
Perovskite Nanocrystals for Optoelectronics and Photovoltaics



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University College

A thesis submitted for the degree of
Doctor of Philosophy
at the University of Oxford

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Abstract

Lead halide perovskite nanocrystals, APbX_3 , are an astounding candidate for optoelectronic and photovoltaic applications. Their tunable band gap, through both composition and quantum size effects, allows for a wide colour gamut spanning the visible to infra-red region. The colour purity achievable through narrow full width at half maximum (FWHM) in their emission spectra, and bright emission with reports of near unity photoluminescence quantum yield (PLQY), place lead halide perovskite nanocrystals at the forefront of research into display technologies. Despite a vast research effort into these materials over the past five years, questions remain regarding their surface chemistry, optimal synthesis for compositional breadth, and their stability.

In this thesis, a mixed cation mixed anion lead halide perovskite nanocrystal synthesis is investigated. Although fine tuning of the band gap is achieved, the miscibility of the inorganic cation, cesium (Cs), and organic cation, formamidinium (FA), is unclear due to concurrent changes in size and shape of the nanocrystals across the compositional range. To resolve this, a new synthesis to perovskite nanocrystals is investigated utilising a phosphine oxide, with the aim to simplify the ligand shell. This is motivated to decouple size and shape control from composition in a mixed cation perovskite nanocrystal synthesis. All inorganic CsPbX_3 nanocrystals are synthesised through this phosphine oxide assisted synthesis, and achieve up to 70 % PLQY whilst maintaining monodispersity at high reaction yields close to the theoretical limit. A simple oleate-only ligand shell is achieved, and confirmed through nuclear magnetic resonance spectroscopy (NMR) and X-ray photoelectron spectroscopy (XPS). The synthesis is translated across to form FAPbBr_3 nanocrystals. Although similar PLQYs are achieved, the size and shape control is lost. This lack of control is attributed to the interaction of the labile ammonium protons on FA with the ligands used in the synthesis, which is determined via NMR.

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When you are in the middle of a story it isn't a story at all, but only a confusion; a dark roaring, a blindness, a wreckage of shattered glass and splintered wood; like a house in a whirlwind, or else a boat crushed by the icebergs or swept over the rapids, and all aboard powerless to stop it. It's only afterwards that it becomes anything like a story at all. When you are telling it, to yourself or to someone else.

Margaret Atwood, Alias Grace

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List of Abbreviations

Cs-oleate	cesium oleate
DLS	dynamic light scattering
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
EDS	energy-dispersive X-ray spectroscopy
EQE	external quantum efficiency
FA	formamidineum
FA-oleate	formamidineum oleate
FFT	fast Fourier transform
FTIR	Fourier-transform infrared spectroscopy
FWHM	full width at half maximum
ICP-OES	inductively coupled plasma optical emission spectroscopy
IIT	Istituto Italiano Di Tecnologia
ITO	indium doped tin oxide
LARP	ligand assisted reprecipitation
LED	light emitting diode
MA	methylammonium

List of abbreviations

MeAc methyl acetate

NC nanocrystal

NMR nuclear magnetic resonance spectroscopy

NPL nanoplatelet

OA oleic acid

ODE 1-octadecene

OLAm oleylamine

PL photoluminescence

PLE photoluminescence excitation

PLQY photoluminescence quantum yield

Poly-TPD Poly(4-butylphenyl-diphenylamine)

ppm parts per million

PSD particle size distribution

rpm revolutions per minute

rT room temperature

TEM transmission electron microscopy

TOPO trioctylphosphine oxide

TPBi 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)

TRPL time resolved photoluminescence spectroscopy

XPS X-ray photoelectron spectroscopy

XRD X-Ray Diffraction

CHAPTER 1

Introduction

Advances in technology, energy, and medicine are being driven by a material that is a thousand times smaller than the width of a single strand of hair. This material is a nanocrystal (NC).

A NC ranges in size from 1 - 100 nm and there has been significant effort in developing NCs, and associated technologies, over recent years. Nanotechnology has revolutionised bio-imaging, and sensing capabilities in medicine, whilst also being applied in drug delivery, and gene therapy. Their applications extend past the biological sphere to energy solutions including water splitting catalysts, and photovoltaic devices. They are also used commercially in display technologies as light emitting diodes (LEDs) or phosphors, such as the Samsung QLED televisions. NCs offer both energy efficiency and colour gamut advantages over other existing screen technologies, for example organic LEDs¹. Their application breadth and success is due to the tunability of the physical, chemical, and biological properties, coupled with an ease of processing.

Semiconducting NCs are of particular interest for optoelectronic and photovoltaic applications, due to their physical and electronic properties. Metal chalcogenide quantum dots, mainly cadmium based, were first used in these applications, with

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core-shell structures required for surface passivation. Toxicity issues surrounding the use of cadmium in quantum dot cores has led to more research into indium phosphide as an alternative. Despite making it to the market, these nanoparticles are limited in their performance due to lack of colour purity and size restrictions.

Lead halide perovskites have the structure APbX_3 , where A is an inorganic or organic cation, and X is the halide anion. They burst on to the photovoltaic research scene in 2012 as a replacement of the dye in a typical dye-sensitised solar cell². Since then, polycrystalline lead halide perovskites have carved out their own field of research for photovoltaics and other applications, such as LEDs and photodetectors. There has been an unprecedented rise in photovoltaic efficiency with records of 25.2 % for single junction and 28.0 % for silicon-perovskite tandem photovoltaic devices³. Polycrystalline perovskites have also shown success in LEDs. However, the field has quickly adapted 2D lead halide perovskites and perovskite NCs for light emission applications, due to their brighter emission in comparison with their polycrystalline counterparts.

The first lead halide perovskite NCs were synthesised by Schmidt et al. in 2014⁴, closely followed by Protesescu et al. in 2015⁵. They have different chemical and physical properties to traditional semiconducting quantum dots, namely their ability to reach near unity PLQY without excessive surface passivation. Due to the structure of the lead halide perovskite, they have a further compositional breadth; different cations (A) and anions (X) can be incorporated into the material, which change the optoelectronic and structural properties. Research into lead halide perovskite NCs is built on the foundations of traditional quantum dots and the progress in the polycrystalline field. The bridging of these two research fields, alongside the astounding properties of perovskite NCs, has allowed for the field to rapidly expand and develop in a short period of time. More than 800 papers were published in 2018 relating to perovskite NCs⁶, just four years after the first reported synthesis.

The application of perovskite NCs in photovoltaics and LEDs is of particular interest. For photovoltaics, perovskite NCs present the opportunity to stably access desired phases of lead halide perovskites, as a result of the inherent differences between

the bulk and nanoscale⁷. Their bright emission, narrow line widths, and band gap tunability make them excellent candidates for display applications. These properties allow them to reach desired colour gamut for optimal high dynamic range display technology, as laid out by the ITU-R Recommendation BT.2020⁸.

Despite this vast growth in application-orientated research, the understanding of fundamental aspects of lead halide perovskites, both polycrystalline and NCs, remains relatively shallow in comparison. Specifically in NC research, there remain questions regarding the surface passivation, achieving near unity PLQY across different compositions, and specifically developing syntheses which can be feasibly scaled without compromising on optical and structural properties. More broadly, the reasons for defect tolerance and stability, or lack of, are gaping holes in the lead halide perovskite research sphere. Targeting these areas is challenging due to the compositional breadth achievable with lead halide perovskites, and the diversity in chemistry for the different compositions. For there to be success in the commercialisation of perovskite NCs, in photovoltaics, LEDs or other applications, their synthesis and surface passivation must be better understood. This thesis contributes to this research area by examining the synthesis of mixed cation perovskite NCs, and introducing a new synthetic route to perovskite NCs with a simpler ligand shell.

CHAPTER 2

Background and Theory

This chapter shall cover relevant concepts for understanding the research presented in this thesis.

First, lead halide perovskites are introduced, outlining their crystal structure, compositional breadth, and notable attributes. Next, the physics of lead halide perovskite nanocrystals (NCs) is presented. This section includes an overview of semiconductor physics, charge carriers, and the quantum confinement effect. Following this, the chemistry of lead halide perovskite NCs is covered. The different synthetic methods, nucleation and growth, the variety of shapes and sizes, and the importance of the ligands and surface chemistry of NCs are highlighted. Finally, the application of perovskite NCs is shown by bringing together their qualities explored in the previous sections.

2.1 Lead Halide Perovskites

A perovskite is the mineral compound calcium titanate (CaTiO_3), and the name can also be used to identify compounds of the same structure. The perovskite structure is

Chapter 2. Background and Theory

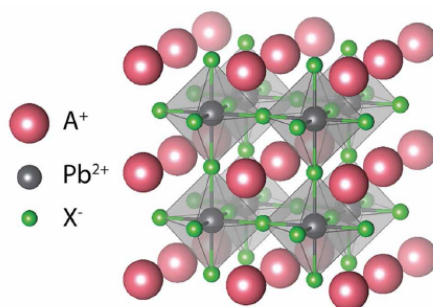


Figure 2.1: Crystal structure of a lead halide perovskite, with cation (A^+ , pink), lead (Pb^{2+} , black) and halide anion (X^- , green). The lead halide octahedra ($[PbX_6]^{4-}$) are denoted by the grey area. Image reproduced from LED Professional¹⁰

ABX_3 and is typically cubic in oxide perovskites. Lead halide perovskites are a subset of this class of materials and adhere to the perovskite structure. They follow the crystal structure of the perovskite-lattice, with corner sharing octahedra of $[PbX_6]^{4-}$ and the cation (A) filling the spaces between, shown in Figure 2.1. B is lead in the 2^+ oxidation state (Pb^{2+}) and the anion X is either a single or mixture of halides: iodide (I^-), bromide (Br^-) or chloride (Cl^-). In the applications discussed here, A can be cesium (Cs^+), methylammonium (MA) ($CH_3NH_3^+$) or formamidinium (FA) ($CH(NH_2)_2^+$). There are variants on this structure, with octahedral tilting and different stoichiometry leading to "perovskite-related" structures⁹.

One of the key advantages of the lead halide perovskite family is the compositional breadth. Mixing of cations, metals, and anions, allows for tuning of the optoelectronic properties for targeted device applications. The above listed cations and anions are not exhaustive of what will fit into the perovskite-lattice; there are examples of metal doping¹¹ and other cations being incorporated^{12,13}, for example. Cation and anion exchanges have also been demonstrated for polycrystalline thin films^{14,15} and NCs^{16–19}. This is of particular note for anion exchange in NCs, which sets perovskite NCs apart from metal chalcogenide NCs where only facile cation exchange is achievable²⁰. The rapid exchange does have drawbacks, with routes to suppress or control the extent of exchange being explored²¹.

There is a large scope of compositional possibilities, but there are limitations on whether the compound will be in the perovskite phase. This limitation can be explained through the Goldschmidt tolerance factor²² (Equation 2.1). This considers

2.2. Physics of Perovskite Nanocrystals

the ionic radii of A, B, and X, and for a stable, 3D perovskite structure, has the range 0.76 - 1.13, with certain perovskite-related structures stable outside this range²³.

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (2.1)$$

The phase transitions of perovskites dictate their stability, and the need for mixing of cations and anions. For example, CsPbI₃ and FAPbI₃ will both readily undergo a phase transition at room temperature (rT) from the perovskite phase to a non-perovskite orthorhombic or hexagonal phase, respectively. This is often called a transition to the yellow phase, due to the associated colour change from black to yellow. Mixing Cs, FA, and MA together can alleviate this phase transition, and keep such materials in the perovskite phase. Such transitions are often triggered by the presence of moisture and air, requiring many of these materials to be handled under inert atmosphere.

What makes lead halide perovskites stand out, and has been the cause for the generation of a new research field, is their outstanding optoelectronic properties. To understand these features, the physics of these materials must be covered. A focus on lead halide perovskite NCs shall be maintained, but certain concepts translate across from polycrystalline lead halide perovskites to the NCs. The rest of this chapter shall focus on perovskite NCs; the physics, chemistry, and application of these materials. There are many excellent reviews on lead halide perovskite NCs which can be referred to for further reading^{9,24–30}.

2.2 Physics of Perovskite Nanocrystals

In this section, the physics of perovskite NCs is presented. First, semiconductors and their band structures are covered in general terms. This is followed by charge carrier dynamics in lead halide perovskites. Quantum confinement of semiconductors is then approached in order to transition over to NCs. The effect of quantum confinement on the optical properties of lead halide perovskites is then discussed. Finally, the

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unique characteristics of lead halide perovskites, and the knock-on effect on lead halide perovskite NCs, are reviewed.

Semiconductors and Band Structure

The content of this subsection is based on the work by Cox³¹ and Shriver and Atkins³². These texts should be referred to for further details relating to semiconductors and band structure.

Semiconductors are a class of materials that sit between a metal and an insulator. There are two main schools of thought for understanding the electronic structure of semiconductors and bulk solids in general. These are the principles laid out in solid-state physics, and in the chemistry-based atomic and molecular orbital approach.

In molecular orbital theory, electrons are spread throughout an entire molecule, and the orbitals that these electrons exist in are constructed through the linear combination of atomic orbitals. For N atomic orbitals combined in a molecule there are N molecular orbitals.

A solid, for example a semiconductor crystal, can be viewed as an infinite molecule, and the combination of orbitals eventually gives rise to a continuum of states. Lower energy and higher energy orbitals combine to form essentially continuous bands. The lowest unoccupied molecular orbital (LUMO) evolves into the conduction band and the highest occupied molecular orbital (HOMO) into the valence band. The space between the two energy bands is the band gap where there are no allowed energy states. In the energy bands there are still discrete molecular orbital levels, however the separation between them is such that individual molecular orbital levels do not need to be considered. The band edges are formed by the fully bonding and anti-bonding extreme cases for both the valence and conduction band. This is demonstrated in a simplistic diagram in Figure 2.2a.

The width of the band remains finite, even as molecular orbital approaches infinity, and it is dependent on the strength of interaction of neighbouring orbitals. The density of states is the number of energy levels in a given energy range divided by volume.

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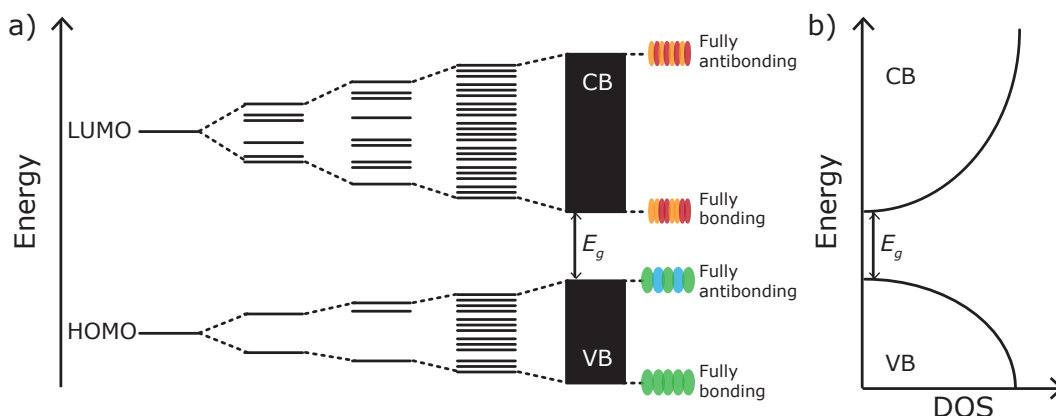


Figure 2.2: Schematic for the extension of molecular orbitals to continuous bands in a semiconductor, as described by Molecular Orbital Theory, and the corresponding density of states (DOS). Abbreviations used: highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), valence band (VB), conduction band (CB), band gap (E_g)

This is not uniform over a band due to an uneven spread of energy levels across the band. At the band gap, the density of states is zero. There are less populated states close to the band edge, as opposed to in the middle of the band, leading to a curved distribution, shown in Figure 2.2b.

Charge Carriers in Semiconductors

The content of this subsection is based on the work by Herz³³, which should be referred to for further details relating to charge carriers in semiconductors, specifically perovskites.

In a semiconductor, the band gap can be overcome with input from energy, for example a photon being absorbed. This energy input promotes an electron, e^- , from the valence band into the conduction band and leaves behind a hole, h^+ . In all cases, there is some level of binding interaction between the e^- and h^+ . The strength of this interaction, or rather the binding energy, dictates if the e^- and h^+ are viewed as free charge carriers (low binding energy) or an exciton (high binding energy). In the case of the exciton forming, the Coulombic attraction between the e^- and h^+ lowers the total energy of the system. There are two types of excitons: Frenkel and Wannier-Mott. The Frenkel exciton is when the e^- and h^+ pair are bound to their parent atom and best describes excitons formed in molecules. These cause large distortions in the

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vibrational mode of the molecule. A Wannier-Mott exciton is when the e^- and h^+ pair are delocalised across a continuous lattice and best describes excitons formed in an inorganic semiconductor. The e^- and h^+ can then go on to recombine. Free charge carriers, also known as photo-carriers, can either move away from each other producing photo-conductivity, or recombine through the decay of the e^- .

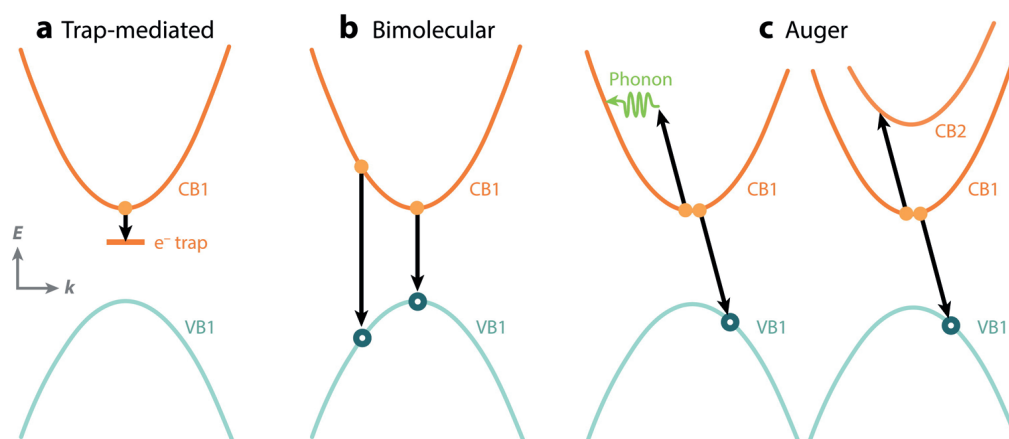
Recombination pathways can be split into radiative and non-radiative pathways. Simply, in radiative recombination a photon is emitted, whereas in non-radiative recombination phonons are emitted. The two processes are not mutually exclusive with radiative and non-radiative pathways occurring concurrently as competing processes. Radiative recombination and the emission of a photon after stimulated excitation from a photon is known as photoluminescence (PL).

