quantitatively reproduce the absorption spectra of the pure Cs$_4$PbX$_6$ NCs for X = I and Br (355 and 319 nm against experimental values for the corresponding NCs of 367 and 314 nm, respectively). The mixed I/Br compositions show an almost monotonic variation of the absorption maxima across the explored compositional range. Notably, for the intermediate PbI$_3$Br$_3$ system, an absorption maximum at 334 nm was predicted, in agreement with the experimental maximum of 343 nm for the mixed halide system. Also, the broadening of the experimental spectrum for the mixed halide system is compatible with a full range of intermediate compositions, which was calculated with a spread of ca. ±0.15 eV from the median PbI$_3$Br$_3$ system. Some preliminary calculations for the X = Cl case (data not shown) were also performed. In that case, however, the optical transitions are underestimated by this approach, providing an absorption maximum of 316 nm against an experimental value of 284 nm for Cs$_4$PbCl$_6$. This is likely due to the unbalanced description of the halide series by (hybrid) DFT, which can be corrected by GW calculations.
Figure 8.4. Data of mixed CsPb(Br:X)$_6$ nanocrystals, with X = Cl$^-$ or I$^-$. TEM images of NCs obtained after inter particle anion exchange of Cs$_4$PbBr$_6$ NCs with (a) Cs$_4$PbCl$_6$ and (b) Cs$_4$Pbl$_6$. (c) XRD patterns confirm intimate crystal phase after exchange; (d) optical absorption spectra recorded on pristine and mixed NCs with intermediate, broadened absorptions; (e) sketch of the PbX$_6$ model used for the calculations, with point charges at the cubic sites; (f) simulated absorption spectra of charge-compensated PbI$_6$, PbBr$_6$ and intermediate compositions. The calculated TDDFT excitation energies and oscillator strengths have been convoluted by Gaussian functions with a $\sigma$=0.075 eV.

8.4 Transforming Cs$_4$PbBr$_6$ NCs into luminescent CsPbBr$_3$ perovskite NCs

The hexagonal Cs$_4$PbBr$_6$ NCs reported in this chapter have high band gaps and therefore are essentially insulators. Also, the lack of strong, excitonic fluorescence prevents their use in applications such as active materials in scintillators. On the other hand, the Cs$_4$PbBr$_6$ NCs could be transformed into CsPbBr$_3$ NCs by a post-synthesis insertion reaction with PbBr$_2$, as shown in figure 8.5a and b. Here, the Cs$_4$PbBr$_6$ NCs were exposed to a solution of PbBr$_2$ dissolved in OlaM, OA and toluene. As shown in figure 8.5c and d as well as in appendix 8.10, this results in the reshaping of the NCs from a spherical/hexagonal shape to cubic NCs. Although the NCs underwent a shape transformation, the overall size was basically preserved. It is important to note that the NCs did not undergo any transformation in the absence of PbBr$_2$, under the same reaction conditions (as shown in appendix 8.11). Due to the monodispersity of the starting Cs$_4$PbBr$_6$ NCs, this resulted in close to monodisperse cubic CsPbBr$_3$ NCs within a wide range of sizes (8.8 nm – 34.0 nm, see also appendix 8.10). These data strongly support the idea that the Cs$_4$PbBr$_6$ NCs did undergo a transformation to CsPbBr$_3$ NCs, and exclude the possibility that they were dissolved and that new CsPbBr$_3$ NCs were nucleated. In this latter scenario, the sizes of the starting Cs$_4$PbBr$_6$ NCs and those of the final CsPbBr$_3$ NCs would be uncorrelated, which is contrary to the presented results. With this approach, large (> 15 nm) and yet nearly monodisperse
CsPbBr₃ NCs could even be synthesized, which currently remains a challenge in conventional CsPbBr₃ NC synthesis methods.³³-³⁴

The formation of the CsPbBr₃ phase resulted in a large shift of the absorption band (from 314 nm to 510 nm) and the emergence of a strong green PL in the 511 - 522 nm range, depending on the size of the pristine NCs (figure 8.5e and appendix 8.12a). Furthermore, no absorption feature from the pristine NCs was observed (appendix 8.12b). Although this implies that the transformation is complete, the PLQYs only ranged from ~26% for the smallest (~9 nm) NCs to 2.4% for the largest (34 nm) NCs. The smallest CsPbBr₃ NCs still exhibited a weak confinement compared to the bulk-like emission of the larger NCs (appendix 8.12a). Yet, for such small NCs, the PLQY was lower than that reported from NCs of similar size and prepared by direct synthesis. Upon increasing the reaction temperature (from 80 °C to 130 °C, and a four fold amount of PbBr₂), the PLQY for the smallest NCs could be increased from 26% to 47%. For now, these lower QY values (compared to those of NCs prepared by direct synthesis) indicate that the transformation from the hexagonal Cs₄PbBr₆ to the cubic CsPbBr₃ phase may entail the formation of structural defects acting as trap states, especially at lower temperatures and lower PbBr₂ concentrations, and suggests that such two-step synthesis would require further tuning. Additional optimizations of this conversion reaction are likely to push the QY to values close to those of directly synthesized CsPbBr₃ NCs. The transformation of the Cs₄PbBr₆ NCs was also confirmed by XRD, as reported in figure 8.5f and appendix 8.12c. Here, the diffraction pattern from the transformed CsPbBr₃ NCs matched that of the cubic/orthorhombic phase, with no measurable diffractions from the pristine NCs. The Cs₄PbCl₆ NCs too could be converted into CsPbCl₃ NCs by the addition of PbCl₂. Figure S13 reports the optical data referred to the Cs₄PbCl₆ → CsPbCl₃ transformation. In the Cs₄PbI₆ → CsPbI₃ case, the CsPbI₃ NCs were quickly degraded and their PL died rapidly, which is expected due to the well-known intrinsic instability of the pure CsPbI₃ phase.³⁵-³⁶ These reactions were not further investigated and will require additional work.
Figure 8.5. Insertion reaction of PbBr₂ into Cs₄PbBr₆ nanocrystals, resulting in the formation of CsPbBr₃ nanocrystals. (a) Reaction of Cs₄PbBr₆ with PbBr₂, forming CsPbBr₃. (b) Phase transformation of the hexagonal Cs₄PbBr₆ phase to the cubic CsPbBr₃ phase after insertion of additional PbBr₂. (c and d) TEM images of different sized Cs₄PbBr₆ NCs before and after their transformation into CsPbBr₃, indicating the preservation of size but transformation of the hexagonal shape to a cubic shape. (e) Optical absorption and PL of Cs₄PbBr₆ before and after the insertion reaction, highlighting the large shift of the band gap, the disappearance of the strong Cs₄PbBr₆ absorption feature and the appearance of a strong green PL after the transformation. (f) XRD patterns before and after the insertion reaction, confirming the rearrangement of the crystal lattice from hexagonal Cs₄PbBr₆ to cubic CsPbBr₃. XRD references patterns are 98-010-9295 for CsPbBr₃ and 98-002-5124 for Cs₄PbBr₆.

8.5 Conclusions
In conclusion, this chapter reports a method for preparing monodisperse Cs₄PbX₆ (X = Cl, Br, I) NCs and discusses their mixed halide compositions. Contrary to recent reports, there was no evidence of a green emission from these 0D NCs. The Cs₄PbBr₆ NCs were used as a starting point to synthesize monodisperse CsPbBr₃ NCs by reacting them with PbBr₂. This transformation further proves that the perovskite crystal structure is extremely versatile, which allows for an extreme reorganization of the lattice. In the case of NCs, this enables the size and crystallinity to be preserved. One important future development in this area of research will be to understand how the detailed structural intermediates of the transformation work and how to use of this type of ‘insertion reaction’ in other classes of NCs.

8.6 Acknowledgements
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8.7 Experimental section

Chemicals. Lead(II) chloride (PbCl₂, 99.999% trace metals basis), lead(II) bromide (PbBr₂, 99.999% trace metals basis), lead(II) iodide (PbI₂, 99.999% trace metals basis), cesium carbonate (Cs₂CO₃, reagentPlus, 99%), n-hexane (HEX, 99.5%), isopropyl alcohol (IPrOH, ≥99.7%), acetonitrile (AcN, anhydrous, 90%), octadecene (ODE, technical grade, 90%), oleylamine (OLAM, 70%) and oleic acid (OA, 90%) were purchased from Sigma-Aldrich. Toluene (TOL, anhydrous, 99.8%) was purchased from Carlo Erba reagents. All chemicals were used without any further purification.