These competing pathways for perovskites can be summarised by the rate equation for the decay of the free carriers, Equation 2.2, where n is the density of free charge carriers, and t is time. The three rate constants are associated with three recombination pathways. k_1 relates to monomolecular recombination, for example trap-assisted recombination. In the latter case, a trap-state is an entity with an electronic energy state that sits in the bandgap of the semiconductor. It generally corresponds to lattice defects in the semiconductor or extrinsic impurities (doping). k_2 represents the bimolecular charge recombination rate of the e^- and h^+ . This recombination usually occurs from the conduction band minima. k_3 represents the Auger recombination rate constant. Auger recombination is a many-body process, involving at least three particles. This is a non-radiative process. All three of these processes for rate constants k_{1-3} are portrayed in Figure 2.3a-c respectively.

$$\frac{dn}{dt} = -k_3n^3 - k_2n^2 - k_1n \quad (2.2)$$

For maximum radiative recombination and light emission, k_2 should dominate over the other two non-radiative rate constants, k_1 and k_3 . Practically, the amount of radiative and non-radiative recombination can be measured through the photoluminescence quantum yield (PLQY) of a material. PLQY is the ratio of photons emitted against

2.2. Physics of Perovskite Nanocrystals



 Herz LM. 2016.
Annu. Rev. Phys. Chem. 67:65–89

Figure 2.3: Schematic for the charge carrier recombination pathways in lead halide perovskites. a) trap-assisted (monomolecular), b) bimolecular recombination which can occur from e^- and h^+ in relaxed state or higher in the band, c) Auger recombination (many-body recombination). Abbreviations used: conduction band (CB) and valence band (VB). Reproduced with permission of ANNUAL REVIEWS in the format Thesis/Dissertation via Copyright Clearance Center³³, see Appendix E

photons absorbed, Equation 2.3. In an ideal case, where only radiative recombination processes occur, a unity PLQY is achieved, or $\phi = 1$. For most semiconductors this isn't the case, due to non-radiative processes which reduce the amount of photons out, and thus causing deviation from unity.

$$\phi = \frac{\text{no. photons emitted}}{\text{no. photons absorbed}} \quad (2.3)$$

The lifetime of the free carriers, τ , is the average time taken to recombine, and is typically measured through time resolved photoluminescence spectroscopy (TRPL). Desirable carrier lifetimes are inherently dependent upon the application of the semiconductor. For example, for a light emitting diode (LED) a short radiative lifetime and long non-radiative lifetime are favourable.

The optical absorption and emission spectra of a semiconductor provide useful information about the electronic structure. Energy levels of excitons can be observed as peaks in the absorption spectra, and the spread of energies in a system is apparent from it's PL. If there is a difference in energy between the absorbed photon and emitted photon, a Stokes shift is observed. This manifests as the offset of the absorption and

Chapter 2. Background and Theory

emission maxima. A material can have an intrinsic Stokes shift caused by band edge fine structure splitting and phonon assisted emission, where energy from the absorbed photon is dissipated through the material as a lattice vibration. In certain cases, there is an apparent Stokes shift that is actually due to photon recycling or polydispersity in the size distribution of the material. Manipulating and understanding the cause for a Stokes shift in a material can be important for device applications.

In perovskites, polycrystalline, single crystal and NC, a small shift between the absorption and emission maxima is noted. The observed apparent Stokes shift has been attributed to photon recycling^{34–42}. Perovskites are prone to photon recycling due to their large absorption coefficients, clear overlap of their absorption and emission spectra, and demonstration of efficient band to band transitions. Photon recycling is where a photon emitted from the recombination of an excited e^-h^+ pair is reabsorbed by the material, generating a new e^-h^+ pair. A knock-on effect of this process is the extension of radiative lifetimes. This was shown for polycrystalline MAPbI₃ films, where an intrinsic bimolecular recombination rate of $k_2^{intrinsic} = 6.8 (\pm 1.4) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ was found⁴². The apparent recombination rate, $k_2^{apparent}$, varies with film thickness and light out coupling abilities of the film, and is related to $k_2^{intrinsic}$ via a correction factor. The apparent recombination rate includes both radiative recombination and photon reabsorption effects, and thus the photon management can be understood by comparing the two values.

Photon recycling is more notable in samples with higher PLQY. In these cases, there is a higher rate of radiative recombination, and thus the recycling can occur more often. Photon recycling also induces a change in the shape of the PL emission spectra. Due to the uneven spread of probabilities of reabsorption of light at given wavelengths, a sharper rise in the PL peak is seen on the side of the absorption onset. At lower energies, or higher wavelengths, a broader tail in the PL is observed.

Nanocrystals and Quantum Confinement

The content of this subsection is based on the work by Alivisatos⁴³, Efros and Rosen⁴⁴, Kambhampati⁴⁵ and Rabouw and de Mello Donega⁴⁶. These texts should be referred to for further details relating to nanocrystals and quantum confinement.

A nanoparticle has a size order of 1 - 100 nm. In terms of its electronic structure, a nanoparticle sits between a molecule with defined discrete energy levels and a bulk crystallite with continuous bands. The size of the nanoparticle induces changes in the density of electronic energy levels, thus changing its optoelectronic properties. This is the quantisation of the energy levels, and is known as quantum confinement.

Quantum confinement can be understood on a basic level by examining a particle in a sphere, which is an extension of the particle in a box. This is a sound qualitative representation, which goes some way to explain changes in optical behaviour of semiconductor NCs too. In this instance, assume a sphere of radius a , which is a homogenous medium of some dielectric constant with no point charges or potential. Outside of the sphere there is infinite potential, therefore inside the sphere there is a non-zero solution to the wavefunction, and outside the wavefunction is zero. Only a certain number of non-zero solutions exist, which gives rise to the allowed quantum energy levels. The energy of the electron (e^-) and hole (h^+) quantum levels (QL) can be described by a parabolic approximation (Equation 2.4). Here, $m_{e,h}$ is the e^- and h^+ effective mass respectively, a is the crystal radius and $\beta_{n,l}$ is the Bessel function dictated by the quantum numbers n and l . This parabolic function assumes single bands for the e^- and h^+ .

$$E_{QL} = \frac{\hbar^2 \beta_{n,l}^2}{2m_{e,h} a^2} \quad (2.4)$$

Due to the inverse proportionality between the energy of the quantum level, E_{QL} , and the radius, a , decreasing the size of nanocrystal increases the energy of these levels. Thus, the total energy of the band edge transition is also increased.

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The Coulomb interaction between the e^- and h^+ must also be considered as both particles are confined in the same nanoparticle volume. This relationship is inversely proportional to the dielectric constant of the semiconductor, κ and the radius, a (Equation 2.5).

$$E_{Coulomb} \propto \frac{e^2}{\kappa a} \quad (2.5)$$

The overall energy of nanoparticle system is a combination of the band gap of the bulk material, E_g , the quantum energy levels, and the Coulombic interaction (Equation 2.6). Quantisation energy is proportional to $\frac{1}{a^2}$ where the Coulombic interaction is proportional to $\frac{1}{a}$. Therefore, in small crystals the Coulombic interaction becomes a minor correction to the quantisation energies of the e^- and h^+ . In larger NCs, the opposite is the case.

$$E_{Total} = E_g + E_{QL} + E_{Coulomb} \quad (2.6)$$

The extent of quantisation is dependent on the size of the NC, and its relative size in comparison to the radius of the Bohr exciton. The Bohr exciton radius, a_B , is the radius of the sphere of volume that the e^- and h^+ pair, the exciton, occupy, and is described in Equation 2.7, where μ is the reduced mass of the exciton. This stems from the Bohr radius of a hydrogen atom, a_0 , which is the distance between the nucleus and electron in a hydrogen atom and is a physical constant. Due to only an e^- and h^+ and their orbitals being considered, the exciton can be related to the nuclei (single proton) and single electron of a hydrogen atom. The Bohr exciton radius is characteristic of a material and in general is of the order 2 - 50 nm⁴³. It has been calculated to be 4.6 nm in MAPbI₃⁴⁷ and approximately 3.5 nm in CsPbBr₃^{48,49}.

$$a_B = \frac{\hbar^2 \kappa}{\mu e^2} \quad (2.7)$$

Three scenarios arise from the relationship between a and a_B . Firstly, there is the weak confinement regime where $a \gg a_B$, which is true for larger NCs. In this case,

2.2. Physics of Perovskite Nanocrystals

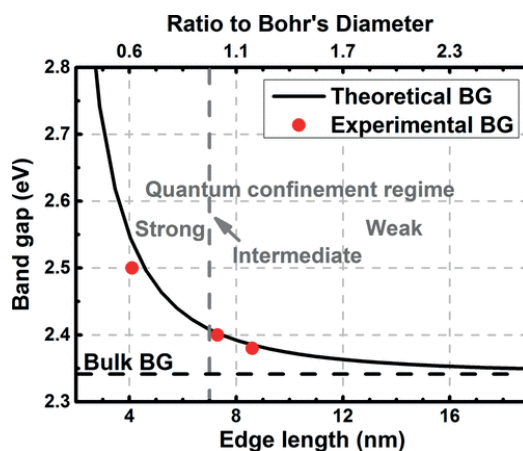


Figure 2.4: Size dependence of band gap on size of CsPbBr₃ NC as a result of quantum confinement. Theoretical band gap as determined by the effective mass approximation. Reproduced with permission from ACS⁴⁸, see Appendix E

the Coulombic attraction has a larger effect on the band gap. Then the intermediate regime where $a \sim a_B$, and thirdly the strong confinement regime where $a \ll a_B$. The latter case is true for very small NCs and the Coulomb interaction only plays a small part in lowering the energy levels. For CsPbBr₃ NCs, there has been shown to be a good match between experimental and theoretical data for the change in band gap energy in these three quantum confinement regimes⁴⁸ (Figure 2.4).

The picture described here is of course a simplified one. The parabolic nature of the electronic bands is only true at the bottom of the conduction band and top of the valence band. As such, it does not explore the higher excitonic states that can be observed. However, it neatly demonstrates the size dependent nature of the electronic properties of a NC. For further explanation the multiband effective mass approximation should be explored. Here, multiple bands of non-parabolic nature are considered for the conduction and valence bands. This approximation was applied to colloidal NCs by Norris, Bawendi and Efros^{44,50–53}. These texts can be referred to for further explanation of this model in the context of NCs.

The particle in a sphere model is sufficient to understand the basic absorption and emission properties of semiconductor NCs of varying size. The introduction of discrete energy levels and widening of the band gap results in colour tunable semiconductor NCs of the same composition, shown in Figure 2.5a. Although a sphere was used

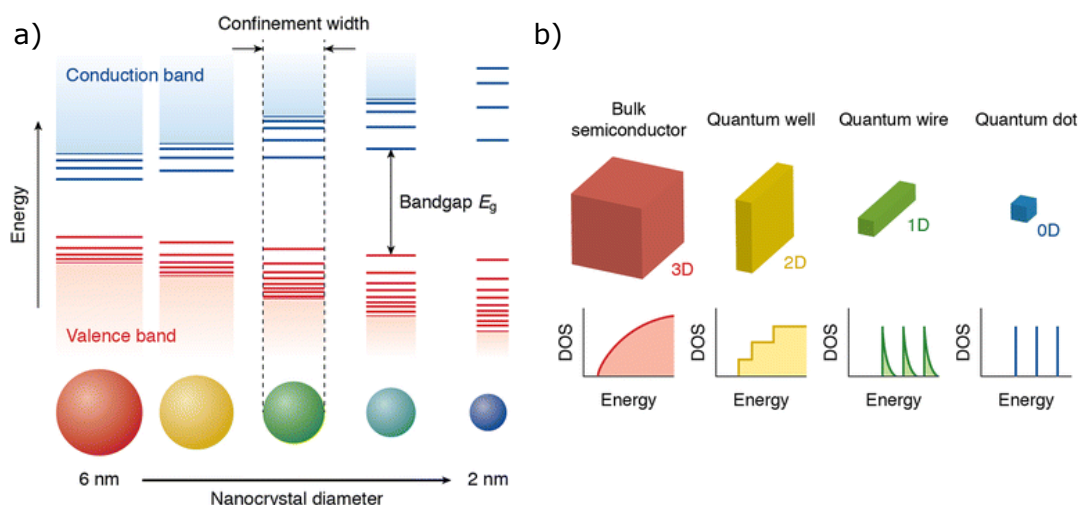


Figure 2.5: a) Schematic representation of the effect of quantum confinement on the electronic structure of a semiconductor and b) the density of states for a semiconductor with reduced dimensionality. Reproduced from Springer Nature⁴⁶

here, the degree of quantum confinement can be different across the three dimensions. As a particle in a sphere is the three dimensional extension of a particle in a one dimensional box, each dimension can be considered in turn to undergo a quantum confinement. This in turn affects the density of states of the NC, and thus explains the shape dependence of the optoelectronic properties.

When the exciton is confined in all three directions, a quantum dot is formed. Two dimensional confinement affords a quantum wire, and one dimension a quantum well. Their density of states compared to a bulk semiconductor demonstrate increasingly discrete levels, as seen in Figure 2.5b.

Optical Properties of NCs

The content of this subsection is based on the work by Efros and Rosen⁴⁴ and Kambhampati⁴⁵. These texts should be referred to for further details relating to optical properties of nanocrystals.

Quantum confinement effects dictate the optical transitions in a NC. Allowed transitions between the discrete energy levels formed as a result of quantum confinement (E_{QL}) make up the optical spectra. The selection rule governing these transitions is that they are only allowed between levels with the same quantum numbers.

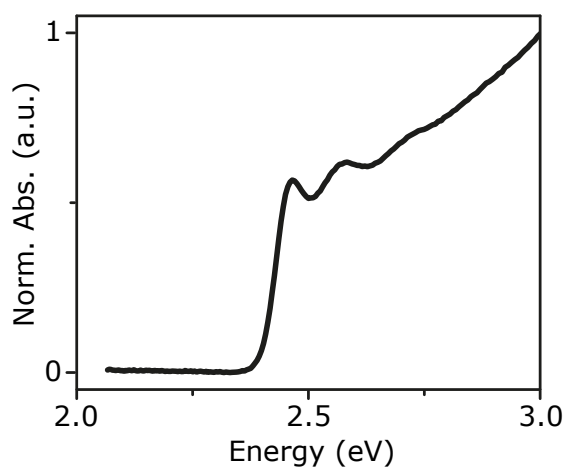


Figure 2.6: UV-visible absorption spectroscopy of monodisperse CsPbBr₃ NCs with defined excitonic peaks

As the NC decreases in size the PL and onset of absorption are blue shifted, reflecting the increase in the overall band gap of the system. The shift in emission is observed for perovskite NCs, for example in CsPbBr₃ where the emission increases from ~ 2.43 eV to ~ 2.66 eV from edge lengths of 11.8 nm to 3.8 nm⁵.

As well as the blue shift, the absorption also offers more insight into the electronic nature of the NCs. The discrete energy levels allow for certain transitions to take place on the absorption of a photon. These transitions are not just between the valence band maxima (HOMO) and conduction band minima (LUMO), with transitions allowed where the quantum number of the energy levels is the same⁴⁴. These transitions, alongside the excitons, dictate the features of the absorption spectra, with peaks forming at the given energies. In theory, each of these peaks can be assigned to either an exciton or a transition from a quantised level. This is clearly shown for GaAs/AlGaAs quantum well structures at room temperature⁵⁴. Excitonic peaks are observable in small, monodisperse perovskite NCs, such as for 6 nm CsPbBr₃ shown in Figure 2.6.

The absorption spectra of CsPbBr₃ can now also be used to determine the size of the NCs. In 2018, Maes et al. determined the intrinsic absorption coefficient, μ_i , for CsPbBr₃ NCs. For a wavelength of 400 nm, with the NCs in hexane a value of 7.7×10^4 cm⁻¹ was obtained⁵⁵. Their results showed that μ_i is size-independent for NCs in

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the range of 4 - 11 nm, but is dependent on the refractive index of the solvent. Further, they demonstrated the ease of conversion of μ_i to the molar absorption coefficient or the absorption cross section of the NCs and thus the size can be determined.

Radiative lifetimes of NCs are expected to be considerably shorter than their bulk counterparts, and are expected to scale with the size of the NC. This is largely due to the removal of carrier diffusion in a NC, and thus a lack of dependence on carrier concentration. The decay in a NC would be expected to follow a monoexponential, assuming a single e^-h^+ pair per NC, and removing the potential for bimolecular and non-radiative recombination pathways.

In practice, faster lifetimes are recorded for perovskite NC than their analogous polycrystalline films. For example, spin coated films of CsPbI_3 NC were recorded to have an average carrier lifetime of 3.8 ns, also showing a reduction from 19.6 ns in solution⁷. A polycrystalline film of CsPbI_3 had a lifetime up to 0.2 μs when spin coated; evaporated films showed extended lifetimes in the order of tens of microseconds⁵⁶. The pathways to recombination in FAPbI_3 NCs, and polycrystalline thin films are examined in a study by Fang et al. They find a significant difference in recombination pathways for the two, owing to the localisation of photogenerated excitons in the NC compared to trap-assisted and bimolecular recombination in the thin films⁵⁷.

As mentioned previously, an apparent Stokes shift is observable for perovskite NCs. One study into the cause of this shift determined the presence of an intrinsic, confined hole state above the valence band edge, which is dependent on the size of the NC⁵⁸. However, photon recycling was not taken into fair consideration in this study. It has since been shown that the assumed size dependence of the apparent Stokes shift can also be explained due to photon recycling.

Gan et al. show that two sets of CsPbBr_3 NCs with average sizes of 6.4 and 9.7 nm and with similar size distributions (σ) have an intrinsic Stokes shift of 71 and 69 meV respectively⁵⁹. They observe a blue shift in the PL as the concentrations of NCs in solution decreases, i.e. increased overlap of the absorption and emission spectra. Therefore, the total shift between absorption and emission maxima has a significant contribution from an apparent Stokes shift, dictated by NC concentration. The smaller

2.2. Physics of Perovskite Nanocrystals

NC feel the effect of the concentration more, with an increased shift of 143.4 meV whereas the larger particles shift only increases to 97.6 meV at higher concentrations. As NC concentration increases, inter-NC distances decrease and the likelihood of photon reabsorption increases⁵⁹. As the absorption coefficient of perovskite NCs is not dependent on size, the smaller NC are more likely to undergo more reabsorption at a given concentration.