Cs₄PbX₆ NCs synthesis and purification. All syntheses were performed in air and without any pre-dried chemicals or solvents. In a typical synthesis, PbX₂ (0.1 mmol) was dissolved in 5 mL ODE, 0.2 mL OA and 1.5 mL OLAM in a 20 mL vial on a hotplate set at 150 °C. After the PbX₂ was completely dissolved (around 100 °C), the vial was moved to a room temperature (RT) hotplate, and the solution was allowed to cool. When the temperature reached the optimal value (80 °C for PbBr₂, 100 °C for PbCl₂ or 60 °C for PbI₂), 0.75 mL of Cs-OA (0.4 g Cs₂CO₃ dissolved in 8 mL OA in a 20 ml vial on a hotplate set to 150 °C) was swiftly injected. After about 30 seconds the reaction turned turbid white and, depending on the required size, was quickly cooled down after 0-10 min to RT with a cold water bath. The NCs were directly washed via centrifugation (at 4500 rpm for 10 minutes), followed by redispersion in 6 ml TOL (or HEX for optical measurements).

Cs₄Pb(Br:X)₆ (X = Cl, I) NCs synthesis and purification via inter-particle anion-exchange. All inter-particle anion-exchange were performed in air and without any pre-dried chemicals or solvents similar to previous reports. In a typical exchange, equal volumetric amounts (from the purified NC solutions as described above) of Cs₄PbBr₆ and Cs₄PbCl₆ or Cs₄PbI₆ and were left stirring overnight at room temperature. The NCs were not further purified.

Reaction of Cs₄PbBr₆ NCs with PbBr₂ to yield CsPbBr₃ NCs and their purification. All syntheses were performed in air and without any pre-dried chemicals or solvents. In a typical reaction, 0.5 ml of Cs₄PbBr₆ NC solution was diluted in 2 ml of TOL and heated on a hotplate set at 80 °C. After the temperature was stable, 50 µl of PbBr₂ precursor was injected (1 mmol PbBr₂ dissolved in 0.5 mL TOL, 0.25 mL OA and 0.25 mL OLAM). Within 1 minute, the solution started turning green and after 15-60 minutes, depending on the size of the Cs₄PbBr₆ NCs, the reaction was cooled down to RT with a cold water bath. The NCs were directly washed by centrifugation (at 4500 rpm for 10 minutes), followed by redispersion in TOL.

Transmission Electron Microscopy (TEM). Conventional TEM images were acquired on a JEOL JEM-1011 microscope equipped with a thermionic gun at 100 kV accelerating voltage. High-resolution TEM (HRTEM) imaging was performed on a JEOL JEM-2200FS microscope equipped with a Schottky gun operated at 80-200 kV accelerating voltage, a CEOS spherical aberration corrector in objective lens enabling a spatial resolution of 0.9 Å, and an in column Ω-filter. The samples were prepared by drop casting diluted NC suspensions onto 200 mesh carbon-coated copper grids for conventional TEM imaging, and 400 mesh ultrathin carbon-coated copper grids for HRTEM imaging, respectively. To avoid or reduce the diffusion of Pb induced by the electron beam, the images were...
taken by summing multiple fast acquisitions (≤0.2 sec) after drift correction, by using a K2 direct detection camera (Gatan, Inc.), allowing low doses (<5e-/pixel·sec).

**Powder X-ray Diffraction (XRD) Analysis.** XRD patterns were obtained using a PANalytical Empyrean X-ray diffractometer equipped with a 1.8 kW Cu Kα ceramic X-ray tube, PIXcel3D 2x2 area detector and operating at 45 kV and 40 mA. The diffraction patterns were collected in air at room temperature using Parallel-Beam (PB) geometry and symmetric reflection mode. All XRD samples were prepared by drop casting a concentrated solution on a zero diffraction silicon wafer.

**Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).** ICP-OES analysis performed on an iCAP 6000 spectrometer (ThermoScientific) was used to quantify the Pb content in the solutions of CsPbBr$_3$ and Cs$_x$PbBr$_6$ NCs. Prior to measurements, the samples were decomposed in aqua regia (HCl/HNO3 = 3/1 (v/v)) overnight.

**Optical Absorption Spectroscopy.** The spectra were taken on a Varian Cary 5000 UV–vis–NIR spectrophotometer. Samples were prepared by diluting the NC solutions in hexane or toluene in 1 cm path length quartz cuvettes.

**Photoluminescence (PL) and Photoluminescence Quantum Yield (PLQY) measurements.** The PL spectra were taken on a Varian Cary Eclipse spectrophotometer. Samples were prepared by diluting the various NC solutions in toluene, in quartz cuvettes with a path length of 1 cm. PLQY measurements were carried out in solutions with an Edinburgh Instruments fluorescence spectrometer (FLS920), which included a xenon lamp with monochromator for steady-state PL excitation. A calibrated integrating sphere was used for PLQY measurements. The NCs/perovskite NCs solutions in toluene were prepared in quartz cuvettes and diluted to 0.1 optical density at the excitation wavelength 400 nm.

**Density functional theory (DFT) calculations.** The Amsterdam Density Functional program package (ADF2014)$^{38, 39}$ has been used for all the calculations. Starting from the experimental molecular geometries of Cs$_3$PbX$_6$ NCs (X= Br, I), DFT single point (SP) energy calculations were carried out in the gas phase on selected NC clusters, modelling the various feasible mixed halide composition. In particular, the B3LYP exchange-correlation functional (including the Vosko-Wilk-Nusair LDA parametrization and 20% of Hartree-Fock) was used, together with a Slater type TZP basis set for all the atoms (the cores 1s-2p, 1s-3p, 1s-4p and 1s-4d were kept frozen, respectively for Cl, Br, I and Pb) and a ZORA Hamiltonian to include relativistic effects. Either the scalar or the spin-orbit (SO) ZORA Hamiltonian were carried out, the latter used in order to consider spin orbit coupling (SOC) effects. Time Dependent (TD) DFT calculations have been performed using the B3LYP exchange-correlation functional. The relativistic TDDFT formalism as implemented in ADF for closed-shell molecules, including SOC, is based on the ZORA two components Hamiltonian.$^{40, 41}$ Relativistic spectra have been evaluated taking into account the SOC in a self-consistent perturbative way.$^6$ The 12 lowest transitions have been considered in each case. The absorption spectra have been simulated by interpolating the computed transitions by Gaussian functions with a broadening $\sigma=0.075$, corresponding to an FWHM of 0.18 eV, thus matching the experimental one. The TDDFT calculations are carried out on negatively-charged [PbX$_6$]$^-$ clusters, where the caesium cations are replaced by including in the Fock operator an electric field due to point charges, fixed in the octahedral corners and formally equivalent to an overall charge of +4. The Pb-X distances are taken from the corresponding 3D perovskite at 3.164 and 2.950 Å for X=I and Br, respectively. The accuracy of the model in reproducing the main electronic features has been validated through comparative calculations on both the neutral Cs$_3$PbX$_6$ NC and the PbX$_6$: anion at the same level of theory showing a variation of the calculated HOMO–LUMO gap within less than 0.2 eV. Periodic Boundary Conditions DFT calculations were performed on the Cs$_3$PbBr$_6$ crystal at its experimental geometry and cell parameters, using the QuantumEspresso simulation package.$^7$ PBE calculations have been performed by using ultrasoft pseudopotentials with a cutoff on the wavefunction of 25 Ry (200 Ry on the charge density) and uniform grid of k-points in the Brillouin Zone.$^8$

References
Appendices

Appendix 8.1. Different sized $\text{Cs}_4\text{PbBr}_6$ NCs. Scale bars correspond to 100 nm.

Appendix 8.2. Additional TEM images of $\text{Cs}_4\text{PbBr}_6$ NCs. (left) Large area of $\text{Cs}_4\text{PbBr}_6$ NCs. (right) Large self-assembled cluster for $\text{Cs}_4\text{PbBr}_6$. 
Appendix 8.3. Structural and optical data of Cs₄PbBr₆ NCs with various sizes. a) Diffraction patterns of different sized Cs₄PbBr₆ NCs. b) Absorption of different sized Cs₄PbBr₆ NCs. Cs₂PbBr₆ reference pattern 98-002-5124

Appendix 8.4. Density of states calculations for CsPbBr₃ and Cs₄PbBr₆.

Appendix 8.5. (left) Large area TEM images of Cs₄PbCl₆ NCs (left) and Cs₄Pbl₆ NCs (right).
Appendix 8.6. XRD patterns for Cs$_4$PbCl$_6$ NCs (top) and Cs$_4$PbI$_6$ NCs (bottom).