Photon reabsorption in perovskite NC has also been shown to be useful in device applications. A set of LEDs were made using films of CsPbI₃ and CsPbCl₃ NCs, which showed little to no halide exchange. It was found that stimulation of the film, through light or electricity, was absorbed by the chloride NCs and the significant majority of emission resulted from the iodide NCs⁶⁰.

Defect Tolerance

As mentioned at the end of the previous section introducing lead halide perovskites, this class of materials have outstanding optoelectronic properties. It is these properties that set them apart from other semiconductor materials currently used in similar applications. One such characteristic is that lead halide perovskites are defect tolerant, and this is a cause of their success⁶¹. These materials can have a high density of points defects, like vacancies, and still operate well as semiconductors.

There is currently not a ubiquitous understanding for the reason behind their defect tolerance in the research field. One theory for the root of their defect tolerance is the liquid-crystalline nature of the perovskite lattice. By being soft and dynamic with partial ionic character, carriers are protected from trapping and scattering through the formation of polarons which screen the Coulombic potential^{24,62,63}. Vacancy defects with low formation energies are the vast majority of defects, with interstitial and antisite defects in the minority. These latter two types of defects would form deep trap states in the electronic structure^{64,65}. These vacancy defects are shallow in energy, due to the anti-bonding character of the valence band maxima and spin-orbit effects in the conduction band.

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This translates over to perovskite NCs, which can be seen to be terminated by a layer of these shallow-energy vacancies. Thus the surface of a perovskite NC will follow the same, muted characteristics as the defect tolerance in a polycrystalline film. As these vacancies do not sit in the middle of the band gap, as is true for other types of semiconducting NCs, high PLQY is achievable with perovskite NCs without the need for a core-shell structure. This allows for an ease of processing in comparison to other semiconductor NCs, such as silicon or cadmium selenide.

Other properties including their high absorption coefficient, charge transport capabilities, and small Urbach energies coupled with large disorder are also cause for sustained intrigue and success of the material. More in-depth discussion of these concepts can be found in the literature^{66–68}.

2.3 Chemistry of Perovskite Nanocrystals

In this section, the chemistry of perovskite NCs is described. The synthetic methods, nucleation and growth, size and shape, and their surfaces, are covered as the four key areas. The examples and specifics used here are those relevant to perovskite NCs.

Synthetic Methods

The content of this subsection is based on the reviews by Shamsi et al.⁹ and Chang and Wacławik⁶⁹. These texts should be referred to for further details on synthetic methods for nanocrystals.

There are two main categories for the synthesis of NCs: top-down or bottom-up approaches. Top-down takes a ready-made material and breaks it up into smaller pieces, whereas bottom-up starts from stitching molecules or atoms together. Bottom-up approaches tend to demonstrate finer control than top-down ones⁶⁹. These approaches are further divided into the four main type of synthesis: vapour, solid, liquid and two phase approaches. Perovskite NCs are largely prepared by a liquid phase approach, although solid state processes such as ball milling have been demonstrated⁷⁰. In the liquid phase approach, the resulting NCs are colloiddally dispersed in a suitable solvent.

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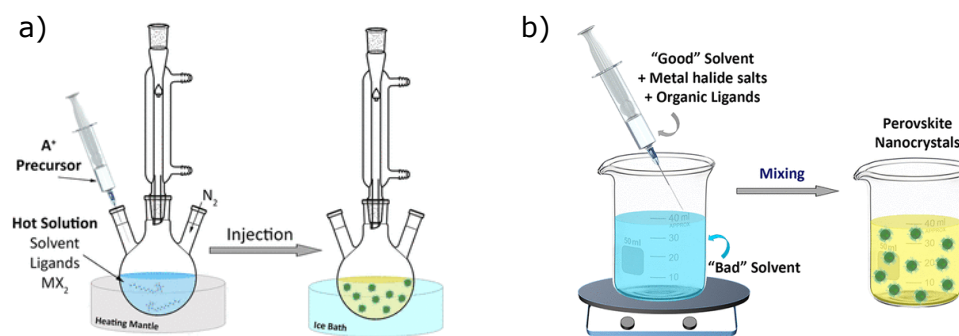


Figure 2.7: Schematics of a) Hot Injection and b) ligand assisted reprecipitation (LARP) synthesis techniques for lead halide perovskite NCs. Reproduced with permission from the ACS⁹, see Appendix E

The key to their dispersion is down to the ligands on their surface and how these interact with the solvent and surface of the NC.

The two main approaches that will be covered here for the liquid phase synthesis of perovskite NC are Hot Injection and ligand assisted reprecipitation (LARP). There are a variety of other, less popular, routes that have been successful in making perovskite NCs. More details on these can be found in numerous reviews on synthetic approaches to perovskite NCs^{9,71,72}. Schematic representation of these two synthetic methods is presented in Figure 2.7.

The fundamental concepts of LARP have been used for centuries across a wide variety of applications from salt crystallisation⁹ to organic nanoparticles⁷³. The general overview is of desired ions being dissolved in a solvent, and then moving the solution to a state of supersaturation. This state can be achieved through temperature, solvent evaporation, or the addition of a miscible solvent that the ions are not as soluble in. The addition of ligands to aid the formation of NCs through this technique is the namesake for this synthesis.

LARP requires the perovskite precursors, PbX_2 and AX , to be dissolved in a suitable polar solvent, typically dimethyl sulfoxide (DMSO) or dimethylformamide (DMF). This mixture is then dropped in to a non-polar solvent, such as toluene or hexane, in the presence of ligands. This mixing induces the supersaturation, and triggers the nucleation and growth of NCs. A wide variety of compositions have been achieved

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through this approach across the halide (I, Br, Cl) and cation (Cs, MA, FA) sites^{74–81}. This synthesis is often carried out in air and is readily scalable^{82,83}.

Hot Injection has been a popular synthesis for semiconductor quantum dots since its first application to cadmium chalcogenides⁸⁴. A precursor is injected into a hot solution of the remaining precursors and ligands in a solvent. It is popular due to the ability to achieve small NCs with narrow size distributions, owed to the separation of the nucleation and growth steps in the synthesis^{69,85–88}. After sufficient growth, the reaction is quenched usually through a rapid change in temperature. This can be introduced by the injection of a cold solvent, or plunging the reaction vessel into an ice bath. These reactions are often carried out under inert atmosphere and can require long degassing steps to remove all air and moisture from the reaction vessel. The resulting NCs are governed by the temperature, time, ratio of ligands to precursors and their concentration. This leaves a large parameter space to be manipulated.

CsPbX₃ NCs were first made via Hot Injection by Protesescu et al. in 2015⁵. Here, lead halide is dissolved in 1-octadecene (ODE) with the addition of long chain aliphatic ligands, oleic acid (OA) and oleylamine (OLAm). Once dissolved and degassed, the mixture is raised to a desired temperature between 120 - 200 °C, and a solution of cesium oleate (Cs-oleate) in ODE is injected. After 5 seconds, the mixture is plunged into an ice bath to quench the reaction. This success arguably triggered the explosion of investigations into perovskite NCs, after narrow emission peaks with easy tunability (12 - 42 nm between 400 - 700 nm) were achieved. Since then, as for LARP, a wide variety of different perovskite compositions have been achieved using this technique across the halide (I, Br, Cl), cation (Cs, MA, FA) and metal (Pb, Sn) sites^{5,9,89–92}.

In both LARP and Hot Injection, the nucleation and growth of the perovskite NCs are vitally important for achieving control in the synthesis. Each synthetic route also offers size and shape control, as well as engineering of the surface chemistry of the resulting NCs. This has been achieved by altering the ligand ratios used in the synthesis, as well as the choice of ligands themselves. Each of these aspects shall be explored in the following sections, with examples for both LARP and Hot Injection given where applicable.

Nucleation and Growth

The content of this subsection is based on the reviews by Chang and Waclawik⁶⁹, Murray et al.⁹³ and Thanh et al.⁸⁸ These texts should be referred to for further details on nucleation and growth of nanocrystals.

Nucleation and growth are the two key processes in the formation of NCs. Any NC synthesis begins with the precursors. Once the concentration of these precursors is above the nucleation threshold, they aggregate and form small nuclei, or seeds, which act as a base for crystal growth. The particles then grow by interaction with remaining precursors in solution and each other. This growth stage is dependent on the particle surface and the monomer diffusion to the surface. Particles must reach a critical radius, above which they will grow and form NCs, and below which they will redissolve. The size distribution of a NC's dispersion is determined by the time over which the nuclei form and by size focusing effects or ripening. These two processes can be explained in a classical description using thermodynamics and kinetics, and a detailed overview of the mathematics behind these processes is presented by Thanh et al⁸⁸.

In order to achieve monodisperse NC, the two processes should be separated. This was conceptually introduced by LaMer in the 1950s⁸⁷, showing that a discrete nucleation should be followed by a slow and controlled growth, Figure 2.8. This is easily achieved through Hot Injection, where the rapid addition of a precursor raises the concentration above the nucleation threshold, and a burst nucleation ensues to relieve the supersaturation. These nuclei continue to grow, with rapid depletion of monomers and ideally no new nuclei. This growth is usually followed by Ostwald ripening, whereby the dissolution of smaller particles enables the larger particles to grow further, leading to size defocusing. This can be mitigated by a rapid quench of the reaction, of course dependent on the reaction kinetics.

Since the first Hot Injection synthesis of CsPbX₃ there have been attempts to unravel the nucleation and growth processes for lead halide perovskite NCs. Microfluidic reactors have been used, coupled with in-situ optical spectroscopy, to form droplets

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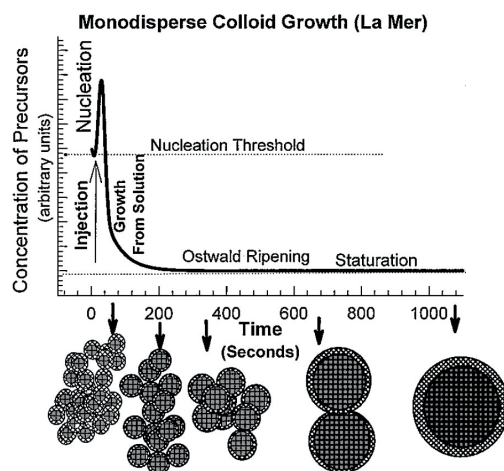


Figure 2.8: Depiction of nucleation and growth stages for the preparation of monodisperse NCs in the LaMer model. Reproduced with permission of ANNUAL REVIEWS in the format Thesis/Dissertation via Copyright Clearance Center⁹³, see Appendix E

of the perovskite NCs and determine their nucleation and growth dynamics^{94,95}. For CsPbX_3 it was found that both processes occurred in the first 1 - 5 seconds of the reaction⁹⁴. Alternatively, transmission electron microscopy (TEM) studies have been used. Koolyk et al. reported a size focusing regime lasting 20 seconds in CsPbI_3 NCs, and that CsPbBr_3 only undergoes a defocusing from the beginning of the reaction with a continued broadening of the size distribution which lasted for 40 seconds⁹⁶. A two-step mechanism involving Pb^0 NCs and orientated attachment was also proposed⁹⁷, but has since been discounted due to the now known formation of Pb^0 forming under electron beam irradiation⁹⁸.

The clear differences found in just these studies alone show the lack of understanding for these key processes in lead halide perovskite NCs. In other traditional quantum dot systems, the nucleation and growth processes have been rigorously studied. One of the margins for error in the studies is that the perovskite forms very rapidly, and this incredibly short time frame impedes studies. In spite of this, the formation of perovskite NCs in a variety of shapes and sizes has still been achieved.

Size and Shape Control

The content of this subsection is based on the reviews by Yin and Alivisatos⁸⁵, Carey et al.⁸⁶, and Shamsi et al.⁹. These texts should be referred to for further details on size and shape control of nanocrystals.

A variety of different shapes of semiconducting NCs are obtainable, including cubes, rods, platelets, wires and tetrapods. The shape evolution during synthesis can be described through a variety of models based on thermodynamics or kinetics. In the thermodynamic rationale, the resulting shape of the NC is due to a minimisation of the free energy, which is dependent on the surface energy of each crystallographic face⁹⁹. Kinetically, the effective monomer model can be applied where the concentration, stability and chemical potential of the precursor monomer governs the parameters for growth shape¹⁰⁰. Other models include the selective adsorption model⁸⁵ and oriented attachment^{101,102}.

The size, and size distribution, of NCs can be altered in post-synthetic treatments. Size selective precipitation or washing steps can result in a narrowing of a size distribution and the isolation of a given size of NC. This can be useful where polydisperse particles are made, or where different sizes of NCs with identical composition are required.

As discussed previously, the shape and size of the NC have an effect on the optical properties through quantum confinement. The extent of quantum confinement is dictated by the regime (weak, intermediate, strong) and the dimensionality (0D, 1D, 2D, 3D). The interplay of these two will determine the band gap of the material, and thus its optoelectronic properties.

Lead halide perovskite NCs are readily manipulated to form different shapes and sizes, and this is possible through both the Hot Injection synthesis and LARP. For Hot Injection, a higher reaction temperature leads to larger particles, due to a faster growth phase. CsPbI₃ nanocubes have been reported to span from 3.4 nm to 12.5 nm with a reaction temperature from 60 to 185 °C⁷. Commonly, the temperature range for CsPbX₃ nanocubes is between 120 - 200 °C. At lower temperatures nanoplatelets

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(NPLs) are formed¹⁰³ and nanowires can be formed at higher temperatures with longer reaction times¹⁰⁴. In most of the studies, the ligands were oleic acid (OA) and oleylamine (OLAm). When the lengths of the aliphatic chain of the ligands are changed, either NPLs or nanocube formation can be promoted with varying thicknesses and/or diameter¹⁰⁵, as shown in the schematic in Figure 2.9a.

The acid-base ratio of the ligand system OA/OLAm has also been shown to effect the size and shape of perovskite NCs. A study by Almeida et al. demonstrated that using the minimum amount of OA and OLAm required to solubilise PbBr_2 (25 mM and 0.25 M respectively), formed monodisperse CsPbBr_3 nanocubes. When the amount of OA was increased, they observed the presence of NPLs and could control the thickness of these NPLs from 2.4 nm to a monolayer thickness. This was done by using high concentrations of OA (up to 0.5 M) and reducing the amount of Cs injected¹⁰⁶. They also demonstrated the formation of hexagonal "0D" Cs_4PbBr_6 through increasing the concentration of both OA and OLAm, but keeping the ratio at 1:1. The cause for this control relates to the interplay of the ligands with the NC surface, which will be discussed further in the next subsection.

In a LARP synthesis of CsPbX_3 at room temperature, varying the aliphatic chain on the ligands also resulted in shape differences. Hexanoic acid and octylamine afforded quantum dots, OA and dodecylamine gave nanocubes, acetate acid and dodecylamine provided nanorods, and oleic acid and octylamine yielded thin NPLs¹⁰⁷, as shown in the schematic in Figure 2.9b. Another example of the shapes achievable through a LARP synthesis was conducted by Seth et al. They reported to be able to change the morphology of CsPbX_3 through altering the solvents, ligands and reaction time. For example, using ethyl acetate as the anti-solvent resulted in quantum dots forming (2.6 nm edge length), which over longer reaction times transformed to nanoplates and then nanobars⁸¹. Size and shape control for the LARP synthesis has also been shown for MAPbX_3 ^{108–112} and FAPbX_3 ⁷⁸ systems.

2.3. Chemistry of Perovskite Nanocrystals

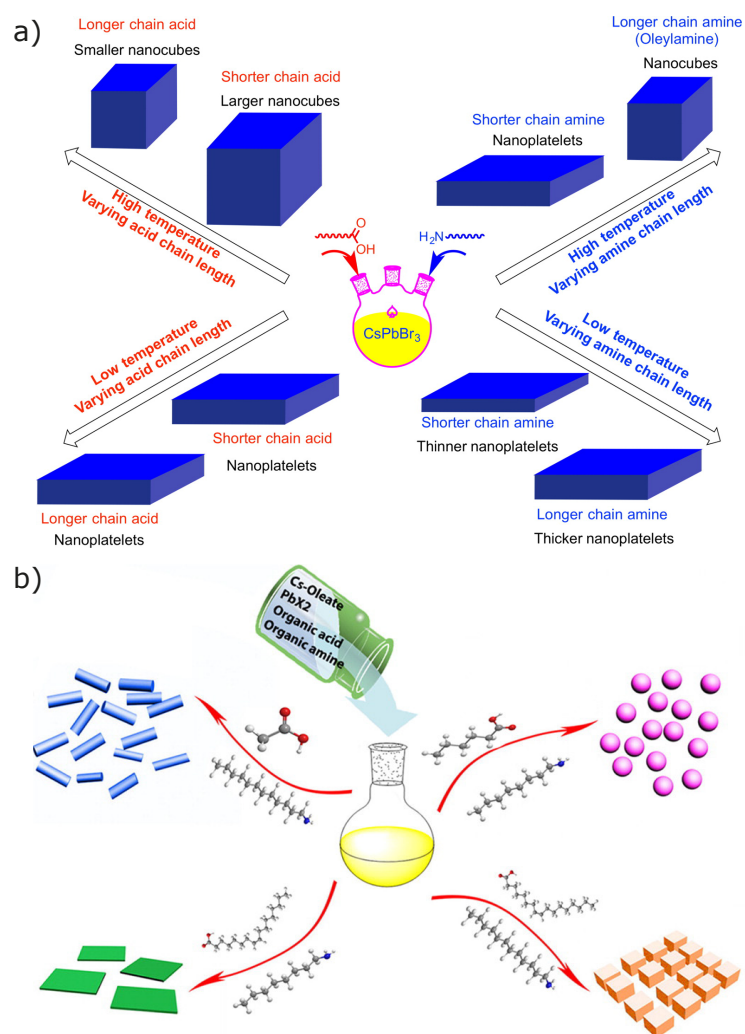


Figure 2.9: Size and shape control in the synthesis of lead halide perovskite NCs via the a) Hot Injection and b) LARP synthesis. Reproduced with permission from the American Chemical Society^{105,107}, see Appendix E

Surfaces and Ligands

The content of this subsection is based on the work by Boles et al.¹¹³ and De Roo et al.^{114,115} These texts should be referred to for further details on surfaces and ligands of nanocrystals.

It is clear that an important factor in NC growth, optical properties, and stability is the ligand shell. The ligand for a NC typically consists of a tethering head, which interacts with the NC surface, and a long hydrocarbon chain. In general, longer chains are better for colloidal stability and the interaction between the surface and tethering head can alter the properties of the NC.

Ligand-NC interactions are classified using the framework in the covalent bond classification in organometallic chemistry. This treats every bond as a covalent 2-centre-2-electron interaction, and the ligand type is dependent on the number of e^- that the neutral ligand contributes to the metal-ligand bond. There are three types, L-, X-, and Z-type ligands, which contribute 2, 1, and 0 electrons respectively in their neutral form. L-type ligands are Lewis Bases, and typically coordinate to surface metal ions, whereas Z-type ligands are Lewis Acids, which coordinate to non-metal atoms. X-type ligands will bind with either metal or nonmetal atoms depending on their affinity to each. A binding motif is built from combinations of the surface stoichiometry of the NC and ligand type. A schematic representation of the binding motif of a NC with L-, X- and Z-type ligands is shown in Figure 2.10a. The NC has to be neutral to be dispersed in non-polar solvents, and the binding motifs reflect this. CsPbBr_3 has the binding motif $\text{NC}(\text{X})_2$, where X is the ammonium (RNH_3^+) and carboxylate (RCOO^-) ions¹¹⁵.

Surface ligands also influence NCs optical and electronic properties. Uncoordinated surface atoms with dangling bonds contribute to electronic states that sit between the conduction band and valence band. These act like defect sites and can trap electrons or holes, and thus quench luminescence. Bonding between NC and ligand generates new molecular orbitals with both bonding and anti-bonding character as normal. Bonding orbitals are more stable than the NC surface, and anti-bonding less stable. A good

2.3. Chemistry of Perovskite Nanocrystals

covalent bond thus removes these trap states from dangling bonds by shifting the energies of the bonding and anti-bonding orbitals outside of the band gap of the NC, effectively cleaning up the trap states. This model is completely dependent on the molecular orbitals of the surface atoms of the NC and those of the ligand. It is possible that the combination of their atomic orbitals could introduce more mid-gap states, and thus quench luminescence even more. Although it is still not fully understood to what extent ligands can be removed, or rather the minimum amount of surface coverage required for a given NC system, it is generally acknowledged that a strongly bound ligand surface is beneficial to optoelectronic properties.

Typically, in perovskite NCs the ligand head groups are carboxylate and primary ammonium, as in oleate (from OA) and oleylammonium (from OLAm), respectively. These ligands are a relic of more traditional quantum dot syntheses, such as metal chalcogenide systems. More recently there has been an emphasis on understanding how these ligands interact with the perovskite surface and if there are binding groups, or ligands in general, that are more suitable.

The surface of a perovskite NC can be viewed as a series of vacancy defects. The surface can either be seen as AX- or PbX_2 -rich depending on the surface termination^{116,117}, which will in turn effect the optoelectronic properties of the NC. Using nuclear magnetic resonance spectroscopy (NMR), De Roo et al. showed that OA and OLAm form a dynamically bound ligand shell on CsPbX_3 NCs¹¹⁴, shown in Figure 2.10b. They showed that it is mainly oleylammonium on the surface of the NCs, in the form of oleylammonium bromide as the main capping ligand. This then interacts with other species such as oleates, bromide, or oleylamine in equilibrium. This complex equilibrium can result in the degradation of the NC if not balanced correctly, for example through washing steps or with concentration and time. If the equilibria is promoted away from the surface of the NC, colloidal stability is risked along with increased luminescence quenching. When the ratio of Pb to Cs was considered for small NCs, it was found to be less than 1. This indicated that smaller NCs are terminated by PbBr_2 , and that the Cs^+ are replaced by oleylammonium ions instead⁵⁵.

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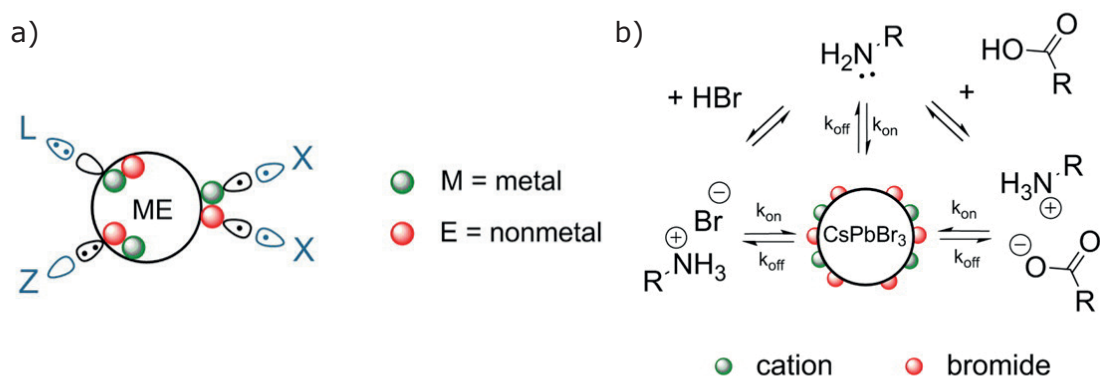


Figure 2.10: a) Schematic representation of binding motifs of ligand types L, X and Z with a NC from the covalent bond classification system, b) the dynamic surface of a CsPbBr₃ NC covered in oleylammonium bromide (left), oleylammonium oleate (right) and oleylamine (top), where R=CH₃(CH₂)₇CH=CH(CH₂)₇. Reproduced from the American Chemical Society¹¹⁴, see Appendix E

This work highlighted the increased lability and dynamics of the perovskite surface in comparison with more traditional quantum dot systems.

The binding motif of a ligand and NC not only includes the ligand tethering head, but also the surface of the NC itself. The surface termination of the perovskite NC makes a large difference on how the ligands will interact, and what is best for stability and PLQY. This was investigated thoroughly for CsPbBr₃ by Bodnarchuk et al. They propose representing the NC as [CsPbX₃](PbX₂)AX', with the core CsPbX₃ terminated by a PbX₂ inner shell and then a capping outer layer of AX'. In this model, A is the monovalent cation (Cs⁺ and/or alkylammonium) and X' is the monovalent anion (halide and/or oleate). It was found that a halogen rich surface, or complete PbBr₆ octahedra, of the inner shell is key to high PLQY and minimisation of surface traps. Then long chain ligands are required in the outershell for colloidal stabilisation. They demonstrated this experimentally by treating a washed CsPbBr₃ NC sample with lead bromide and didodecyldimethylammonium bromide to restore PLQY from 30-40 % to 90-100 %¹¹⁸.

The stability of NC can be split into colloidal stability, which concerns the NC dispersion in a solvent, and the phase or chemical stability of the NC, which concerns, for example, their susceptibility to moisture. Both types of stability issues can be tackled through the manipulation of the ligand chemistry, which often encompasses a

2.3. Chemistry of Perovskite Nanocrystals

boost in PLQY due to a better passivated surface. One such exploration by Krieg et al. investigated the use of zwitterionic capping ligands on CsPbBr₃ NCs. Here, they showed that sulfobetaines, phosphocholines, and γ -amino acids were favourable ligands due to their lack of mutual or external neutralisation through acid-base equilibria, and that the added chelating effect from these ligands stabilised the NC surface. They were able to form more concentrated colloidal solutions with these ligands, as well as NCs that were more stable to a variety of washing techniques and over time¹¹⁹. Other surface treatments have been conducted on perovskite NCs, including thiocyanate treatments¹²⁰, lead halide treatments¹²¹ and softer Lewis bases¹²². A common strategy to tackle the chemical stability of lead halide perovskite NC films is to embed them in a host matrix. This has been shown to be successful with polymers¹²³, silica-based matrices^{124–126} or coating films with aluminium oxide¹²⁷.

It is noteworthy, that the vast majority of studies into the surfaces of perovskite NCs have focused on CsPbBr₃. This is often seen as the model system, due to its ease of synthesis and lack of phase change. There are some studies into the surface of NCs with different halogens, for example for CsPbI₃¹²⁸. However, there is little research into the other cations, particularly FA. Changing the cation will undoubtedly cause large differences on the surface of the NC and the binding affinity to different ligands. There is scope in the literature for further investigation in this area, and the research presented in this thesis contributes to this.

Ligand Exchange

The perovskite NC ligand shell is dynamic, and so it is possible to induce ligand exchanges as a post-synthetic treatment. Due to the more ionic nature of the perovskite NC-ligand interaction, compared to the covalent nature of traditional quantum dots, ligand exchanges have to be treated differently. Harsher treatments can result in the dissolution of the perovskite, or trigger phase changes^{129–134}. There have been examples of ligand exchange on perovskite NC both in solution^{120,135,136} and directly on films^{129,137,138}.

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Long chain ligands impede charge transport across a NC film, and so ligand exchange is desirable to improve device performance. For photovoltaic applications strong coupling is required between the NCs, with compact surface species and the removal of residual precursors essential. Wheeler et al. investigated a two step strategy for CsPbI₃ NCs, using methyl acetate (MeAc) to remove oleates, and a combination of formamidinium iodide (FAI) in ethyl acetate to remove oleylammonium¹³⁹. They showed the importance of water in this process for the hydrolysis of MeAc, to exchange oleate for acetate ligands. Their use of FAI did result in some incorporation of FA into the perovskite lattice, which proved unfavourable for device performance. Short time scales were essential, with an exchange time of 10 seconds determined to be enough for complete removal of long chain ligands and little cation exchange¹³⁹. This highlights the extremely labile environment of OA and OLAm on the surface of these NCs.

In general, a thinner film of perovskite NCs is required for an LED compared with a photovoltaic device. Therefore, even though the long chain ligands are still insulating, operational LEDs are able to be made without conducting ligand exchanges^{140,141}. For an LED, the primary aim of the ligand exchange is maintaining or improving the PLQY of the material whilst removing excess precursors.

The ease of ligand exchange reflects the dynamic nature of lead halide perovskite NC and their surfaces. This is further highlighted by their ability to anion and cation exchange with ease. The first two reports of anion exchange in lead halide perovskite NC emphasise that this is a unique quality for this material; traditional semiconductor quantum dots cannot anion exchange^{16,17}. These exchanges are possible through a variety of halide precursors, such as ammonium halides, organometallic Grignard reagents, and lead halide salts. It is also achievable by mixing two compositionally different NCs together, and this has been shown for both anion¹⁷ and cation¹⁴² exchange. With a rigid ligand system, these exchanges would be hugely impeded, and thus these exchanges are testament to the malleable nature of lead halide perovskite NCs.

2.4 Applications of Perovskite Nanocrystals

To date, perovskite NCs have been used in a variety of lab-scale applications, including LEDs and phosphors²⁷, solar cells^{7,143,144}, lasers¹⁴⁵, photodetectors¹⁴⁶ and photocatalysis¹⁴⁷. Their narrow and efficient emission at tunable wavelengths makes them particularly desirable to light emission technologies, allowing for higher colour purity to be achieved. In this section, the state-of-the-art in perovskite nanocrystal LED advances will be presented along with what sets this material apart from the current commercial technologies.

LEDs

Lead halide perovskite NC LEDs have a very similar device architecture to that of organic and quantum dot LEDs. One way to characterise the efficiency of LEDs is to measure their external quantum efficiency (EQE). The EQE is the ratio of electrons injected to photons emitted. In order to mimic colours seen in real life in display technologies, a wide colour gamut is required. To achieve this three wavelengths of light, corresponding to red, green, and blue components, are selected to give the widest range across the visible spectrum. At time of writing these wavelengths of light for red, green and blue light were 630 (1.97), 532 (2.33), and 467 (2.66) nm (eV) respectively⁸. The colour gamut achievable with these wavelengths is shown by the triangle in Figure 2.11.

There are a variety of characteristics that set lead halide perovskite NCs apart from other semiconducting quantum dots for display technologies. Their compositional breadth, and subsequent band gap tuning, allow for finer tuning of their emission properties, without needing to be in the strong quantum confinement regime. This also broadens the scope for optimisation and decreases the influence of intrinsic limitations. They do not require a core-shell structure to achieve high PLQYs, which reduces synthetic steps and opportunities for complications. Another key quality is their narrow emission widths. Indium-phosphide quantum dots, as used in commercial TVs, are

Chapter 2. Background and Theory

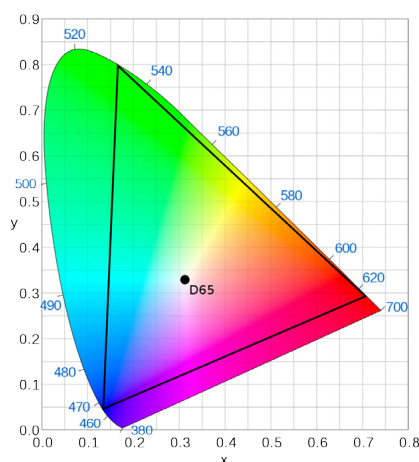


Figure 2.11: Chromaticity diagram showing the Rec. 2020 color space inside the triangle which has points at 467, 532 and 630 nm for blue, green, red primary colour. The point D65 represents white as denoted by the Rec. 2020 standard. Reproduced with permission, see Appendix E

limited to a full width at half maximum (FWHM) of 40 nm (~ 170 meV) at 530 nm (~ 2.34 eV) due to intrinsic properties of the few-nm sized core²⁴. Perovskite NCs are able to achieve FWHM at least half as narrow as this at the same wavelength, which has been shown numerous times in literature and in the results in this thesis.

There are many examples of perovskite NC LEDs devices in the literature. However, the emission wavelength is more often than not at less commercially relevant wavelengths, especially in the red region. MAPbI₂Br NC LEDs achieved an EQE of 2.75 % at 635 nm¹⁴⁸. For green LEDs, FAPbBr₃ NC made in-situ during film formation emit at 528 nm and were shown to achieve a maximum EQE of 16.3 %¹⁴⁹. Ochsenbein et al. recently made an advancement in achieving stable electro-luminescence at 463 nm from CsPb(BrCl)₃ with a maximum EQE of 1 %¹⁵⁰.

Toxicity is a major factor in assessing commercialisation of a new technology. Recently, the commercial processing of toxic cadmium-based quantum dots has declined, with Samsung Electronics introducing the first cadmium free quantum dot TV in 2015 (SUHD TV) and actively moving away from using this family of quantum dots. Although lead does raise some toxicity concerns, it is widely used in industry across various applications, such as lead-acid batteries and solder for silicon solar cells. This is also reflected in less stringent restrictions by the European Restriction of Hazardous Substances Directive on lead based electronics compared to cadmium²⁴.

2.4. Applications of Perovskite Nanocrystals

Despite this, research is on-going into lead-free perovskites. Aldakov and Reiss recently reviewed ways for safer-by-design NCs for commercial applications, covering both traditional quantum dots and perovskite nanocrystals¹⁵¹. They highlight the progress of lead-free perovskite NCs and the differences in strategy required between the two families of quantum dots.

The rapid success of perovskite NCs in LEDs and other device applications is due to the historical foundations laid by conventional semiconductor quantum dots and their LEDs, organic LEDs and polycrystalline perovskites. As cross-pollination between these fields continues, coupled with an increased understanding of the surface chemistry and stability of lead halide perovskite NC, it is likely that these NCs will have a large impact in the electronics world.

This thesis presents research regarding perovskite NCs for optoelectronic and photovoltaic applications. The tunability of the band gap of perovskite NCs using mixed cation compositions is first explored, Chapter 4. Their optical properties, ease of mixing, and structural effects associated with this compositional landscape are examined. Then, a novel approach to CsPbX₃ NCs utilising a phosphine oxide in the synthesis is presented in Chapter 5, with a focus on the NC surface chemistry and comparison to more traditional synthetic techniques. This optimised synthesis is then applied to FAPbBr₃ NCs in Chapter 6, with the motivation to replicate the successes seen for the inorganic perovskite. NMR is used to understand the differences in the results between these two compositions. It also sheds light on to why synthesis of mixed cation perovskite NCs across an extensive compositional range will require further control of the ligand and surface chemistry.

CHAPTER 3

Methods

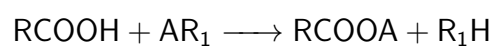
All syntheses and characterisation techniques detailed in this chapter are those conducted by the author of this thesis. Where additional syntheses or characterisation from a third party is used, their contribution is noted at the end of the relevant experimental chapter.

3.1 Precursor Syntheses

This section will cover general synthetic procedures for precursors in perovskite nanocrystal (NC) synthesis. Standard air free techniques with a Schlenk line are used.

Oleates

In general terms, oleic acid (OA) is reacted with cation salt to form a cation-oleate and side product. The reaction can be represented with the following equation:



Sodium Oleate

NaOH (0.71 g, 17.6 mmol) and OA (5.6 mL, 17.6 mmol) are stirred overnight at room temperature in ethanol (50 mL). Excess solvent is removed under reduced pressure, to afford white, soapy sodium oleate, Na-oleate.

Cesium Oleate

0.15 M in 1-octadecene (ODE) Cs₂CO₃ (0.406 g, 1.25 mmol) and OA (1.7 mL, 5.39 mmol) are degassed in 15.0 mL ODE in a 3-neck round-bottomed flask under vacuum at 100 °C for 1 hour followed by reacting under nitrogen at 140 °C. The colourless cesium oleate (Cs-oleate) solution is stored in a nitrogen filled vial for further use.

0.15 M in OA Cs₂CO₃ (0.122 g, 0.38 mmol) and OA (5.0 mL, 15.8 mmol) are degassed in a 3-neck round-bottomed flask under vacuum at 100 °C for 1 hour followed by reacting under nitrogen at 140 °C. The colourless Cs-oleate solution is stored in a nitrogen filled vial for further use.

For both of these reactions CH₃COOCs can be used in replacement of the carbonate¹⁰⁵ and the concentration of Cs-oleate readily tuned depending on reaction specifics. Research into the concentration limits and homogeneity of Cs-oleate solutions have been carried out by Lu et al¹⁵².

Formamidinium Oleate

0.125 M in ODE from Na-oleate Na-oleate (1.08 g, 3.55 mmol) is reacted with formamidinium acetate (0.366 g, 3.52 mmol) in 20 mL toluene at room temperature for three hours. The product is separated under reduced pressure and then dissolved in hot ODE to achieve a 0.125M solution of formamidinium oleate (FA-oleate).