Appendix 8.7. Cs$_4$PbX$_6$ NCs after 1 month of storage. TEM images of (a) Cs$_4$PbCl$_6$, (b) Cs$_4$PbBr$_6$, and (c) Cs$_4$PbI$_6$ NCs stored for one month under ambient conditions. (d) Absorption spectra indicated no degradation of NCs.
Appendix 8.8. Cs$_4$PbCl$_6$ NCs and Cs$_4$PbPb$_6$ NCs after washing twice with isopropanol and acetonitrile.

a) XRD patterns for Cs$_4$PbCl$_6$ NCs and Cs$_4$PbPb$_6$ NCs after washing twice with isopropanol and acetonitrile. TEM images of b) Cs$_4$PbCl$_6$ NCs and c) Cs$_4$PbPb$_6$ NCs after washing. d) The optical absorption spectra indicated no degradation of NCs after washing with polar solvents.

Appendix 8.9. Cs$_4$Pb(Cl:Br)$_6$ and Cs$_4$Pb(Br:I)$_6$ NCs obtained via direct synthesis. TEM images of (a) Cs$_4$Pb(Cl:Br)$_6$ NCs and (b) Cs$_4$Pb(Br:I)$_6$ NCs obtained via direct synthesis. (c) XRD patterns prove the mixed halide Cs$_4$PbBr$_6$ NCs and confirm intermediate lattice parameters compared to the pure phases. (d) Optical absorption spectra of the mixed halide NCs and the pristine NCs. Scale bars in (a) and (b) correspond to 100 nm.
Appendix 8.10. Overview of CsPbBr₃ NCs obtained via insertion reaction of PbBr₂ on Cs₄PbBr₆. All scale bars correspond to 100 nm.
Appendix 8.11. Blanc experiments for transformation reactions. **a)** TEM image and **b)** absorption of Cs$_4$PbBr$_6$ NCs after (45 min) insertion reaction, without the addition of PbBr$_2$

Appendix 8.12. Optical and structural data from different sized CsPbBr$_3$ NCs obtained through the insertion reaction of PbBr$_2$ into Cs$_4$PbBr$_6$. **a)** PL and PLQY, **b)** absorption and **c)** XRD data of different sized of CsPbBr$_3$ NCs CsPbBr$_3$ XRD reference pattern 98-002-5124.

Appendix 8.13. Insertion reaction of PbI$_2$ into Cs$_4$PbBr$_6$. Optical absorption of Cs$_4$PbCl$_6$ NCs (magenta) and optical absorption (black) and PL (blue) spectra of the CsPbCl$_3$ NCs obtained through the insertion reaction of PbCl$_2$ into CsPbCl$_3$. The absorption tail for the CsPbCl$_3$ NCs at longer wavelengths is most likely due to aggregation effects.
Chapter IX

A case study into the optical properties of Cs$_4$PbBr$_6$
Chapter IX: A case study into the optical properties of Cs₄PbBr₆*

Abstract: Although the optical properties of Cs₄PbBr₆ are dominated by optical transitions which are localized in the individual octahedra, recent results have demonstrated a highly efficient green photoluminescence from Cs₄PbBr₆ powders and single crystals. These results are controversial, and they contradict the results that were discussed in the previous chapter. This chapter provides a closer look at this material, in the form of both nanocrystals and bulk crystals/thin films, and will discuss the contrasting opinions on their properties. It will also propose potential applications and provide some suggestions for future experiments.

9.1 Introduction

As discussed in chapter 4, the remarkable properties of LHPs can directly be related to their peculiar crystal structure, the ABX₃ perovskite structure, in which corner sharing BX₆ octahedra form a cubic framework, and A⁺ cations fill the voids. The first account of lead halides crystalized in the perovskite structure dates back to 1893, when different colored powders with a CsPbX₃ composition, with the color depending on the halide, could be prepared. As was reported in that same work, cesium lead halides can also crystalize as white powders with a CsPbX₆ stoichiometry, regardless of the type of halide that is used. In this phase, the PbX₆⁻⁴ octahedra are no longer corner shared, thus the photoexcited carriers in these materials experience a much stronger quantum confinement than that of CsPbX₃. For this reason, the Cs₄PbX₆ phase is often called a “zero dimensional (0D) perovskite”, although it bears no structural resemblance to the perovskite structure. The Cs₄PbX₆ phase remained almost completely forgotten during the 20th century, with only a few works investigating their optical properties (specifically by Nikl and Kondo et al. during the 1990s and 2000s). It was not until 2016 that these Cs₄PbX₆ compounds started to generate interest again, mainly as a result of the surging pursuit in LHP and related metal halides, and papers began to report Cs₄PbBr₆ powders with strong and stable green photoluminescence (PL). Soon after, the first publications on Cs₄PbX₆ nanocrystals (NCs) emerged. Interestingly, in stark contrast to the highly emissive CsPbX₃ NCs that were first synthesized in 2015 and the highly green emitting Cs₄PbBr₆ powders, these Cs₄PbX₆ NCs exhibited no PL; instead, they had optical properties that were similar to those described in the first reports on Cs₄PbX₆ in 1893 and in the 1990s. Furthermore, these optical properties were also similar to those of individual [PbBr₄]⁴⁻ clusters. Although the majority of papers on this topic agree that these materials have a large bandgap (>3.2 eV), the origin of the absorption in the visible spectrum and of the green PL that has been reported for various Cs₄PbBr₆ NCs, powders and single crystals is still under debate. The

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proposed origin of the green PL is either intrinsic to Cs$_4$PbBr$_6$ (due to the presence of defects),\textsuperscript{11-12, 14, 17-26} or from contamination by CsPbBr$_3$ NC-like impurities.\textsuperscript{13, 27-42}

In this chapter, the literature on OD cesium metal halides, focusing on Cs$_4$PbX$_6$, both in their bulk form and as NCs, will be discussed. Both old and recent literature concerning this phase will presented, and current attributions to the origin of the strongly downshifted PL compared. First, section 9.2 will give a general description of the crystal structure of Cs$_4$PbBr$_6$. The following section, 9.3, will overview of the green luminescence reported in Cs$_4$PbBr$_6$ films, single crystals and powders. Section 9.4 will summarize the know defects and defect emission in perovskite and perovskite-like materials, and section 9.5 will compare this with the observed green luminescent reported in Cs$_4$PbBr$_6$. The bulk Cs$_4$PbBr$_6$ materials will be compared to their NCs counter parts in, in section 9.6, as well as how Cs$_4$PbBr$_6$ can be transformed in CsPbBr$_3$, and vice versa. The final section, section 9.7 will propose further experiments that will help to clarify the optical properties as well as discuss potential future applications with these materials.

9.2 A closer look at the Cs$_4$PbBr$_6$ crystal structure

We start the perspective with a description of the cubic (3D) LHP crystal structure, due to its relation with the Cs$_x$PbX$_y$ phase. In this structure, [PbX$_6$]$^4^-$ octahedra corner share each X anion between two octahedra, resulting in a cubic (or pseudo cubic, like orthorhombic/tetragonal, depending on the sizes of the A and X ions) Pb-X-Pb framework,\textsuperscript{43} as is shown in figure 9.1a. To charge balance and provide geometrical stability, the lead-halide framework can be stabilized by monovalent cations (often depicted as ‘A’) which can be in the form of Cs$^+$, or organic cations like methylammonium (MA) or formamidinium (FA). The rules on whether perovskite structures are stable or not (the so called Goldschmidt tolerance factor) are mainly defined by the ionic radii (r) of A, B and X, and can be determined by using formula 9.1:

$$(9.1) \text{Goldschmidt tolerance factor, } t = \frac{r_A + r_X}{\sqrt{2(r_b + r_X)}},$$

with stable perovskites generally forming with $t \ 0.7 - 1.1$.\textsuperscript{1} Long before LHPs became popular in photovoltaics and NC chemistry, it had already been reported that cesium lead halides can crystallize in two other stoichiometries: CsPb$_2$X$_5$ and Cs$_4$PbX$_6$.\textsuperscript{2} The Cs$_4$PbX$_6$ phase has a crystal structure that is very different from that of CsPbX$_3$; while the [PbX$_6$]$^4^-$ octahedra in Cs$_4$PbX$_6$ are still surrounded by 8 Cs$^+$ atoms, which is similar to the cubic LHP phase, the halides in Cs$_4$PbX$_6$ are no longer shared between [PbX$_6$]$^4^-$ octahedra. Furthermore, the Cs$^+$ atoms in Cs$_4$PbX$_6$ are no longer all occupying identical crystallographic sites, but actually two distinct sites.\textsuperscript{29} Overall, this results in a rhombohedral (R$\overline{3}$c) Cs$_4$PbX$_6$ phase, as is shown in figure 9.1a. An alternative way to perceive Cs$_4$PbBr$_6$ is to take the CsPbBr$_3$ phase and remove $\frac{3}{4}$ of the PbX$_2$ while still maintaining the cubic framework of Cs$^+$ ions and keeping the remaining PbX in [PbX$_6$]$^4^-$ octahedra. Due to the large voids that are created by the removal of PbX$_2$, the system strongly compresses and distorts, resulting in a Cs$_4$PbX$_6$ phase.\textsuperscript{29} In contrast to the cubic LHP phase, OD cesium lead halides seem to be less sensitive to the ratios of the ionic radii of the A, Pb, and X components, as a wide variety of A-Pb-X systems can crystallize in the rhombohedral A$_4$PbX$_6$ structure (with A = Cs, Rb, K; X = F, Cl, Br, I).\textsuperscript{44} This general rhombohedral A$_4$BX$_6$ structure is often referred to as the ‘K$_6$CdCl$_6$ structure’,\textsuperscript{45} and it can be found in a wide range of metals halides ($M = Sn, Cd, Mn, Mg, Ca$)
etc. and with $A = (\text{NH}_4, \text{Cs}, \text{Rb}, \text{K})$ with a set of formation rules that are similar to those of the Goldschmidt tolerance factor and are based on the ionic $B/X$ and $A/X$ radii.\textsuperscript{45} Although it is beyond the scope of this review, the 0D $A_4BX_6$ crystal structure can even be found in oxides such as $\text{Sr}_4\text{IrO}_6$ and $\text{Ca}_2\text{RuO}_6$.\textsuperscript{46}

Due to the (almost) perfect linear alignment of the $\text{Pb}^{2+}$ ions and the halide ions in the LHP framework, the $p$ orbitals of each $X^-$ ion perfectly overlap the $s$ and $p$ orbitals of the two $\text{Pb}^{2+}$ atoms it is shared with (figure 9.1b). This orbital overlap leads to a large orbital hybridization, resulting in a marked decrease in the bandgap from a single $[\text{PbX}_6]^{4-}$ cluster (about 4 eV in solution for $[\text{PbBr}_6]^{4-}$\textsuperscript{16} to CsPbBr$_3$ (about 2.15 eV, bulk). Due to the symmetry of the Cs$_4$PbX$_6$ phase, which is lower than the cubic/orthorhombic CsPbX$_3$ phase, one $[\text{PbX}_6]^{4-}$ octahedron in Cs$_4$PbBr$_6$ has two different $[\text{PbX}_6]^{4-}$ octahedra as its nearest neighbors, with $\text{Pb}-\text{Pb}$ distances of 8.7 Å and 10 Å, respectively (compared to a 5.9 Å $\text{Pb}-\text{Pb}$ distance between neighboring $[\text{PbX}_6]^{4-}$ octahedra in orthorhombic CsPbBr$_3$).\textsuperscript{29} As mentioned above, in Cs$_4$PbX$_6$, the $[\text{PbX}_6]^{4-}$ octahedra do not share halides, thus they exhibit negligible orbital overlap between neighboring octahedra, as is shown in figure 9.1b. As was reported in 1893 alongside with the first works on CsPbX$_3$, Cs$_4$PbX$_6$ powders are colorless, independent of the type of halide.\textsuperscript{2} Indeed, the reported bandgaps are all in the UV region, with Cs$_4$PbCl$_6 = 4.37$ eV, Cs$_4$PbBr$_6 = 3.95$ eV, and Cs$_4$PbI$_6 = 3.38$ eV, as is shown in figure 9.1c.\textsuperscript{3, 6, 8-9} The decoupled $[\text{PbX}_6]^{4-}$ octahedra in Cs$_4$PbX$_6$, compared to the halide coupled $[\text{PbX}_6]^{4-}$ octahedra in LHP, cause the bandgap Cs$_4$PbX$_6$ to shift towards values of free $[\text{PbX}_6]^{4-}$ clusters in solutions, and essentially leads to single molecule-like, excitonic absorption bands.\textsuperscript{13, 16, 29} The fact that Cs$_4$PbX$_6$ phases have bandgap values close to their respective free $[\text{PbX}_6]^{4-}$ clusters is also evident from the optical properties of a series of alkali metal halides ($AX$, $A = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$, $X = \text{Cl}, \text{Br}, \text{I}$) doped with $\text{Pb}^{2+}$.\textsuperscript{47} For these materials, the spectral position of the excitonic absorption is almost independent of the alkali metal ($\text{NaBr}:\text{Pb}^{2+} = 304$ nm, $\text{CsBr}:\text{Pb}^{2+} = 313$ nm Cs$_4$PbBr$_6 = 314$ nm),\textsuperscript{47-48} while it is strongly dependent on the halide ion. The single cluster behavior of $\text{Pb}^{2+}$ in Cs$_4$PbBr$_6$ is also supported by various density functional theory (DFT) calculations, which have confirmed that Cs$_4$PbX$_6$ compounds have large bandgaps (figure 9.1d).\textsuperscript{13, 17, 19, 29, 41}

That the dimensional reductions of the Pb-X-Pb framework in LHPs has a strong effect on the optical properties, is also evident in the lead iodide perovskites. For instance, cubic CsPbl$_3$ is thermally unstable at room temperature, and it undergoes a phase transition to an orthorhombic phase. Here, the lead iodide octahedra are disconnected and reordered into linear chains so that the dimensionality in the interconnection of the $[\text{PbX}_6]^{4-}$ octahedra is reduced from 3D to 1D,\textsuperscript{49} and an increase in the bandgap from 1.73 to 2.25 eV can be observed. Similarly, cubic FAPbl$_3$ undergoes a transition to a more stable non-perovskite hexagonal phase at low temperatures, with the lead iodide octahedra completely disconnected, resulting in the bandgap being significantly higher than in the cubic phase.\textsuperscript{50} Moreover, 2D Ruddlesden–Popper phases, as well as layered CsPb$_2$X$_5$, exhibit electronic, absorption and PL properties that are very different to those of the corresponding LHPs.\textsuperscript{51, 52
9.3 Green photo luminesces in Cs$_4$PbBr$_6$

Despite the wide band gap of Cs$_4$PbBr$_6$, several groups have recently reported a strong green PL as well as an absorption in the green region of the spectrum from Cs$_4$PbBr$_6$ powders, single crystals and NCs. This green PL from Cs$_4$PbBr$_6$ had already been observed in the early 1990s by Nikl et al., who conducted a series of experiments on CsX:Pb$^{2+}$, Cs$_4$PbX$_6$ and CsPbX$_3$, with the aim of studying the optical properties of Pb$^{2+}$ in different cesium halide matrices. It was noticed that the Cs$_4$PbBr$_6$ absorption around 4 eV often was accompanied by both a weak absorption and a strong PL in the green region around 2.4 eV (figure 9.2a and b). Nikl et al. concluded that “it is difficult to hold back the occurrence of CsPbX$_3$ (X = Cl, Br) phase completely”, and that “the unwanted coexistence of these two phases in the Cs$_4$PbX$_6$ crystals most probably arises because of an unavoidable incongruent melting crystal growth process”. Kondo et al. performed a similar series of experiments, and also concluded that “Cs$_4$PbBr$_6$ crystals usually coexist with the CsPbBr$_3$ and/or CsBr phases”. Nikl et al. further studied the coexistence of CsPbBr$_3$ and CsBr, and they hypothesized that the green luminescence that is seen in Pb-doped CsBr single crystals arose most likely from the presence of CsPbBr$_3$ quantum dots. Similarly, CsPbCl$_3$ NC-like clusters with a PL and absorption around 400 nm could be crystallized inside CsCl, and CsPbI$_3$ (in the yellow δ-phase) impurities were observed in Cs$_4$PbI$_6$ and CsI. The procedure of embedding perovskite NCs in a halide-based matrix was recently also extended to hybrid organic-inorganic perovskites, in which...
MAPbBr₃ NCs were embedded in a MABr matrix. All these works indicated that the CsX, Cs₄PbX₆ and CsPbX₃ phases are miscible, that they often coexist, and that the PL originates from small NC like CsPbX₃ impurities (figure 9.2c and d).