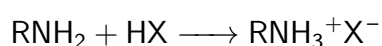
0.2 M in ODE Formamidinium acetate (0.347 g, 3.33 mmol) and OA (2.3 mL) are mixed in 14.4 mL ODE. The mixture is degassed at 50 °C until no more bubbles are formed, then under nitrogen the temperature is raised to 150 °C until the reaction

has completed. The FA-oleate solution is then cooled and stored under nitrogen until further use.

0.4 M in OA OA (40 mL) is dried at 120 °C for 1 hour. Formamidineum acetate (1.66 g, 15.9 mmol) is added and the mixture is degassed at 50 °C for 15 minutes. The temperature is raised to 130 °C under nitrogen until all the formamidineum acetate has dissolved. The FA-oleate solution is then cooled and stored under nitrogen until further use.

Oleylammonium Halides

In general terms, an amine is reacted with a hydrohalic acid to form an ammonium halide. The reaction can be represented with the following equation:



Oleylamine (12.5 mL, 38 mmol) and ethanol (100 mL) are combined and stirred in an ice bath until homogeneous. Hydrohalic acid (76 mmol) is added dropwise; 8.56 mL for 48 % aq. HBr. The solution is then left to stir for a minimum of six hours. The excess solvent is removed under reduced pressure, and the resulting solid is washed with diethyl ether before drying overnight in a vacuum oven to give a white, waxy solid of oleylammonium halide (OLAmX).

3.2 Common Chemicals

Figure 3.1 documents the most common chemicals used throughout this thesis, and their chemical structures.

These are split up into four sections: ligands, solvents, washing solvents (which can also be referred to as anti-solvents), and perovskite organic cations.

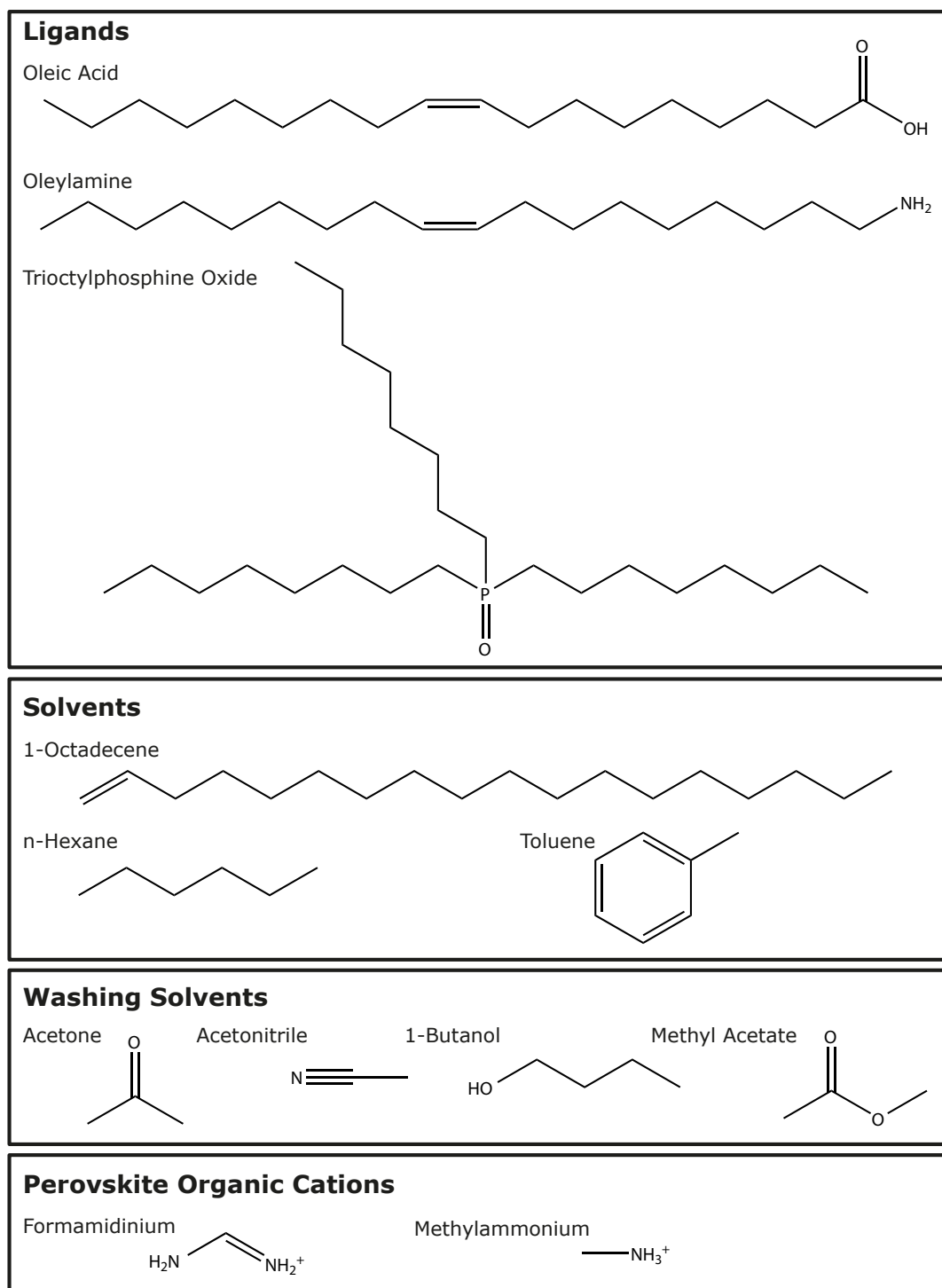


Figure 3.1: Common chemicals and their structures

3.3 Characterisation Techniques

As this thesis includes data from experiments conducted at Istituto Italiano Di Tecnologia (IIT), Central Research Laboratory, Genova, both sets of characterisation equipment are listed here. For the relevant chapters, data collected at IIT is highlighted.

Optical

Measurements are either recorded on colloidal solutions or on thin films. Films are either drop cast or spin coated onto a substrate, with or without a polymer host. Where measurements in solution have been carried out, 1 cm quartz cuvettes have been used.

Steady-State PL Spectroscopy

PL is conducted on a Horiba Scientific Fluorolog in Oxford and a Varian Cary Eclipse Fluorescence Spectrophotometer at IIT.

Time Resolved Photoluminescence Spectroscopy

A Picoquant FluoTime 300, using a 405 nm laser, is used for time resolved photoluminescence spectroscopy (TRPL) measurements. Time-correlated single photon counting is used. To determine carrier lifetimes, the data is fitted to a stretched exponential, and the code for this fitting can be found in Appendix A. Results and use of this fit are documented in Chapter 4.

Photoluminescence Quantum Yield

To measure photoluminescence quantum yield (PLQY), a CNI Low Noise Violet Blue 405 nm 200 mW laser is used with an integrating sphere and Ocean Optics Maya2000 Pro spectrometer. The integrating sphere allows for redistribution of light isotropically, regardless of angular dependence of emission. The system, including the sphere, fibre

Chapter 3. Methods

and spectrometer, was calibrated using a calibration halogen lamp. The PLQY, ϕ , is calculated according to De Mello et al, taking reabsorption into account¹⁵³.

For a given measurement, four spectra are collected:

1. *Background* - no laser, no sample
2. *Empty* - laser, no sample
3. *In* - laser, sample in path of laser
4. *Out* - laser, sample out of path of laser

There are two key spectral characteristics - the light from the laser, L , and the light from the photons emitted from the sample, P , the PL. The intensity of the excitation light, L , and emitted light, P , is estimated by integration of the peaks. For each spectrum, corresponding L and P values are assigned and then combined to give the final PLQY, ϕ .

To calculate an accurate ϕ , any contribution to P from light that is reabsorbed by the sample from the integrating sphere must be known. When the sample is *Out*, a portion of light, μ will be reabsorbed by the sample from the scattered laser light in the sphere. When *In* a portion of the light, A , will be absorbed by the sample, a portion will be transmitted or reflected, $(1 - A)$, and a fraction of this unabsorbed light will be scattered in the sphere and then absorbed by the sample, μ . From these, the absorbance, A , can be calculated.

$$L_{out} = L_{laser}(1 - \mu) \quad (3.1)$$

$$L_{in} = L_{laser}(1 - A)(1 - \mu) \quad (3.2)$$

$$A = 1 - \frac{L_{in}}{L_{out}} \quad (3.3)$$

3.3. Characterisation Techniques

The number of photons detected in the *Out* spectrum are denoted as $L_{out} + P_{out}$. For the total photons *In* spectrum, $L_{in} + P_{in}$, there are two major contributions - that of light emitted due to absorption of laser light, $\phi L_{laser}A$, and that scattered in the integration sphere, $(1 - A)(L_{out} + P_{out})$. Combining these, rearranging and substituting in Equation 3.3, the PLQY is obtained in Equation 3.4

$$\phi = \frac{P_{in} - (1 - A)P_{out}}{L_{laser}A} \quad (3.4)$$

There are certain limitations with this approach, for example the presence of stray light in the spectrometer is difficult to account for. The closer the lower limit of the PL range to the upper limit of the laser range, the larger the error becomes due to a broadened laser spectrum and some amount of spectral overlap. The integration of peaks is also dependent on the number of points that make up the peaks. One way to overcome this is to fit the laser and PL peaks to a suitable equation and integrate that. Due to the asymmetric nature of the peaks, especially the laser, a straight forward Gaussian is not acceptable. Other models, such as Lorentz, were used but due to the little gain in accuracy achieved when fitted, these fits are not included in the calculation package.

Measurements conducted at IIT used an Edinburgh Instruments FLS920 spectrofluorometer equipped with an integrating sphere.

An error of $\pm 5 \%$ is attributed to all PLQY measurements.

In-situ Steady State Photoluminescence Spectroscopy

This is set up with a Thorlabs 405 nm Laser Diode Module COS405 connected to a Thorlabs LDS5 power supply, a cuvette holder with heating and stirring controlled by a Quantum Northwest TC 125 Temperature Controller, and an Ocean Optics Maya2000 Pro detector. A schematic of the set up alongside a photo is shown in Figure 3.2. To avoid interference from ambient light, experiments were conducted in the dark, with the background file taken to account for stray light.

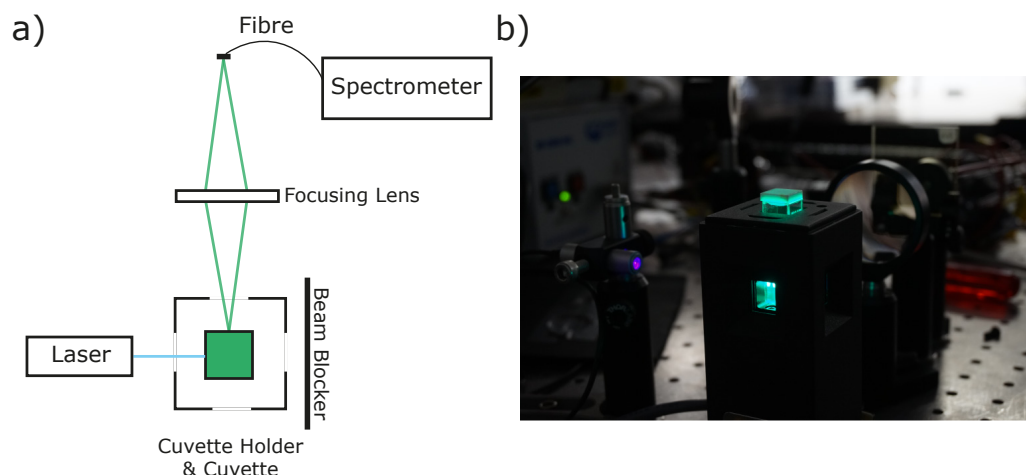


Figure 3.2: a) Schematic for in-situ PL measurements and b) photo of set up with CsPbBr₃

Ultraviolet-Visible Absorption Spectroscopy

For absorption spectroscopy, an Agilent Technologies Cary 60 UV Vis is used. Measurements conducted at IIT used a Varian Cary 300 UV-Vis spectrophotometer.

Structural

X-Ray Diffraction

NC dispersions are drop cast onto either quartz or glass substrates for X-Ray Diffraction (XRD) measurements. A PANalytical X'Pert Pro powder diffractometer is used, with a Cu-K α radiation operating at 40 kV and 40 mA.

At IIT, concentrated NC dispersions are drop-cast onto a zero diffraction silicon substrate for measurement in a PANalytical Empyrean X-ray diffractometer equipped with a 1.8 kW Cu K α ceramic X-ray tube and PIXcel3D 2×2 area detector, operating at 45 kV and 40 mA.

Transmission Electron Microscopy

For transmission electron microscopy (TEM), a Jeol JEM-2100 microscope with LaB₆ source, operating at an accelerating voltage of 200 kV is used. It has an Oxford Instruments 80 mm thin window energy-dispersive X-ray spectroscopy (EDS) detector

3.3. Characterisation Techniques

and Gatan Orius CCD camera. TEM is carried out in the David Cockayne Centre for Electron Microscopy, Department of Materials, University of Oxford. NC dispersions are drop cast onto holey-carbon coated 300 mesh copper grids.

Measurements conducted at IIT were done with NC dispersions drop cast on carbon coated 200 mesh copper grids and a JEOL JEM-1100 microscope operating at an accelerating voltage of 100 kV.

Nuclear Magnetic Resonance Spectroscopy

For ^1H nuclear magnetic resonance spectroscopy (NMR) residual d-toluene peaks are used for reference. For ^{31}P NMR, an external standard of triethylphosphate is used.

A 2-channel Bruker Avance III HD 400 MHz nanobay instrument running TOPSPIN 3 equipped with a 5 mm z-gradient Broad Band Fluorine Observation probe is used. Measurements conducted at IIT used a Bruker Avance III 400 MHz spectrometer, equipped with a Broad Band Inverse probe to investigate the acid-base interactions of OA and trioctylphosphine oxide (TOPO). To perform NMR studies on NCs, a Bruker DRX400 spectrometer 400.13 MHz equipped with a Bruker 5 mm Broad Band Inverse Z-gradient probe head affording a maximum gradient strength of 53.5 G/cm is used.

Synthesis of Mixed Cation Perovskite Nanocrystals

In this chapter, the development and assessment of a synthesis for mixed cation mixed anion perovskite nanocrystals (NCs) is presented. Firstly, the general synthesis and considerations for mixed cation systems are described, followed by a review of results for $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_y\text{Br}_{3-y}$. These NCs are discussed in detail, with a critical review of the oleate-based synthesis and how the synthetic conditions affect the optical and structural properties. $\text{FA}_x\text{Cs}_{1-x}\text{PbBr}_y\text{Cl}_{3-y}$ NCs are also investigated. Finally, an acetate-based synthesis is explored and compared to the oleate-based synthesis.

Key Findings

- Tuning of the emission of mixed cation mixed anion perovskite NCs across the visible spectrum
- FA and Cs are miscible, but lack of control of incorporation
- Decoupling size and shape effects from compositional change is challenging

4.1 Motivation

Polycrystalline thin films of mixed inorganic-organic cation perovskites have been shown, in certain cases, to have superior phase stability from their single cation counter parts. For example introducing small amounts of cesium (Cs) into formamidinium (FA) lead tri-iodide allows for the α -perovskite phase to be stabilized, as opposed to the non-perovskite yellow phase present in the neat FA perovskite^{154–156}. There have also been examples of a third cation being introduced to increase the phase and stability and process-ability of the polycrystalline thin films, resulting in $(MA_xFA_yCs_{1-x-y})PbX_3$ ¹⁵⁷.

Inorganic lead halide perovskites have proved to be efficient light-emitting materials, but they are also subject to phase instability. For example, $CsPbI_3$ based photovoltaic devices have only been demonstrated to overcome an intrinsic phase instability, when films were formed from NCs⁷, and even then it is likely that they are only metastable in a dry environment. For polycrystalline thin films, the cubic perovskite undergoes fast conversion into an orthorhombic yellow phase¹⁵⁸.

It has been shown that mixing cations (specifically Cs and FA) stabilize mixed halide perovskites against phase transformation, and yield well-performing photovoltaic devices^{154,155}. Introducing mixed cation compositions of perovskite NCs may help to alleviate issues of phase instability, which are also seen on the nano-scale.

The main synthetic routes to lead halide perovskite NC focus on single cation systems^{4,5,107}. Mixed cation perovskite NCs are still relatively scarce in the literature in comparison to the single cation and mixed anion systems; there has been work on a top-down approach, showing mixing two single cation perovskite NCs together yields the mixed cation perovskite¹⁴². Research regarding synthesising mixed cation perovskite NCs from a bottom-up approach has been successful for ligand assisted reprecipitation (LARP), but there has been little follow up or demonstrations of effects on stability shown¹⁵⁹. Where Hot Injection has been used only a limited range of compositions are achieved, such as $FA_{0.33}Cs_{0.67}PbX_3$ ¹⁶⁰ or $FA_{0.1}Cs_{0.9}PbI_3$ ⁹⁰.

Controlling the ligands and cation precursors is crucial to achieve mixed cation perovskite NCs without compromising on optical and structural properties. Here,

4.2. Oleate-based Synthesis Overview

two different Hot Injection based syntheses are investigated. Firstly, an oleate-based synthesis is explored followed by an acetate-based one. The aim of this research is to further understand the miscibility of FA and Cs cations and determine the most effective way to control the ligand shell.

4.2 Oleate-based Synthesis Overview

General Considerations

In the development of a synthesis for mixed cation perovskite NCs, $\text{FA}_x\text{Cs}_{1-x}\text{PbX}_3$, a number of considerations must be made. Firstly, due to FAPbX_3 NCs requiring an excess of FA to Pb, and CsPbX_3 NCs requiring a deficiency of Cs to Pb⁸⁹, the tuning of FA:Cs:Pb ratios in the injection step is not a equimolar relationship. The amount of ligand is also crucial, and for CsPbX_3 NCs an excess of both oleic acid (OA) and oleylamine (OLAm) is suitable. Conversely, in FAPbX_3 NCs an excess of amines proves detrimental to the formation of stable crystals. It has been postulated that this is related to the amines deprotonating FA and thus rendering it unreactive in the formation of perovskite NCs⁸⁹. An excess of OA is suggested to counter this, especially in the synthesis of FAPbI_3 ⁹⁰.

Temperature must also be considered, as in reported syntheses for the two systems different temperature ranges are used: 80 - 140 °C for FAPbX_3 ⁸⁹ and 120 - 200 °C for CsPbX_3 ⁵. Although there is a small window for overlap, this narrower temperature range indicates it may be harder to access a wider range of sizes whilst maintaining mixed cation compositions⁹⁰. These considerations set a challenge for the formation of compositionally-tuned mixed cation perovskite NCs. The method described below was developed with the aim of tackling all three considerations at once.

Method

Mixed cation NCs are made through a modified Hot Injection method, in a round bottom flask with stirring and normal Schlenk line techniques. Lead halide, (PbX_2 ,

Chapter 4. Synthesis of Mixed Cation Perovskite Nanocrystals

FA-Oleate			Cs-Oleate		
mL	mmol	Ratio		mmol	mL
3.2	0.40	1.0	0.0	0.00	0.00
2.6	0.32	0.8	0.2	0.01	0.09
1.9	0.24	0.6	0.4	0.02	0.18
1.3	0.16	0.4	0.6	0.03	0.26
0.7	0.08	0.2	0.8	0.04	0.34
0.0	0.00	0.0	1.0	0.05	0.43

Table 4.1: Amount of 0.125M cation oleates used for the synthesis of $\text{FA}_x\text{Cs}_{1-x}\text{PbX}_3$, with the proposed ratio for the resulting NCs



Figure 4.1: Photo of perovskite NCs made via Hot Injection synthesis under UV illumination. From Left to Right: $\text{FA}_x\text{Cs}_{1-x}\text{PbBr}_3$ ($x = 0.2, 0.4, 0.6, 0.8$), $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_{1.5}\text{Br}_{1.5}$ ($x = 0.2, 0.4, 0.6, 0.8$) and $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_3$ ($x = 0.2, 0.4, 0.6, 0.8$)

0.2 mmol) is dried in 1-octadecene (ODE) for 1 hour at 120 °C. Dried OA (0.5 mL, 1.58 mmol) and dried OLAm (135 μL , 0.41 mmol) are added to the PbX_2 solution under nitrogen at 120 °C. Once all PbX_2 is solubilised, the temperature is raised to 130 °C. Cation oleate solutions are individually preheated to 120 °C and are injected simultaneously at amounts calculated for the desired composition, Table 4.1. Synthesis of both cesium oleate (Cs-oleate) and formamidinium oleate (FA-oleate) (0.125 M in ODE), can be found in Chapter 3. After 5 seconds the flask is plunged into an ice bath to quench the reaction. NCs are separated by adding 1-butanol (3 - 4 mL) to the reaction mixture and then centrifuging at 8,000 rpm for 10 minutes. The NCs are then redispersed in hexane or toluene.

4.3 Iodide-Bromide Systems

The synthesis described above is first applied to bromide and iodide containing NCs, spanning the visible spectrum from 2.51 to 1.59 eV.

Optical Properties

Emission and absorption properties of $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_y\text{Br}_{3-y}$ NCs can be seen in Figure 4.2. A continuous shift in emission peak is seen for tuning values of x and y in Figure 4.2a, but this shift is not completely linear, as demonstrated in Figure 4.2b where $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_{1.5}\text{Br}_{1.5}$ NCs deviate from an evenly graduated shift. For these, the absorption onset is less steep, Figure 4.2d, in comparison to the single anion case, Figure 4.2c & e. This could be a result of the extent of incorporation of the anion species in each case, an additional factor in the tuning of the band gap of the material.

The full width at half maximum (FWHM) and photoluminescence quantum yield (PLQY) for these NCs are documented in Table 4.2. The mixed anion have the lowest PLQY of all the NCs synthesised through this route. Overall, the PLQY are lower than literature reported values for the single anion compositions, where near unity has been reported^{5,120,122}. This could be due to the amount of OLAm in the synthesis. Restricting the OLAm concentration may allow for a lack of negative interaction with FA, but there is not a sufficient concentration to push the dynamic equilibrium of the ligands on to the surface of the NCs resulting in a heavily populated trap state surface, and lower PLQY. For the mixed anions, this could be more heavily pronounced due to the binding strengths of the different halides towards ligands or due to strain on the lattice from mixed halide compositions¹⁶¹.

Interestingly, the FWHM for all anion stoichiometries is widest at low incorporations of FA, indicating a lack of homogeneity in potentially both size and composition in these NCs. As mentioned previously, an excess of FA to Pb is required to form FAPbX_3 NCs⁸⁹, implying that forming the perovskite is not favourable. The opposite is true for CsPbX_3 NCs which readily form at low concentrations of Cs to Pb. In a mixed cation system where only a small amount of FA is trying to be incorporated, the thermodynamic drive to form a Cs-rich perovskite is much higher and may result in competing pathways and the formation of a heterogeneous batch of NCs, as seen here.

This rationale is in agreement with previous work on a mixed cation perovskite NCs. In work by Protesescu et al. they find that even varying the FA to Cs ratio

Chapter 4. Synthesis of Mixed Cation Perovskite Nanocrystals

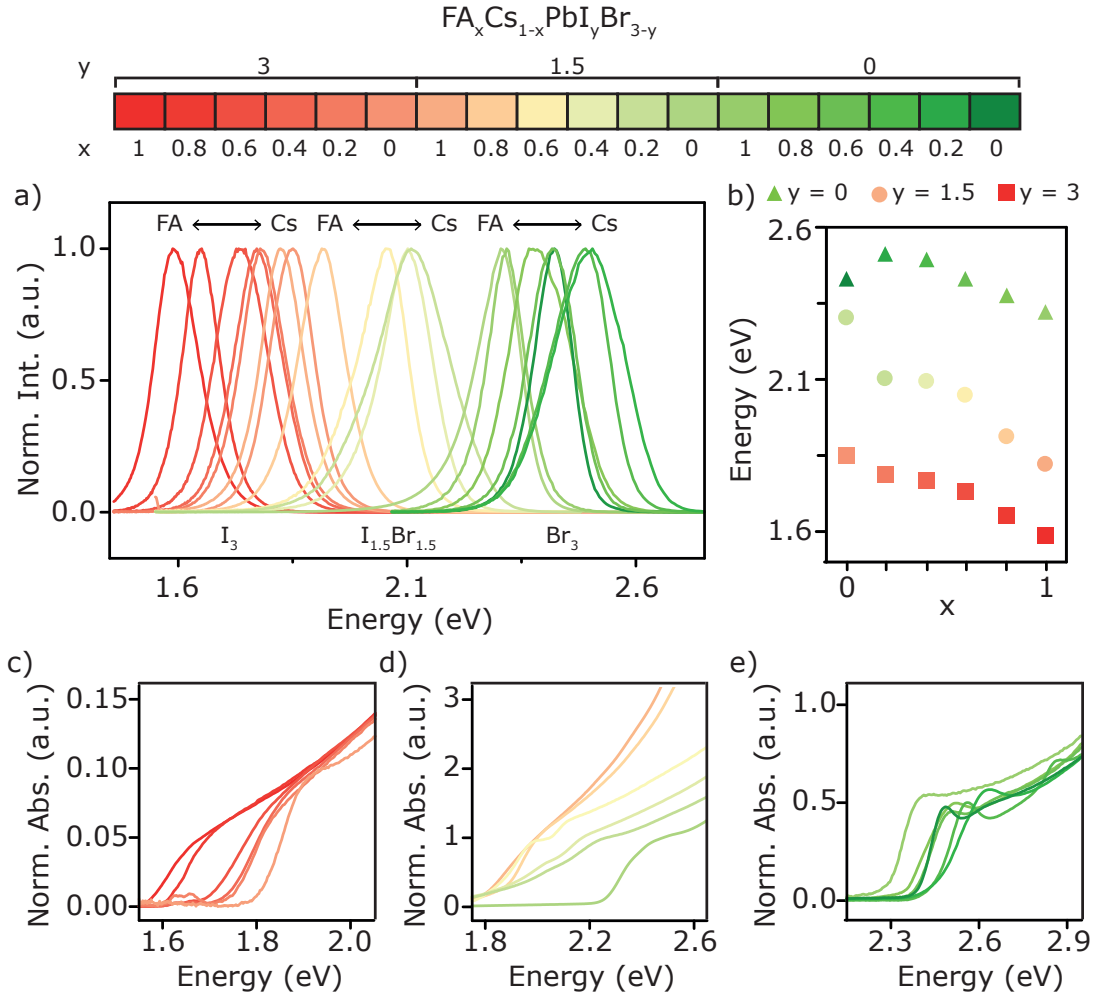


Figure 4.2: Absorption and emission properties of mixed cation perovskite NC, $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_y\text{Br}_{3-y}$. a) PL spectra, b) PL peak position and c) absorption spectra are shown

to 6:1 doesn't change the photoluminescence (PL) emission peak of $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_3$. From this it is concluded that there is either a single mixed stoichiometry of 10 % FA possible, or that the FA cations are only in the outermost layer of the NCs⁹⁰.

Size and shape could also be a cause for a widening in the FWHM. Again, due to the ligand engineering at play in the synthesis to curb disruption of FA, the growth of different shapes and sizes of NCs is highly likely. As reported previously, and discussed in Chapter 2, perovskite NCs can be promoted to form cubes and platelets in varying sizes by changing the concentration of the acid and base ligand in the reaction^{105,107}. The size and shape of these NCs will be reviewed in section 4.3 of this chapter, where transmission electron microscopy (TEM) images are presented and analysed.

4.3. Iodide-Bromide Systems

To determine the photo-carrier lifetime of the NCs time resolved photoluminescence spectroscopy (TRPL) is conducted. Normalised decays are shown in Figure 4.3a. The decays are fitted to a stretched exponential, Equation 4.1, the first moment of which gives the average lifetime, τ , Equation 4.2. The stretching factor, β , is a representation of the deviation from a monoexponential decay; when $\beta = 1$, a normal exponential decay is recovered, Equation 4.3. For such a case, τ is given by the time at which the decay is reduced to $\frac{1}{e}$ of it's initial value. For NCs, a monoexponential decay indicates a homogeneous system, and thus the stretching factor can indicate the deviation from homogeneity. The MatLab code used for fitting this data can be found in Appendix A.

$$f(t) = Ae^{(\frac{t}{\tau})^\beta} + B, \quad \text{where } 0 \leq \beta \leq 1 \quad (4.1)$$

$$\langle \tau \rangle = \left(\frac{\tau}{\beta} \right) \Gamma \left(\frac{1}{\beta} \right) \quad (4.2)$$

$$f(t) = Ae^{(\frac{t}{\tau})} + B \quad (4.3)$$

The average lifetime and stretching factor for the NCs are plotted against their cation composition, x , in Figure 4.3b & c respectively. The first observation is that with increasing FA content, the photo-carrier lifetime increases. Reported FA perovskite NCs have been shown to have long lifetimes of a similar order to those reported here⁸⁹. Often, however, these values are acquired by finding the time at which the decay is reduced by $\frac{1}{e}$ of it's initial value. In order to corroborate values obtained here using the stretched exponential with those in the literature, the $\frac{1}{e}$ lifetime is also calculated. These values can be found in Table 4.2. Although exact values differ, the general trend remains: more FA results in a longer lifetime. Not only does this show that the values here are comparable to those in the literature but also it indicates that the stretched exponential offers an extra insight into nature of the decay through the stretching factor.

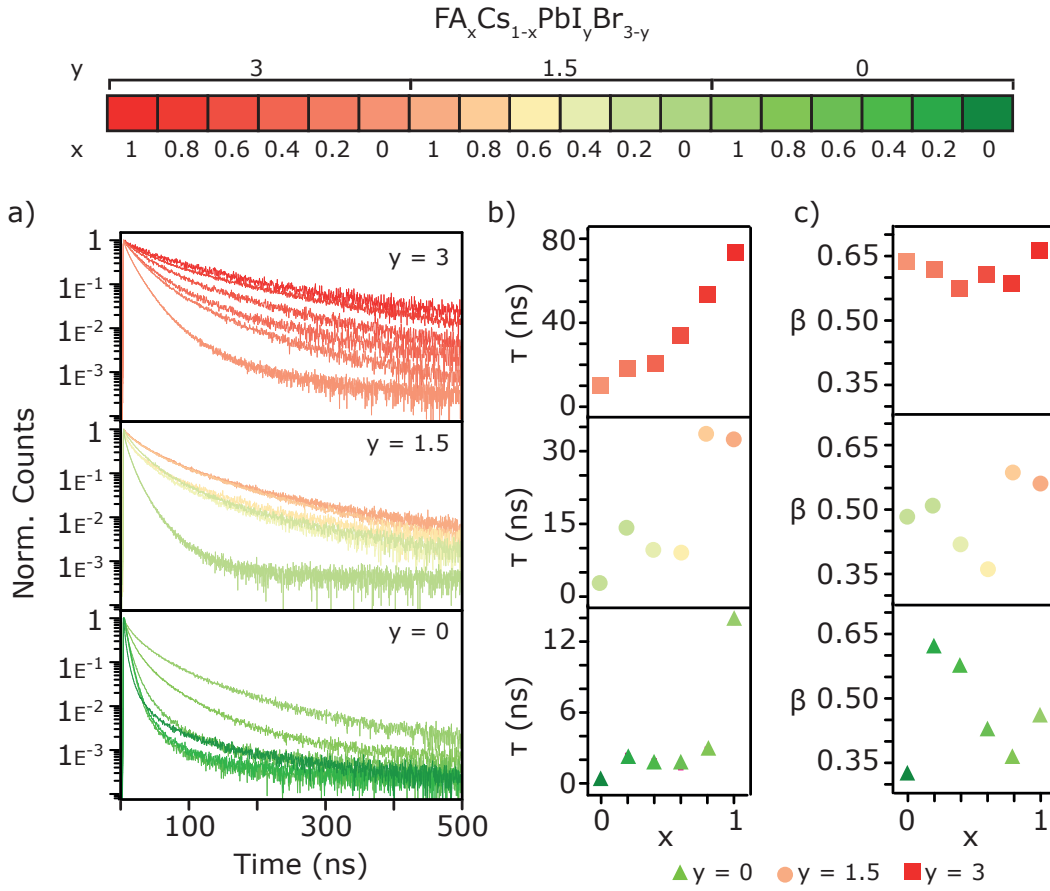


Figure 4.3: TRPL data for $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_y\text{Br}_{3-y}$ NCs. a) Normalised decays alongside b) average lifetime, τ , and c) stretching factor, β , plotted against cation composition, x

For tri-iodide NCs there is little variance in β . For both neat bromide NCs and $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_{1.5}\text{Br}_{1.5}$, the story is quite different. There is significant variation in β , clearly shown by the change in shape of the decays in Figure 4.3a, middle and bottom panel. This reflects a higher proportion of inhomogeneity across the bromide containing systems as more FA is present. This variance is concurrent with a larger range in FWHM for $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_{1.5}\text{Br}_{1.5}$ and $\text{FA}_x\text{Cs}_{1-x}\text{PbBr}_3$, 78 meV and 87 meV respectively, in comparison to $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_3$, 49 meV.

On review of the optical properties, there is successful demonstration of band gap tunability but the homogeneity of systems formed with this synthesis are questionable.

4.3. Iodide-Bromide Systems

Entry	Composition		Peak (eV)	FWHM (meV)	PLQY %	Stretched Fit		1/e τ (ns)
	x	y				τ (ns)	β	
i	1	3	1.59	111	47	72	0.68	73
ii	0.8	3	1.65	96	50	53	0.62	56
iii	0.6	3	1.73	74	50	33	0.66	40
iv	0.4	3	1.77	123	51	20	0.64	28
v	0.2	3	1.78	115	59	18	0.70	26
vi	0	3	1.85	113	47	9	0.64	17
vii	1	1.5	1.82	109	10	33	0.58	40
viii	0.8	1.5	1.91	121	28	34	0.60	40
ix	0.6	1.5	2.05	129	3	8	0.35	23
x	0.4	1.5	2.10	128	6	10	0.42	22
xi	0.2	1.5	2.11	187	10	16	0.55	25
xii	0	1.5	2.30	112	10	2	0.45	12
xiii	1	0	2.32	95	57	14	0.46	25
xiv	0.8	0	2.37	161	45	3	0.36	15
xv	0.6	0	2.42	123	51	1.4	0.42	11
xvi	0.4	0	2.49	151	30	1.7	0.57	10
xvii	0.2	0	2.51	182	55	2	0.62	10
xviii	0	0	2.42	98	10	0.1	0.32	9

Table 4.2: Optical properties of $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_y\text{Br}_{3-y}$ NCs. Average lifetime and stretching factor calculated using a stretched exponential fit are alongside the lifetime calculated at the time decay is reduced to $\frac{1}{e}$ of it's initial value

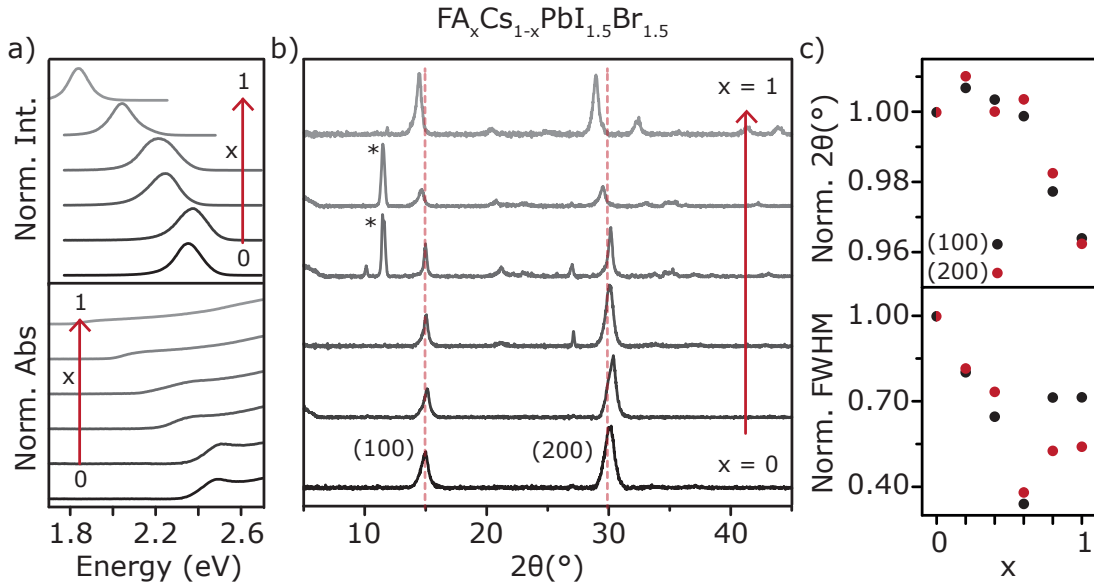


Figure 4.4: a) Normalised emission (top) and absorption spectra of $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_{1.5}\text{Br}_{1.5}$ NCs, b) corresponding X-Ray Diffraction (XRD) with (100) and (200) planes identified for $x = 0$, and lead halide peaks starred (*), and c) the relative change in peak position and FWHM against composition, x

Structural Properties

The structural properties were investigated to elucidate if the optical properties are a result of inhomogeneity in the composition, size, or shape of the NCs. To begin with, XRD for $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_{1.5}\text{Br}_{1.5}$ is measured, Figure 4.4. There is a noticeable shift in the band gap of the material from the optical spectra, Figure 4.4a, and this is mirrored by a peak shift and broadening in the XRD, Figure 4.4b. If the shift in band gap is a result of the size or shape of the NCs alone, then only a change in the width of the XRD peak would be expected. If the NCs are compositionally different then a shift in peak position is expected^{154,162,163}. Both relative line broadening and peak position (normalised to $x = 0$) are plotted against composition in Figure 4.4c.