More recently, small CsPbBr₃ NCs encapsulated in a Cs₄PbBr₆ matrix were found to have high photoluminescence quantum yields (PLQYs) and were used to fabricate temperature-insensitive frequency-upconverted lasers, as was proven by HRTEM. Xu et al. proposed a type-I heterostructure for such system, and they prepared a light-emitting diode (LED) in which the carriers from the Cs₄PbBr₆ host were injected into the CsPbBr₃ NCs. In addition, another LED based on silica encapsulation of the Cs₄PbBr₆-passivated CsPbBr₃ NCs was also reported. Moreover, several groups have used transmission electron microscopy (TEM) to identify the presence of green luminescent CsPbBr₃ NCs in Cs₄PbBr₆ microcrystals, as well as in Cs₄PbBr₆ NC solutions (figure 9.2e). Figure 9.2. Overview of studies describing the embedment of CsPbBr₃ in Cs₄PbBr₆. (a) Cs₄PbBr₆ thin films exhibiting a small absorption around 520 nm, (b) accompanied by a narrow PL at 550 nm originating from the presence of CsPbBr₃. Adapted from ref. (c) Schematic representation of a band structure and absorption/PL spectrum of CsPbBr₃ NCs embedded in a Cs₄PbBr₆ matrix. The absorption spectrum exhibits a strong excitonic absorption around 315 nm due to the Cs₄PbBr₆ host, and a broad absorption up to 515 nm due to the absorption of the CsPbBr₃ NCs which emit at the band edge (around 515 nm). (d) Theoretical model for a Cs₄PbBr₆|CsPbBr₃ composite material, with various embedded cubic CsPbBr₃ NCs in a rhombic Cs₄PbBr₆ prism matrix, adapted from ref. (e) TEM image and electron diffractogram of a Cs₄PbBr₆|CsPbBr₃ composite, indicating the existence of small CsPbBr₃ NCs in the Cs₄PbBr₆ host, adapted from ref.

9.4 Defect emission in cesium lead halides

Although all of these accounts point towards the coexistence of CsPbX₃ aggregates in CsX and Cs₄PbX₆, more recent literature has proposed alternative reasons for the green PL in Cs₄PbX₆. These recent works start with the assumption that there is no clear evidence that CsPbX₃ is present, as the X-ray diffraction (XRD) patterns of Cs₄PbBr₆ show no peaks that are ascribable to CsPbBr₃, and elemental analysis yields Cs:Pb:X ratios much closer to 4:1:6 than 1:1:3. Many of these works provide an alternative explanation to the origin of green PL and absorption, namely the presence of structural
defects in Cs₄PbBr₆, which have been previously reported to cause down-converted PL in 3D and 2D (layered) perovskites. De Bastiani et al. proposed that, in Cs₄PbBr₆, the luminescence originates from the presence of bromide vacancies (V₈) which form shallow or deep trap states within the bandgap (figure 9.3a and b). Feng et al. proposed another type of defect, which arises from the incorporation of –OH (hydroxide) groups into Cs₄PbBr₆. Through DFT calculations, they indicated that the incorporation of –OH can form a 2.6 eV sub-bandgap state in Cs₄PbBr₆. Recombination from mid-bandgap states due to crystal defects was also hypothesized as being the origin of the green PL in Cs₄PbBr₆ microdisks.

Although the formation of defect states is a plausible explanation for the existence of intrinsic green PL in Cs₄PbBr₆, it is not in agreement with the current view of the effect of defects in perovskites. The hypothesis of V₈ as a luminescent center is mainly based on the halogen vacancies being the most prominent type of defect in LHPs that are synthesized under halogen-poor conditions. In halide-based materials, halogen vacancies are generally considered as deep traps, and this, in addition to other factors such as the high hole effective mass, accounts for their low carrier transport properties. On the other hand, in LHP, deep traps often have rather high formation energies and are not easily formed, and the few shallow trap states that are formed often have little effect on the optical properties. Therefore, LHPs are often described as ‘defect tolerant’ materials. For instance, the superior properties of MAPbI₃ arise from the absence of deep traps, and iodine vacancies (V₁) only form shallow traps. Similarly, in its bromide counterpart, V₈ are generally described as shallow defects. However, V₈ and chlorine vacancies (VCl) in the cubic MAPbX₃ (X = Cl, Br) are significantly deeper traps than V₁ in the tetragonal MAPbI₃. In the case of bromide perovskites, it was concluded that high V₈ concentrations result in a lower radiative recombination efficiency, and a consequent decrease in PLQY. In the case of CsPbBr₃, using a small excess of CsBr precursor (compared to PbBr₂), results in decreased V₈ concentration and, thus, an enhanced PLQY. The different nature of halide vacancies in perovskites is also evident in lead-free Cs₂AgInBr₆ and Cs₂TlBiBr₆ double perovskites (elpasolites), where halide vacancies have been reported both as shallow (Cs₂AgInBr₆) and deep (Cs₂TlBiBr₆), respectively. Furthermore, deep traps and mid-bandgap states in LHPs are often considered band-to-band PL quenchers, therefore they should not lead to a strong mid bandgap PL. Emissive mid-bandgap states are sometimes observed in LHPs, but only under vacuum, and the observed PL in these cases is weak, broad and Stokes shifted. Thus, it is evident that the nature of the halogen vacancies strongly depends on the crystal structure and the chemical nature of the B cation. Hence, the marked difference in the crystal structures of CsPbBr₃ and Cs₄PbBr₆ raises the question: are defects, in particular V₈, in CsPbBr₃ and Cs₄PbBr₆, of a similar nature? Proper calculations on the effect of defects in Cs₄PbX₆ are still lacking, and drawing parallels between halide vacancies in CsPbX₃ and Cs₄PbX₆ should be done with caution. Also, due to the rather different types of bonding of the halides in Cs₄PbX₆, the formation energy of a Vₓ is likely very different than that in CsPbX₃. For instance, unlike CsPbBr₃ and its hybrid perovskite counterpart, which are usually found to be bromine-deficient, Cs₄PbBr₆ is often reported to have a Br:Pb ratio that is usually higher than 6, thus implying that Cs₄PbBr₆ are rather halide rich. One could therefore expect a rather low density of V₈.

Although it is difficult to experimentally prove or disprove the existence of a vacancy based trap emission in Cs₄PbX₆, one can observe several PL and absorption features
in luminescent Cs$_4$PbBr$_6$ and compare these with defect emissions in other LHPs. For instance, several marked differences between the reported green PL in an “allegedly” pure 0D Cs$_4$PbBr$_6$ and that of a general trap and defect emission in both 2D and 1D organic lead halides, which consist of either layered PbX$_6^{4-}$ clusters (2D) or linear PbX$_6^{4-}$ chains (1D), can be seen in the full with at half maximum (FWHM) and in the Stokes shift of the PL. In the 2D and 1D systems, the defect emissions exhibit a broad PL, often with FWHMs larger than 100-200 nm, which is attributed to efficient exciton self-trapping that acts as an excited state defect instead of a permanent defect (figure 9.3c).$^{84-85}$ Examples of 2D and 1D organic lead halides materials exhibiting a Stokes shifted and broad PL include (EDBE)[PbBr$_4$] (EDBE = 2,2’-(ethylenedioxy)bis(ethylammonium)) and Cs$_4$N$_2$H$_{14}$PbBr$_4$. Another class of materials with a broad and Stokes-shifted PL are 0D (and also 1D) organic-inorganic Sn$^{2+}$ bromides such as (Cs$_4$N$_2$H$_{14}$X)$_4$SnX$_6$ (X = Br or I).$^{83-87}$ In these 0D materials, the large organic cations completely isolate each SnX$_6^{4-}$ octahedron. Thus, these materials are considered to exhibit the intrinsic properties of the individual SnX$_6^{4-}$ clusters, and the photoluminescent properties are explained to be not as a result of lattice defects but rather due to an excited state structural reorganization within individual SnX$_6^{4-}$ clusters. This results in them having a long lifetime, in the range of a few microseconds. Hence, Zhou et al. concluded that the SnX$_6^{4-}$ octahedra could be thought of as either “crystal lattice points” or “molecular species”. In stark contrast with the optical behavior of these compounds, the green PL in Cs$_4$PbBr$_6$ is often reported to have a very narrow FWHM (15-25 nm), as is shown in figure 9.3d and e.$^{12,18,21}$ This narrow PL matches that of CsPbX$_3$ NCs (12-42 nm, figure 9.3f) and that of the first accounts of CsPbBr$_3$ NCs embedded in CsBr (0.11 eV, compared to 0.12 eV for colloidal 8 nm CsPbBr$_3$ NCs).$^{15,56,88}$ It is also similar to other confined NCs with a band edge PL.$^{89}$ As mentioned above, the defect emission in LHP is often observed with a large Stokes shift, as defect states are formed mid-bandgap (Figure 3b-c). Although the green PL in Cs$_4$PbBr$_6$ is sometimes referred to as being Stokes shifted or as having a down shifted PL (originating from the 3.9 eV bandgap of Cs$_4$PbBr$_6$), almost all green luminescent Cs$_4$PbBr$_6$ nano/micro/bulk crystals clearly also absorb strongly in the green region (this can be simply deduced by their green/yellow color, figure 9.3d and e).$^{11,18,21,90}$ If the green PL were to originate from a mid-gap state or a trap state, then the absorption of the Cs$_4$PbBr$_6$ host would remain unaltered, i.e. it would have no features in the visible range. Take, for example, the case of fluorescent, low-dimensional organic-inorganic lead or tin halides,$^{83,85,91-94}$ in which the dimensionality (whether 2D, 1D or 0D) is tuned by using specially designed amines, like 2,2’-(ethylenedioxy)bis(ethylamine), Cs$_4$N$_2$H$_{14}$Sn$^{2+}$ or Cs$_4$N$_2$H$_{14}$Br$^+$. In all these low dimensional organic lead and tin halides, the strong dimensional confinement results in large bandgaps in the ultraviolet region of the spectrum, and powders of all these materials are, indeed, white in color. These lower dimensional organic lead halides materials exhibiting a Stokes shifted and broad PL include (EDBE)[PbBr$_4$] (EDBE = 2,2’-(ethylenedioxy)bis(ethylammonium)) and Cs$_4$N$_2$H$_{14}$PbBr$_4$. Another class of materials with a broad and Stokes-shifted PL are 0D (and also 1D) organic-inorganic Sn$^{2+}$ bromides such as (Cs$_4$N$_2$H$_{14}$X)$_4$SnX$_6$ (X = Br or I).$^{83-87}$ In these 0D materials, the large organic cations completely isolate each SnX$_6^{4-}$ octahedron. 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In all these low dimensional organic lead and tin halides, the strong dimensional confinement results in large bandgaps in the ultraviolet region of the spectrum, and powders of all these materials are, indeed, white in color. These lower dimensional organic lead and tin halides can also exhibit a down-converted (100-200 nm) emission in the visible spectrum, and their PL excitation (PLE) matches their absorption spectra.$^{86-87}$ In the case of the green luminescent Cs$_4$PbBr$_6$, the absorption and PLE spectra show features in the visible range (around 510-520 nm), which is in the same range as the green PL. The green PL in the Cs$_4$PbBr$_6$ is therefore often reported with a very small Stokes shift of only 28 meV,$^{11,21}$ suggesting that that the green PL originates from a direct band-band transition in the visible, rather than from an emission from a mid-gap defect state (figure 9.3e). Additionally, the PLE spectra from allegedly “pure” Cs$_4$PbBr$_6$ and from samples of CsPbBr$_3$ encased in a Cs$_4$PbBr$_6$ matrix are identical.$^{92}$ In both cases, a strong absorption at visible wavelengths along with a sharp
absorption decrease (with most cases no absorption at all) at shorter wavelengths (315 nm) are observed (figure 9.3d). This can be explained by the presence of two band edges which correspond to two different materials (Figure 2b). Furthermore, the green PL reported for the “pure” 0D phase was actually completely quenched when excited at the bandgap of Cs₄PbBr₆ (around 4eV).¹¹ In the work by Wang et al., in which they reported CsPbBr₃ NCs in a Cs₄PbBr₆ matrix, excitation at around 4eV resulted in a dwindled green emission, and the spectrum was instead dominated by a broad ultraviolet emission (~370 nm).³² This again indicates that the green PL does not originate from Cs₄PbBr₆, but rather from a lower bandgap material (CsPbBr₃). In addition, in thin films of CsPbBr₃|Cs₄PbBr₆ composites, the intensity of the absorption in the green region decreases as the concentration of the 3D material is reduced.⁴⁰ This observation might explain the absence of an absorption peak in the visible range for the small (26 nm) green-emitting Cs₄PbBr₆, for which only an absorption tail is recorded.¹⁴ So far, no explanation has been given for the absorption in the green region for supposedly pure Cs₄PbBr₆.

The aforementioned defect emission properties (i.e. the large stokes shift and large FWHM) are also observed in different binary and ternary chalcogenide quantum dots. For instance, selenium vacancies in CdSe NCs give rise to a broad and Stokes shifted deep trapped emission, and a higher defect emission is observed for smaller NCs due to their larger surface/volume ratio.⁹⁵ Doping chalcogenide NCs can also cause a defect emission; a typical example of this can be seen in Ag-doped CdSe NCs, which manifest an enhanced band edge emission compared to the undoped NCs. However, these Ag-doped CdSe NCs also show a broad, Stokes shifted emission, which is attributed to a defect emission.⁹⁶ Another example is the donor-acceptor defect emission in highly emissive CuInS₂ NCs, which is characterized by a large Stokes shift and PL FWHM of about 100 nm.⁹⁷
Figure 9.3. Overview of proposed defect emission in Cs$_4$PbBr$_6$. (a) Sketch of a bromide vacancy in Cs$_4$PbBr$_6$. (b) Schematic representation of a band structure with a mid-bandgap defect state, causing mid-bandgap emission. (c) Defect-related PL emission in a layered 2D organic lead bromide (N1-methylethene-1,2-diammonium)PbBr$_4$, adapted from ref 98. (d) Absorption, PL, and PLE from green emitting 26 nm Cs$_4$PbBr$_6$ NCs, showing a narrow PL FWHM and a strong quenching of the PL around 315 nm, adapted from ref 14. (e) Absorption and PL of a green emitting Cs$_4$PbBr$_6$ single crystal, showing a narrow band edge like PL, adapted from ref 21. (f) Absorption and PL from CsPbBr$_3$ NCs, exhibiting a very similar PL and absorption, with a narrow PL and small stokes shift, adapted from ref 13.

9.5 A more detailed look at the green photo luminesces reported in Cs$_4$PbBr$_6$

In addition to the directly observable green PL and absorption, several other optical measurements on green luminescent Cs$_4$PbBr$_6$ raise questions about its origins. Recent transient absorption measurements on green luminescent Cs$_4$PbBr$_6$ films by Yin et al. were interpreted by assuming a short polaron lifetime of ~2 ps, and the hypothesis of polaronic features in Cs$_4$PbBr$_6$ was confirmed by other groups. However, the transient absorption data strongly resemble those of colloidal CsPbBr$_3$ NCs, as was reported by Wu et al. In both the works of Yin et al. and Wu et al., at fast delay times (0.2–0.5 ps), an exciton bleach was observed at the lowest energy excitonic band, and an exciton absorption feature was observed 15 nm above the band edge. Moreover, in both the green luminescent Cs$_4$PbBr$_6$ films of Yin et al. and the CsPbBr$_3$ NCs of Wu et al., the exciton-induced shift almost completely disappeared after 2 ps, and the TA spectra only exhibited an exciton bleach at the bandgap. Since Yin et al. did not consider the possibility of inclusions of CsPbBr$_3$ NCs in their model, and they did not compare their results with Wu et al.’s data, it would be interesting to re-analyze the TA-measurements taking the consideration of CsPbBr$_3$ NCs in mind.

The uncertainty regarding the optical properties of the green-emitting pure Cs$_4$PbBr$_6$ extends to PL lifetimes. Here, again, the short PL lifetimes of the green PL from
Cs₄PbBr₆ are very similar to those of CsPbBr₃ NCs.¹¹, 2¹, 3⁰, ⁵³ For instance, in the work on Cs₄PbBr₆ single crystals, De Bestiani et al., concluded that “This PL lifetime is closer to the lifetime of perovskite-quantum dots (QD) than usual perovskite single crystals.”²¹ Similarly, Saidaminov et al. reported a PL lifetime of Cs₄PbBr₆ powders that is two orders of magnitude faster than that of the LHP single crystals.¹¹ On the other hand, results by Cha et al. disagree with the above reports, as they measured average PL lifetimes of 19.58 ns and 2.43 ns for Cs₄PbBr₆ and CsPbBr₃ single crystals, respectively.⁵³ Ling et al., found that the PL lifetime of their CsPbBr₃ | Cs₄PbBr₆ composite increased as the Cs₄PbBr₆ ratio increased.⁴⁰ In the case of Cs₄PbBr₆ microdisks, an average PL lifetime of 11.95 ns was recorded at the center of the disks only,²⁰ whereas a shorter PL lifetime (9.26 ns) was recorded at the disks’ edges, indicating that there is a spatial inhomogeneity within the disks. Generally, PL lifetimes of the bulk (single crystals and powders) green emitting Cs₄PbBr₆, in most reports discussed above and others, are in agreement with PL lifetimes of CsPbBr₃ NCs suggesting that the high PLQY is due to Cs₄PbBr₆-passivated CsPbBr₃ NCs.¹², ⁶²

One final interesting observation is with regard to annealing luminescent Cs₄PbBr₆ single crystals. De Bastiani et al. observed that through annealing, aggregates of CsPbBr₃ NCs were formed within the single crystals. It was observed that annealing above 250 °C results in the formation of 10 nm sized CsPbBr₃ NCs (as determined by XRD).²¹ This was explained as triggered by the VₓBr defects in Cs₄PbBr₆ samples, which act as “initialization centers”. Although the PLQYs of 10 nm CsPbBr₃ NCs is often found to be in the range of 80-95%,¹⁵, ¹⁰⁰ it was reported that the formation of the formed CsPbBr₃ NCs within the single crystal actually strongly quenches the PL. This is rather contradictory, as one would expect an increase in the PLQY when CsPbBr₃ NCs are formed.