There are three significant insights from this data. Firstly, that there are substantial shifts in the XRD peaks from $x = 0.6$ - 1, but below that there is little change. This confirms the lack of graduated incorporation of FA into the NCs from this synthetic route, and that there might be preference to forming more Cs-rich compositions instead. This is preceded in the polycrystalline thin film literature where it is noted that only certain ratios of FA to Cs are achievable^{155,164,165}.

Secondly, lead halide peaks are only observed in the XRD of $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_{1.5}\text{Br}_{1.5}$ NCs when $x = 0.6$ and $x = 0.8$. There are three most plausible reasons for the presence of lead halide; that it is an unreacted remnant from the synthesis, a product of degradation or a result of the washing technique on the NCs. Given that all the NCs are washed in the same way with 1-butanol, it is unlikely that the washing causes for more lead halide to be present, unless there is heightened sensitivity to the anti-solvent at given anion ratios.

Thirdly, there is considerable change in the broadening of the peaks across the compositional range. This confirms that the change in optical properties and the band gap tunability presented is a consequence of both changes in size and shape as well as composition.

To further examine size, shape and composition, TEM and energy-dispersive X-ray spectroscopy (EDS) are conducted. Figure 4.5 presents TEM images of

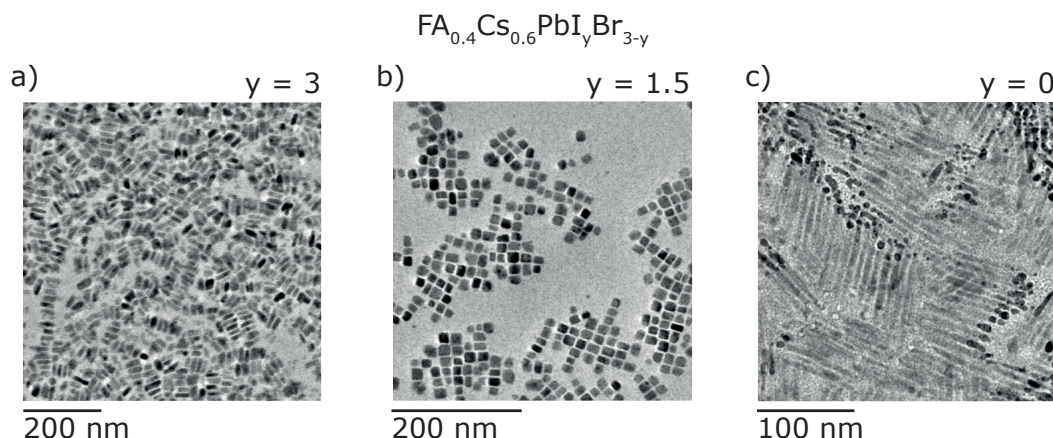


Figure 4.5: TEM images of $\text{FA}_{0.4}\text{Cs}_{0.6}\text{PbI}_y\text{Br}_{3-y}$ NCs with a) $y = 3$, b) $y = 1.5$, c) $y = 0$

$\text{FA}_{0.4}\text{Cs}_{0.6}\text{PbI}_y\text{Br}_{3-y}$ NCs. As suspected from the optical characterisation, a range of shapes are produced through this synthesis for different compositions. For tri-iodide, $y = 3$, nanoparticles more similar to nanoplatelets (NPLs) are formed, whilst for tri-bromide, $y = 0$, small nanorods are formed, Figure 4.5a & c respectively. Despite showing the lowest quality optical properties, the mixed anion NCs are cubes as expected, Figure 4.5b. This change in shape, and size, is most likely a result of the restriction of OLAm coupled with the reaction temperature.

The width of NCs in the $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_{1.5}\text{Br}_{1.5}$ are measured and a particle size distribution is shown in Figure 4.6. As the FA content increases, the particles decrease in size and polydispersity. For $x = 0.2$ there is average edge length of 14.2 ± 3.0 nm ($\sigma = 21$ %), whereas for $x = 0.8$ the average diameter is 12.3 ± 1.8 nm ($\sigma = 14$ %). The polydispersity explains the shallow absorption onset and large FWHM of the PL spectra.

The shape of the NCs are also important. At lower FA content, cubic or rectangular shapes are formed consistently, however at a higher FA content, $x \geq 0.8$, the particles are more spherical. As a result of this, their width was calculated using the diameter of a circle, as opposed to the edge length of a cube. At $x \geq 0.6$, the XRD peak shift and narrowing is more pronounced, as well as additional peaks being present. Given the more spherical shapes of the high FA content NCs as well, it could be plausible

Chapter 4. Synthesis of Mixed Cation Perovskite Nanocrystals

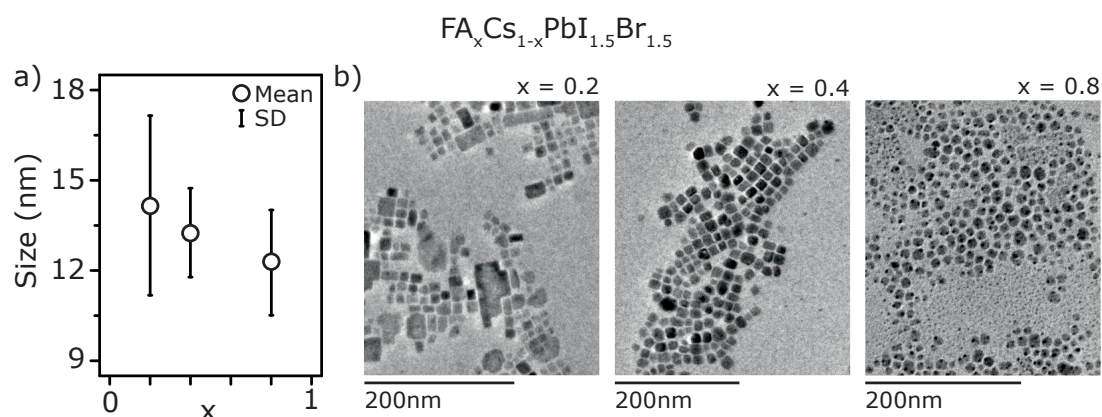


Figure 4.6: a) Average width of NCs and b) representative TEM images of $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_{1.5}\text{Br}_{1.5}$. It should be noted that to determine the width of $x = 0.8$, the diameter of a circle was used as opposed to a square

Entry	Composition		Ratio Pb:Cs	
	x	y	Predicted	EDS
i	0.8	1.5	0.2	0.34
ii	0.6	1.5	0.4	0.67
iii	0.4	1.5	0.6	0.89
iv	0.2	1.5	0.8	0.71

Table 4.3: EDS results for $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_{1.5}\text{Br}_{1.5}$ NCs. The EDS results are an average calculated from X sites across a sample. In all cases, the amount of Pb has been set to 1

that these are in a different phase or stoichiometry compared to the low FA content NCs.

EDS is conducted to investigate the accurate composition of $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_{1.5}\text{Br}_{1.5}$. Using high-angle annular dark-field imaging (HAADF) scanning TEM (STEM), points across a sample are selected and EDS is measured, with an average calculated for each composition. The average ratio of Pb to Cs is presented in Table 4.3. For the ratios stated Pb has been set to 1, and the predicted ratio is alongside the measured value. Though the measurements do not reflect the predicted compositions, there are still significant differences between each sample. This suggests that FA and Cs are miscible across a larger range than previously reported⁹⁰, but that there is a lack of control through this synthetic route. At higher FA content, there is significantly more Cs present than expected as observed in Table 4.3 Entry i & ii.

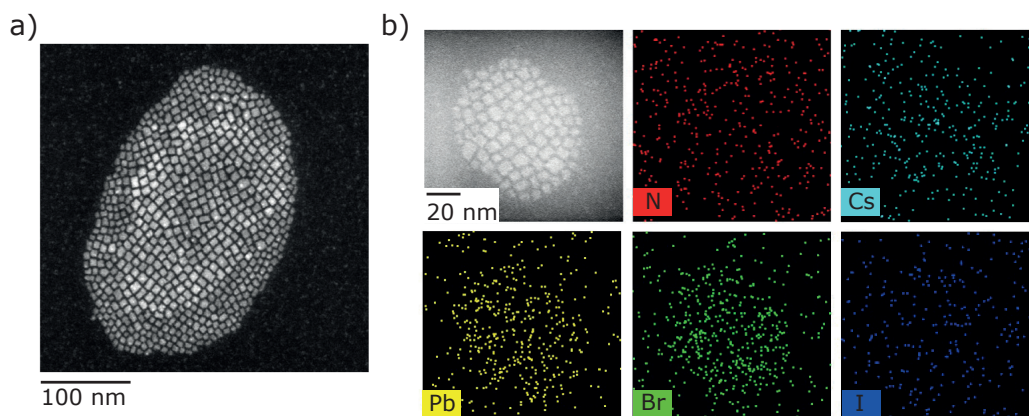


Figure 4.7: a) HAADF STEM image for a cluster of $\text{FA}_{0.8}\text{Cs}_{0.2}\text{PbI}_{1.5}\text{Br}_{1.5}$ NCs and b) another HAADF STEM image with associated EDS maps for nitrogen (N, red), cesium (Cs, light blue), lead (Pb, yellow), bromide (Br, green) and iodine (I, dark blue)

For further insight, EDS mapping is conducted on $\text{FA}_{0.8}\text{Cs}_{0.2}\text{PbI}_{1.5}\text{Br}_{1.5}$, Figure 4.7, using HAADF STEM. From this mapping the Cs:Pb:Br ratio calculated is 0.53:1:1.7. Bromide is known to desorb from the sample under electron irradiation, hence why a 1:3 ratio for Pb:Br is not obtained^{98,166–169}. Although nitrogen is mapped, a value cannot be associated with it to determine FA content due to nitrogen being attributable to the ligands on the surface and environmental effects. The Cs content here is again significantly higher than the predicted value (0.53 vs 0.2). This, alongside the EDS point data described above, supports earlier discussion of CsPbX_3 NCs being more favourable to form. The imbalance between the Cs:Pb and FA:Pb precursor ratio also reflects this^{89,90}.

The structural characterisation presented supports conclusions from the optical data regarding the lack of homogeneity in the NCs. It is clear that the effect of size and shape on the band gap cannot clearly be decoupled from the compositional tuning in this scenario.

Exchange Reactions

In order to understand more about the miscibility of FA and Cs, cation exchange reactions were monitored with in-situ PL.

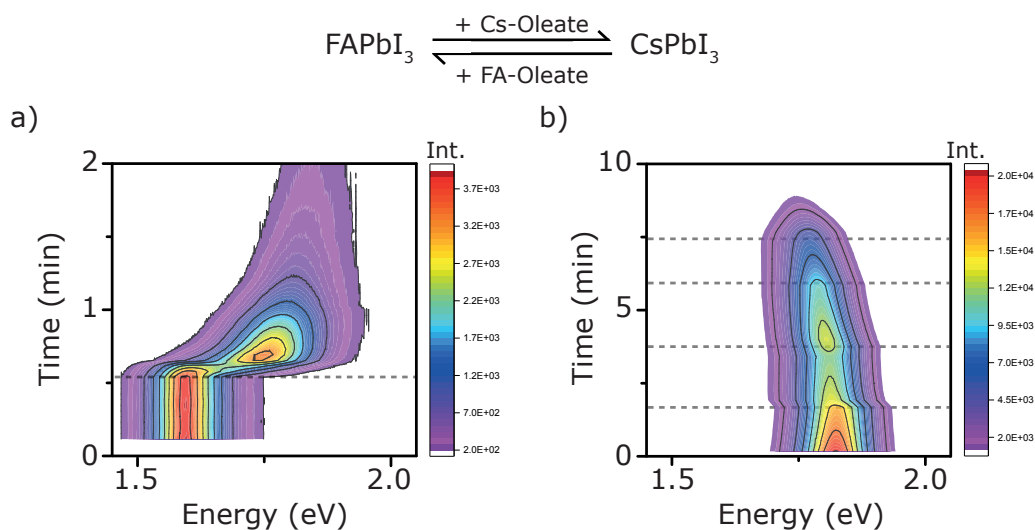


Figure 4.8: In-situ PL data collected for exchange reactions of a) FAPbI₃ with Cs-oleate and b) CsPbI₃ with FA-oleate. Grey dotted lines indicate the addition of cation source. Intensity below 5 % of the initial intensity maxima is not colour-mapped (i.e. is white)

Method

FAPbI₃ and CsPbI₃ are made according to the Hot Injection synthesis described at the beginning of this chapter. The exchange reactions are conducted as follows:

FA → Cs: 1 mL of 0.125M Cs-oleate in ODE is diluted with 1 mL of hexane. 100 μL of this solution is added to 3 mL of FAPbI₃ in a cuvette with stirring in the in-situ PL set up.

Cs → FA: 1 mL of 0.125M FA-oleate solution in ODE Four 10 μL additions of 0.125M FA-oleate in ODE are added at roughly two minute time intervals to 3 mL of CsPbI₃ in a cuvette with stirring in the in-situ PL set up.

Results

The change in PL during the exchange reaction is presented in Figure 4.8. For FA → Cs, Figure 4.8a, there is a drastic change in both peak position and intensity after the addition of Cs-oleate. If there were to be a gradual exchange of the two cations, a single peak would be expected to gradually shift, as shown for anion exchanges^{16,17}. Instead, a second peak forms and grows in intensity whilst the original peak decreases in intensity.

4.4. Bromide-Chloride Systems

Although the original peak does experience a slight blue shift over time, as does the second peak, the coexistence of two separate emission peaks indicates the formation of two compositionally different perovskite NCs coexisting as opposed to a gradual cation exchange from one composition to another. At the concentrations for this reaction, the change happens swiftly and is completed in under sixty seconds from the introduction of the cation source.

For $\text{Cs} \rightarrow \text{FA}$, any change occurs over a much longer time scale and requires a greater concentration of the cation source to be present. Even so, the red shift in PL is minimal over this time period, Figure 4.8b. As previously seen, the size and shape will play an important role in the PL emission from the NCs, and without further structural characterisation it is difficult to conclude if either of these exchanges went to completion. One important observation is that $\text{FA} \rightarrow \text{Cs}$ appears to be more favourable than vice versa.

4.4 Bromide-Chloride Systems

The synthesis is applied to a mixed bromide-chloride system. Optical data for the resulting NC is presented in Figure 4.9a & b.

In this case, a further washing step with methyl acetate was carried out after wide and double peaks were found in the emission spectra. After washing, there is no gradual change in onset of absorption or emission peak across the range $0 \leq x \leq 0.6$, indicating that mixed cation NCs have not been formed. Also, the PL emission remains broad and shoulder peaks are seen for $x = 0.2$ and $x = 0.4$. The TEM shown in Figure 4.9c & d, demonstrates the polydispersity of the NCs before washing and thus the lack of growth control.

4.5 Acetate-based Synthesis

The oleate-based synthesis explored in this chapter presents substantial issues for mixed A-site compositions. This includes both controlling the composition and the size and shape of NCs. One route proposed for the synthesis of FAPbBr_3 NCs replaces

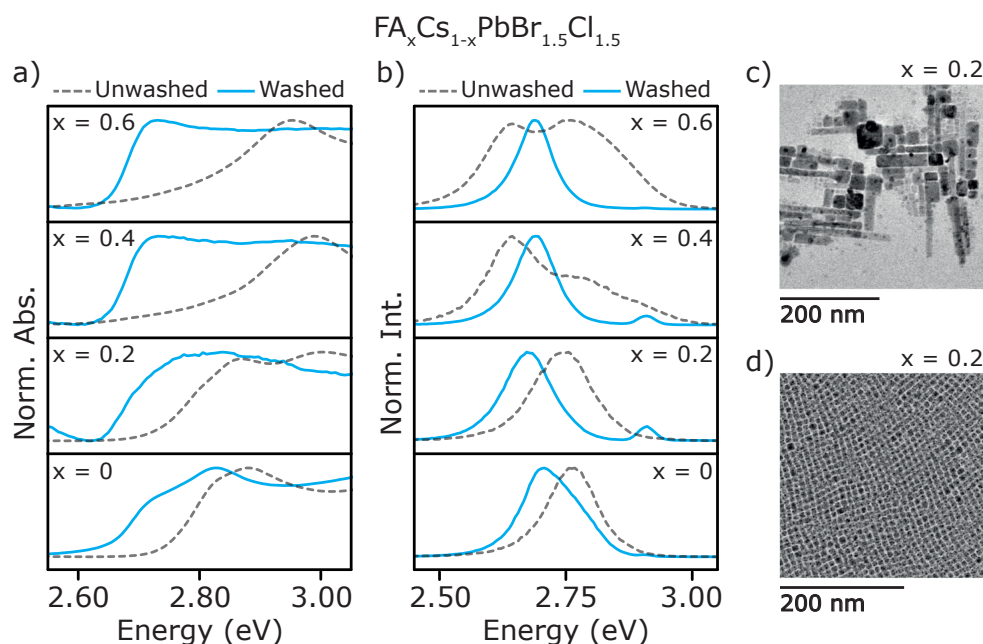


Figure 4.9: a) Absorption spectra and b) PL spectra of $\text{FA}_x\text{Cs}_{1-x}\text{PbBr}_{1.5}\text{Cl}_{1.5}$ before (black dotted) and after washing (blue solid) and TEM images of both c) larger particles and d) monodisperse particles co-existing in $\text{FA}_{0.2}\text{Cs}_{0.2}\text{PbBr}_{1.5}\text{Cl}_{1.5}$

the injection of cation oleates with oleylammonium halides to control the interaction of oleylamine with FA⁸⁹. This synthesis is carried out on mixed cation systems to evaluate if added control of size and shape alongside improved optical properties can be achieved.