As mentioned earlier, the argument that is generally used to prove that the green emission is an intrinsic property of Cs₄PbBr₆ is the lack of CsPbBr₃ diffractions peaks. For instance, no CsPbBr₃ diffractions peaks were reported in various Cs₄PbBr₆ samples, including powders, single crystals and NCs.¹¹, ¹⁴, ¹⁷-¹⁸, ²⁰-²¹ The authors were able to demonstrate that the presence of any CsPbBr₃ impurity phase down to 0.5% in weight could be detected by XRD (Figure 4a). Nevertheless a similar experiment, in which non-luminescent Cs₄PbBr₆ NCs were mixed with a small amount (2% molar, 0.5 wt%) of highly luminescent CsPbBr₃ NCs, indicated that this small amount of CsPbBr₃ did not result in any clear CsPbBr₃ features in the XRD pattern (Figure 4b).¹³ Furthermore, XRD patterns of Cs₄PbBr₆ | CsPbBr₃ composites, also indicated that there were not any detectable CsPbBr₃ XRD diffractions.⁴⁰, ⁶² This is expected, as diffractions from CsPbBr₃ NCs should be extremely low in intensity, not only due to their low concentration, but also due to the very broad and low intensity diffraction peaks of NCs. This is clear from the XRD patterns of borosilicate glass doped with 4 nm CsPbX₃ NCs, which hardly exhibit any perovskite XRD peaks even though the glasses are strongly absorbent and brightly luminescent, indicating that there is a high concentration of NCs.¹⁰¹
Figure 9.4. XRD measurements on Cs$_4$PbBr$_6$, both in bulk and as nanocrystals, with and without 0.5 wt% CsPbBr$_3$ nanocrystals. (a) XRD calibration experiment indicating that the synthesized Cs$_4$PbBr$_6$ single crystals were either pure or contained less than 0.5 wt% of CsPbBr$_3$, adapted from ref 21. (b) A similar experiment performed with NCs, in which Cs$_4$PbBr$_6$ NCs were mixed (2% molar, 0.5 wt%) with CsPbBr$_3$ NCs, indicating a strong green PL after mixing, but no detectable CsPbBr$_3$ XRD diffraction peaks.

9.6 Cs$_4$PbBr$_6$ nanocrystals and their transformation reactions

Thus, it is very tempting to suggest that the optical properties of the green emitting Cs$_4$PbBr$_6$ originate from CsPbBr$_3$ NCs impurities since they have similar PLs and absorptions, PLQYs, and lifetimes. One more synthetic clue towards the formation of CsPbBr$_3$ NCs inside bulk Cs$_4$PbBr$_6$ derives from the results of the synthesis of non-luminescent Cs$_4$PbX$_6$ NCs. These Cs$_4$PbX$_6$ NCs exhibit no PL and no absorption in the visible region, with only a strong excitonic absorption in the UV, and can be synthesized in the 10-100 nm size range. These Cs$_4$PbX$_6$ NCs are spherical or hexagonally shaped for small NCs (<20 nm) and often rhombohedral for larger NCs, which strongly differs from the highly cubic CsPbX$_3$ NCs, and strongly reflects their hexagonal crystal structure.

Interestingly, these NCs are often synthesized under similar conditions to those of the highly luminescent CsPbBr$_3$ NCs, but they use a higher amount of alkylamine. Here, the nucleation of CsPbBr$_3$ can be completely suppressed, since OLAM strongly binds to Pb$^{2+}$. Even though these NCs are synthesized under stoichiometric conditions closer to CsPbBr$_3$ (Cs: Pb: Br = 2.2:1:2), only the Cs$_4$PbBr$_6$ phase was formed, therefore no green PL was observed. This would then explain how both green luminescent and non-luminescent Cs$_4$PbBr$_6$ NCs could be synthesized by the simple addition of more ligands: the increased ligand amount suppresses the formation of CsPbBr$_3$. Furthermore, these Cs$_4$PbX$_6$ NCs were also the first to reported with mixed halide compositions, as both confirmed with absorption and XRD. These mixed halide Cs$_4$PbX$_6$ NCs exhibit rather broadening of their excitonic absorption compared the single halide Cs$_4$PbX$_6$ NCs. The broadening of the absorption is a direct result of the individual decoupled, mixed halide [PbBr$_n$X$_{6-n}$]$^{4-}$ clusters, which can only be populated with integer n = 0, 1, 2, up to 6, resulting in a broad absorption due to the contributions of different [PbBr$_n$X$_{6-n}$]$^{4-}$ octahedra within the NC.

Although Cs$_4$PbX$_6$ | CsPbX$_3$ composites exhibit a low potential for applications, Cs$_4$PbX$_6$ NCs can be transformed into CsPbBr$_3$ NCs by various reactions (Figure 5).
A case study into the optical properties of Cs\textsubscript{4}PbBr\textsubscript{6}

can be done via the insertion of PbBr\textsubscript{2}, the extraction of CsBr with water or with Prussian Blue, or through the extraction of Pb\textsuperscript{2+} with amines.\textsuperscript{13, 27-28, 33, 37} Several groups have reported that the size and shape of the starting Cs\textsubscript{4}PbBr\textsubscript{6} NCs can be used to tune the size of the final CsPbBr\textsubscript{3} NCs (Figure 5b).\textsuperscript{13, 27-28, 33, 37} The transformed CsPbBr\textsubscript{3} NCs exhibit a strong green PL, similar to the PL of directly synthesized CsPbBr\textsubscript{3} NCs, and they show no excitonic absorption in the UV from their parent Cs\textsubscript{4}PbBr\textsubscript{6} NCs (Figure 5c). Similarly, no Cs\textsubscript{4}PbBr\textsubscript{6} diffractions are observed in XRD analyses after the transformation (Figure 5d). Interestingly, the formed CsPbBr\textsubscript{3} NCs can be transformed back into Cs\textsubscript{4}PbBr\textsubscript{6} NCs via the addition of OA (Figure 5c-d).\textsuperscript{33} One interesting advantage of using this pathway to make CsPbX\textsubscript{3} NCs is that the Cs\textsubscript{4}PbX\textsubscript{6} NCs can be synthesized with a large tunability over their size (from about 10 nm up to 50 nm), while remaining near monodisperse. The monodispersity of the Cs\textsubscript{4}PbBr\textsubscript{6} NCs can be used to make large (20-50 nm), monodisperse CsPbBr\textsubscript{3} NCs, which currently still remains a challenge to overcome by direct CsPbBr\textsubscript{3} NC syntheses. Finally, Hu et al. have used a Cs\textsubscript{4}PbBr\textsubscript{6} to CsPbBr\textsubscript{3} exchange reaction (via the extraction of Cs\textsuperscript{+} with water) to synthesis the CsPbX\textsubscript{3}|SiO\textsubscript{2} and CsPbBr\textsubscript{3}|Ta\textsubscript{2}O\textsubscript{5} Janus NCs,\textsuperscript{36} which are among the first examples of colloidal LHP NC heterostructures.

**Figure 9.5.** Overview of transformation reactions of Cs\textsubscript{4}PbBr\textsubscript{6} nanocrystals into CsPbBr\textsubscript{3} nanocrystals and back. (a) Proposed reaction mechanisms for the exchange reaction via the extraction of CsBr, or the insertion of PbBr\textsubscript{2}. (b) TEM image showing the preservation of NC size from Cs\textsubscript{4}PbBr\textsubscript{6} NCs to CsPbBr\textsubscript{3} NCs, adapted from ref \textsuperscript{13}. (c) First excitonic absorption peak and (d) XRD pattern of NCs after several reversible exchanges from CsPbBr\textsubscript{3} to Cs\textsubscript{4}PbBr\textsubscript{6} and back, adapted from ref \textsuperscript{37}.

### 9.7 Open question and the use of Cs\textsubscript{4}PbBr\textsubscript{6} in applications

Although the green PL in Cs\textsubscript{4}PbBr\textsubscript{6} can indeed be explained by the presence of small CsPbBr\textsubscript{3} NCs, there are still a few observations which require further scrutiny. One striking
and consistent feature of the green PL in the reported luminescent Cs$_4$PbBr$_6$ is its peak position. For many Cs$_4$PbBr$_6$ single crystals, powders and NCs, the PL is always found in a rather narrow range, from 515 to 524 nm. Although this is coincidentally in the same range as for 8-15 nm-sized CsPbBr$_3$ NCs, it would mean that the formed CsPbBr$_3$ NCs would always be in the same range of sizes, and would never be formed with a size smaller than ~ 5 nm, as this would result in a blue shifted PL due to the quantum confinement effects on CsPbBr$_3$. However, recently it has been demonstrated that the size of the formed CsPbBr$_3$ NCs is highly dependent on the synthetic procedure, including synthesis temperature and ligands ratios.$^{102}$ Blue emitting Cs$_4$PbBr$_6$ composites were only very recently reported by Chen et al., who were able to synthesize both blue and green emerging Cs$_4$PbBr$_6$ cm-sized single crystals embedded with CsPbBr$_3$ NCs.$^{34}$ Here, it was observed that during the crystallization, first small blue emitting NCs were formed. Interestingly, it was reported the blue PL slowly shifted towards the green, even if the single crystals were isolated from their growth media, thus indicating that small blue emitting CsPbBr$_3$ NCs are thermodynamically less stable than the larger green emitting CsPbBr$_3$ NCs. Although it was speculated that the CsPbBr$_3$ NCs were formed due to Pb$^{2+}$ vacancies,$^{34}$ a proper study on the formation and growth of these embedded CsPbBr$_3$ is still lacking.

One additional open question is whether the high PLQY in Cs$_4$PbBr$_6$|CsPbBr$_3$ composites is only due to the formation of CsPbBr$_3$ NCs, or does it also arise from a synergistic effect at the CsPbBr$_3$|Cs$_4$PbBr$_6$ interface. Quan et al., proposed that the lattice matching at the CsPbBr$_3$|Cs$_4$PbBr$_6$ interface improves the surface passivation of CsPbBr$_3$ NCs.$^{62}$ Ling et al. suggested, however, that the shallow traps that are generated at the CsPbBr$_3$|Cs$_4$PbBr$_6$ interface cause an enhancement in the PL.$^{40}$ Furthermore, Xu et al. suggested that the change in dielectric constant from the CsPbBr$_3$ NCs to the Cs$_4$PbBr$_6$ host, could result in an increase of the oscillator strength of the excitons in the imbedded nanocrystal, which increases the radiative decay.$^{30}$ It is vital, therefore, to understand whether the CsPbBr$_3$|Cs$_4$PbBr$_6$ interface further enhances the PL properties of the CsPbBr$_3$ NCs or not, as this might lead to a better understanding of the requirements for encapsulating CsPbBr$_3$ NCs in other materials, while maintaining high and stable PLQYs. Finally, it is interesting to note that the CsPb$_2$Br$_5$ phase, which is a layered 2D structure, is currently facing the same green PL discussion as Cs$_4$PbBr$_6$. Various different optical properties have been reported, ranging from a non-luminescent wide indirect bandgap material$^{52, 103-105}$ to a green material with a strong green PL (again, around 515 nm)$^{22, 106-109}$.

Cs$_4$PbX$_6$ phases also exhibit very different electronic properties from CsPbX$_3$ due to their marked structural difference from CsPbX$_3$. In contrast to the highly conductive perovskite phase of CsPbX$_3$, the decoupling of the PbX$_6^{4-}$ octahedra in Cs$_4$PbX$_6$, and the large increase in distance between these octahedra, carriers are strongly confined to the single octahedra, meaning that Cs$_4$PbX$_6$ essentially act as insulators.$^{53, 111}$ A similar argument stands for Cs$_4$SnBr$_6$, which has the same crystal structure as Cs$_4$PbBr$_6$. This material was reported to have an electrical conductivity that is more than 200 times lower than that of CsSnBr$_3$.$^{111}$ A single crystal of Cs$_4$PbBr$_6$ was found to have an ultralow photovoltaic (in the order of nA). One work did use the luminescent Cs$_4$PbBr$_6$ (reported as a CsPbBr$_3$|Cs$_4$PbBr$_6$ composite, with a PLQY of 30%) for an LED.$^{30}$ The composites showed an increase in the external quantum efficiency (EQE) compared to that of CsPbBr$_3$, presumably due to the increase in the PLQY, the achieved maximum EQE was only 10$^{3\%}$, which is several orders of magnitude lower than LEDs using CsPbBr$_3$ NCs. This demonstrates
that, even though CsPbBr$_3$|Cs$_4$PbBr$_6$ composites have a high PLQY, their lack of conductivity hinders their use in LEDs. On the other hand, Tong et al. recently demonstrated that the addition of Cs$_4$PbBr$_6$ to a MAPbI$_3$|CsPbBr$_3$ photodetector lead to an increased and faster deep ultraviolet detection. However, it is important that the electronic and photo conductivity are first properly characterized, before Cs$_4$PbX$_6$ can be considered as interesting material for electron injected applications such as LEDs and photodetectors. One recent work by Yin et al. indeed confirmed that “intrinsic large band gap, heavy charge carriers, and low electrical conductivity of 0D perovskites limit their application in photovoltaic devices”. As a result of the stable and high PLQYs, Cs$_4$PbX$_6$|CsPbBr$_3$ materials are still interesting for down converting applications like down conversion LEDs, in which the emissions of the material are achieved via excitation with a blue LED. To this end, there have been only very few publications that have reported proper devices. For instance, Chen et al. recently combined highly luminescent Cs$_4$PbBr$_6$|CsPbBr$_3$ single crystal with a K$_2$SiF$_6$:Mn$^{4+}$ phosphor as red emitter and blue a emitting GaN chip to create high quality white light with luminous efficiency of $\approx$1.51 lm W$^{-1}$ and color gamut of 90.6% Rec. 2020 at 20 mA, which was reported to be “much better than that based on conventional perovskite nanocrystals”. Furthermore, Wang et al. demonstrated that the Cs$_4$PbX$_6$|CsPbBr$_3$ composites exhibited a temperature-insensitive gain, and they used this for a vertical cavity surface emitting laser which could operate at temperatures as high as 100 °C. One other problem with having Cs$_4$PbX$_6$ as host material for CsPbX$_3$ is the toxicity of the Cs$_4$PbX$_6$. If the active luminescent CsPbBr$_3$ is only several %wt, or even less, the majority of the host (Cs$_4$PbBr$_6$) will be inactive. Consequently, this would strongly limit the use of these materials in applications, due to the Pb$^{2+}$ toxicity. One alternative could be to find new synthesis approaches that are similar to those used for Cs$_4$PbBr$_6$|CsPbBr$_3$. These types of matrices, as discussed earlier, were already used in the 90s’ in the first reports CsPbBr$_3$ quantum dots, which were imbedded in CsBr and which were also recently used for organic MABr|MAPbBr$_3$ composites. Although others concluded that traces of CsBr in Cs$_4$PbBr$_6$|CsPbBr$_3$ quenched the PL, it would be of great interest to revive these types of host materials for CsPbBr$_3$, as it would significantly lower the required amount of lead. Recently pre-synthesized CsPbX$_3$ NCs were, for instance, embedded in potassium halide salts, and they exhibited high PLQYs and long term stability, which demonstrates the advantage of embedding LHP NCs in other halide based salts. Novel synthesis approaches for pure CsX NCs have recently been reported and could aid in designing synthesis routes towards CsBr|CsPbBr$_3$ composites. Furthermore, devices have so far been limited to Cs$_4$PbBr$_6$|CsPbBr$_3$, and it remains to be seen whether or not other halide based composites, like Cs$_4$Pbl$_6$|CsPbI$_3$, are stable enough to use in devices.

## 9.8 Conclusions

This chapter provided an overview of the contradicting literature on Cs$_4$PbBr$_6$. Due to the insulating bandgap and the very low conductive properties of Cs$_4$PbX$_6$ (either luminescent or non-luminescent), it remains to be seen whether or not this material will ever be used in widespread in applications. On a brighter note, the field of “zero dimensional perovskites” gives us inside knowledge on how to synthesize and stabilize CsPbX$_3$ NCs, without the aid of large, bulky, non-conductive ligands, directly into powders and single crystals, and this is still challenging today with regard to colloidally synthesized CsPbX$_3$. While defects such bromine vacancies are proposed as being the origin of the green
PL, additional calculations and optical studies will be required to assess the nature of defects in Cs₄PbBr₆ and of radiative decay mechanisms. Furthermore, more extensive studies are required in order to correlate the properties of Cs₄PbBr₆ with those of other all-inorganic 0D phases, such as Cs₂SnX₆ and Cs₃Bi₂I₉, for example.

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