Method

Mixed cation NCs are made in a round bottom flask with stirring and normal Schlenk line techniques. Lead acetate, (PbAc_2 , 0.2 mmol) and a combination of cesium acetate (Cs-acetate) and FA acetate (FA-acetate) in desired ratio (see Table 4.4) are dried in a pre-dried mixture of ODE (8 mL) and OA (2 mL, 6.3 mmol) for 30 minutes at 50 °C. Once all precursors are solubilised, the temperature is raised to 130 °C under nitrogen. 0.3 M oleylammonium halide (OLAmX) solutions are made by mixing OLAmX (0.6 mmol) in 2 mL dried toluene. Synthesis of OLAmX can be found in Chapter 3. The OLAmX solution is then injected into the precursor solution. For mixed halide NCs, the individual OLAmX solutions in toluene are premixed prior to injection. After 10 seconds the flask is plunged into an ice bath to quench the reaction. NCs are separated

4.5. Acetate-based Synthesis

FA-acetate			Cs-acetate		
mg	mmol	Ratio		mmol	mg
78	0.75	1.0	0.0	0.00	0
62	0.60	0.8	0.2	0.04	8
46	0.45	0.6	0.4	0.08	15
31	0.30	0.4	0.6	0.12	23
15	0.15	0.2	0.8	0.16	31
0	0.00	0.0	1.0	0.20	38

Table 4.4: Amount of cation acetate used for the synthesis of $\text{FA}_x\text{Cs}_{1-x}\text{PbX}_3$, with the proposed ratio for the resulting NCs

by adding 1-butanol (6 mL) to the reaction mixture and then centrifuging at 8,000 rpm for 10 minutes. The NCs are then redispersed in hexane or toluene.

Results

Optical data is presented for $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_3$ NCs in Figure 4.10. There is a gradual red shift in absorption onset and PL peak position from 1.75 to 1.64 eV (0.11 eV difference) as more FA is incorporated from $x = 0.2$ to 0.8, Figure 4.10a and Table 4.5 Entries i & iii. Across the same x range there is a similar PL red shift for the oleate-based synthesis where there is a difference of 0.13 eV, Table 4.2 Entries ii & v.

There is little change in photo-carrier lifetime calculated from a stretched exponential fit for all three samples, Figure 4.10b and Table 4.5. From $x = 0.2$ to $x = 0.8$ there is only a 5 ns difference. This is significantly different to the oleate-based synthesis where across the same range a 35 ns difference was seen, Table 4.2 Entries ii & v. Previously, as more FA in the synthesis correlated with longer photo-carrier lifetimes, the lifetime was speculated as a marker of FA incorporation in the NCs. However, as this is not the case here due to the narrow change, this is not an appropriate indicator.

Optical data is presented for $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_{1.5}\text{Br}_{1.5}$ NCs in Figure 4.11. Here a significant red shift of 0.33 eV in the PL peak and absorption onset is seen between $x = 0.2$ to $x = 0.4$, Figure 4.11a and Table 4.5 Entries v & vi. The size and shape of these two sets of NCs are shown in the TEM images, Figure 4.11b-e. At a larger incorporation of FA, a mixture of platelets (Figure 4.11b) and cubes (Figure 4.11c) are

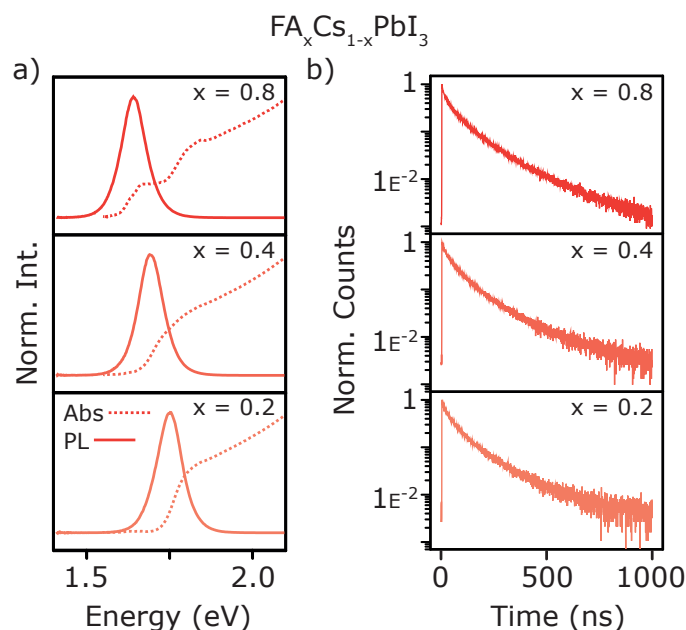


Figure 4.10: Optical characterisation of $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_3$ NCs showing a) absorption and PL spectra and b) TRPL

Entry	Composition		Peak (eV)	FWHM (meV)	PLQY %	Stretched Fit	
	x	y				τ (ns)	β
i	0.8	3	1.64	88	-	50	0.53
ii	0.4	3	1.69	88	-	55	0.58
iii	0.2	3	1.75	90	-	55	0.58
iv	0.6	1.5	1.83	100	10	-	-
v	0.4	1.5	1.97	102	15	21	0.59
vi	0.2	1.5	2.30	96	1	6	0.42

Table 4.5: Optical properties of $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_y\text{Br}_{3-y}$ NCs synthesised using OLAmX. Average lifetime and stretching factor calculated using a stretched exponential fit

observed. For the lower FA content sample, highly crystalline nanocubes are observed (Figure 4.11d & e). Therefore the larger shift observed in the optical characterisation could be a result of differences in size and shape between the two sets of NCs as well as any compositional change.

For all samples made through the acetate-based synthesis, narrower FWHM are reported between 88 meV and 102 meV, Table 4.5. In the oleate-based synthesis there is a much larger FWHM range from 74 meV to 187 meV, suggesting more homogeneous systems are afforded via the acetate-based route. This could be a result of better control of the OLAm-FA relationship.

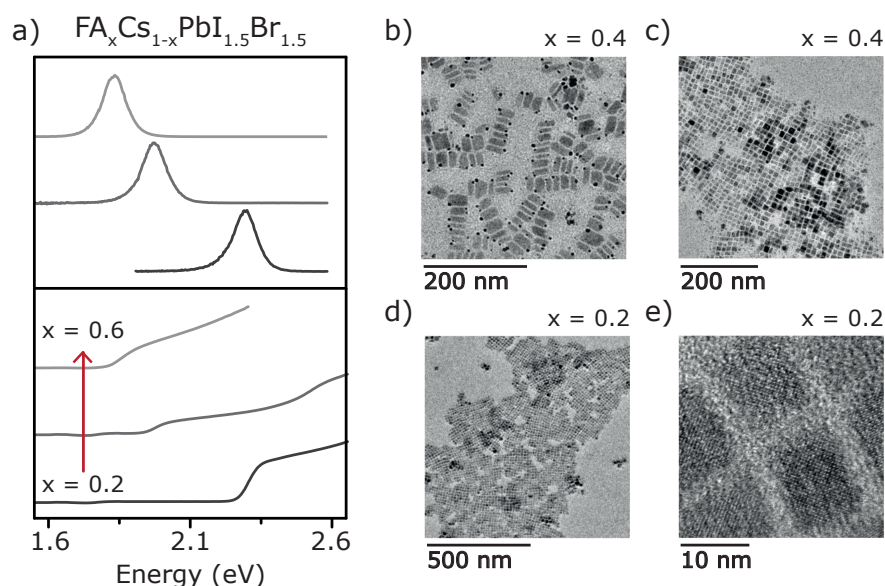


Figure 4.11: a) Optical characterisation of $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_{1.5}\text{Br}_{1.5}$ NCs absorption and PL spectra and TEM images of b) & c) $\text{FA}_{0.4}\text{Cs}_{0.6}\text{PbI}_{1.5}\text{Br}_{1.5}$ and d) & e) $\text{FA}_{0.2}\text{Cs}_{0.8}\text{PbI}_{1.5}\text{Br}_{1.5}$

4.6 Conclusion

An oleate based synthetic route to $\text{FA}_x\text{Cs}_{1-x}\text{PbX}_3$ NCs has been presented. The results highlight challenges of accommodating both organic and inorganic cations whilst maintaining control over size and shape of the NCs. Although miscibility between FA and Cs is achieved, the extent to which this can be harnessed is called into question. The role of the ligands and their different interactions with FA and Cs requires further exploration before further compositions are attempted.

An acetate-based synthesis utilising oleylammonium halide was shown to produce more homogeneous systems. The replacement of the source of the oleylammonium ligand was an attempt at improving control. The results demonstrate that although there was improvement, there are still obvious interplays between composition and size and shape that need to be decoupled.

To tackle these issues, the ligands must be reviewed. A simpler ligand shell with a less dynamic nature would be beneficial. If the binding site is the same for both FAPbX_3 and CsPbX_3 NCs, mixing the cation sites will be more straightforward.

Chapter 4. Synthesis of Mixed Cation Perovskite Nanocrystals

Overall, as the acetate-based synthesis provides more control over the ligands, it would be more useful to expand on this synthesis to further look at mixed cation perovskite NCs. However, a longer term strategy is to examine changing the ligand shell altogether. This would provide a new foundation for mixed cation and mixed anion perovskite NCs, and a key to their stability.

Contributions

EDS mapping shown in Figure 4.7 was conducted by Dr Zhiya Dang at Istituto Italiano Di Tecnologia (IIT) Central Research Laboratory, Italy. Dr Bernard Wenger assisted with TRPL fittings.

Phosphine Oxide Route to Cesium Lead Halide Nanocrystals

In this chapter, the development of a synthesis of CsPbBr₃ nanocrystals (NCs) using trioctylphosphine oxide (TOPO) and oleic acid (OA) is presented. Bright, size-tunable CsPbBr₃ nanocubes, with narrow size distributions and in high yields (61 % at. in Pb), are made by varying the reaction temperature in the range of 25 – 140 °C and the [TOPO]:[OA] ratio. These two parameters, which influence the OA-TOPO acid-base equilibrium, regulate the solubility and reactivity of PbBr₂ and consequently the mean size and size distribution of the NCs.

Firstly, the relationship between reaction precursors is explored by ³¹P and ¹H nuclear magnetic resonance spectroscopy (NMR). This is followed by an examination of the synthesis and influence of key factors on the properties of CsPbBr₃ NCs. Thirdly, analysis of the surface chemistry is evaluated to demonstrate the formation of a simple ligand shell. The results are then contextualised by a comparison to the traditional Hot Injection synthesis, and finally the expansion and application of the synthesis in related systems is discussed.

Key Findings

- Lower reaction temperatures in comparison to the typical Hot Injection synthesis
- Reactions conducted in air
- Yield close to theoretical limit
- Monodisperse nanocubes free from impurities and bi-products
- Photoluminescence quantum yields up to 61 % via optimising surface coverage
- Simple, Cs-oleate only ligand shell which is dynamically bound

5.1 Motivation

The fabrication and growth of both thin films and single crystals of metal halide perovskites are typically done using highly polar solvents such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF) or γ -butyrolactone (GBL). It is notable that these solvents all contain the functional group $R=O$. Conversely, the synthesis of perovskite NCs employs a combination of non-polar solvents and weaker aliphatic amines and carboxylic acids, which act as the ligands and are required to solvate PbX_2 .

Concerns have been raised regarding the toxicity of polar solvents in thin film and single crystal fabrication for industrial scale applications^{170–172}, and the role of primary amines and carboxylic acids in the stability of perovskite NCs. In the synthesis of $APbX_3$ NCs, primary amines (usually oleylamine (OLAm)) are found in equilibrium with their protonated form, alkylammonium ions. These ions compete for the same lattice sites as A cations and promote the formation of nanosheets, nanoplatelets (NPLs) or even layered phases¹⁰⁶. Concurrently, the carboxylic acids (usually OA) are found in their deprotonated form, carboxylate ions. These ions compete with the X anions for the same lattice sites. They are also in equilibrium with one another, forming a dynamic and complex ligand shell that can cause an unstable NC surface by promoting the formation of defects. Furthermore, several works have shown that amines can

5.2. TOPO interactions with PbX₂ and OA

drive the dissolution of lead halide perovskite NCs and their transformation into an insulating phase^{106,173,174}.

A bridge between the know-how developed in macro-scale syntheses and the NC syntheses is required. This would enable progress by bringing together the successes and advantages of both systems whilst remedying the shortcomings. Exploration of the application of TOPO ((C₈H₁₇)₃P=O) to synthesise CsPbX₃ NCs allows for replacement of the labile amine ligand and mirrors the R=O group required in the macroscale synthesis. It should be noted that TOPO has already been used in the synthesis of CsPbX₃ NCs however, it was either employed in combination with primary amines¹⁷⁵ or in combination with octylphosphonic acid¹⁷⁶. In the latter case the role of TOPO in the synthesis was not investigated.

5.2 TOPO interactions with PbX₂ and OA

TOPO is able to solubilize PbBr₂ in the absence of a solvent, forming a clear TOPO:PbBr₂ solution above 50 °C. This solidifies to a white solid upon cooling, matching with the melting point of TOPO (~ 50 °C). The resulting product fluoresces orange under ultraviolet excitation, which is similar to lead bromide dissolved in DMSO and DMF, Figure 5.1a. From this it can be inferred that the phosphine oxide TOPO complexes PbBr₂ in a similar way as carbonyl and thionyl groups¹⁷⁷.

The interaction of TOPO with PbBr₂ is further examined by ³¹P NMR in dilute toluene solutions. As shown in Figure 5.1b, the ³¹P signal of TOPO is shifted down-field in the presence of PbBr₂ (24:1 mol ratio), and this is attributed to an interaction of the oxygen atom of TOPO with PbBr₂¹⁷⁸. The addition of the protic acid OA to dilute TOPO:PbBr₂ solutions leads to the precipitation of PbBr₂, determined by X-Ray Diffraction (XRD), Figure 5.1c. This is due to a competing interaction between the OA and PbBr₂ for TOPO.

¹H and ³¹P NMR are employed in order to study the acid-base interaction between OA and TOPO in d-toluene, Figure 5.2. In the presence of TOPO, the α-CH₂ resonances of OA shift down-field, Figure 5.2a, which is attributed to hydrogen

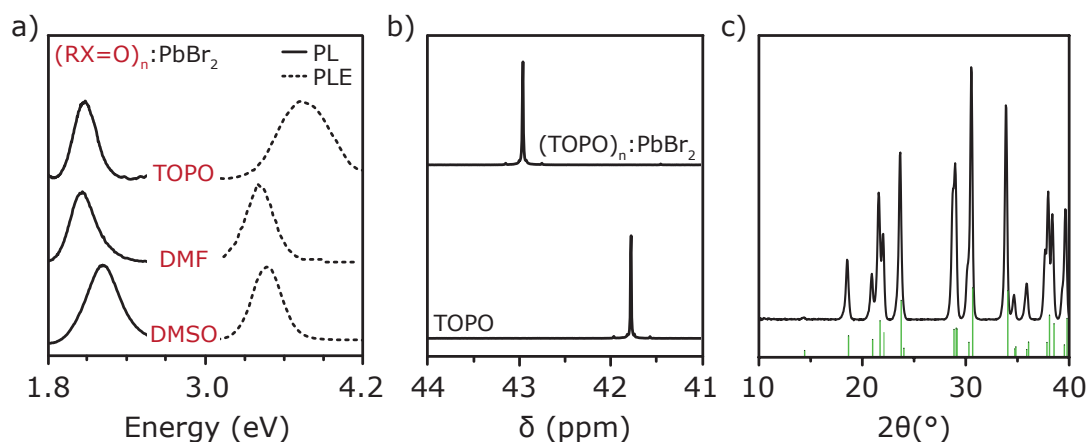


Figure 5.1: a) photoluminescence (PL) (solid line) and photoluminescence excitation (PLE) (dashed line) spectra of TOPO, DMSO and DMF solutions of PbBr_2 ($[\text{PbBr}_2] = 93$ mM in the TOPO solution and ≤ 50 mM for DMSO and DMF solutions). b) ^{31}P NMR spectrum of TOPO and $\text{TOPO}:\text{PbBr}_2$ in d-toluene ($[\text{TOPO}] = 0.81$ M, $[\text{PbBr}_2] = 0.03$ M). c) XRD pattern of PbBr_2 precipitated out of TOPO and OA in 1-octadecene (ODE) at 75 °C, reference pattern for PbBr_2 (shown in green) is taken from ICSD 98-003-6170.

bonding of OA with TOPO. This is analogous to previous work on acid-base equilibria between OA and OLAm¹⁰⁶. To confirm that the shift observed is due to interactions with TOPO and not due to concentration alone, ^1H NMR of neat OA at the same concentrations as in the TOPO:OA solutions are recorded, see Table 5.1 for ratios and concentrations. Although at high OA concentrations a splitting of the $\alpha\text{-CH}_2$ is observed, it is not to the same extent as when TOPO is present, thus concluding that the shift seen in the TOPO:OA mixture is largely due to the acid-base interaction.

In comparison to OLAm, TOPO induces a smaller downfield shift to the $\alpha\text{-CH}_2$ resonances of OA at equimolar concentrations, Figure 5.2c. This is in agreement with previous reports showing that the proton affinities of $\text{RX}=\text{O}$ bases are lower than those of amines¹⁷⁹.

Over the same range of acid:base ratios, Table 5.1, a tenfold larger down-field shift is observed for the narrow ^{31}P signal of TOPO, Figure 5.2b. This is as a result of hydrogen bonding or protonation of TOPO, and aligns with previous studies¹⁸⁰. The greater shift that is observed with respect to the ^1H signal is due to the contribution of paramagnetic shielding to the chemical shift, which is the dominant term for the ^{31}P nuclide (and in general for hetero nuclei) and is absent for the ^1H nuclide¹⁸¹. The ^{31}P

5.2. TOPO interactions with PbX₂ and OA

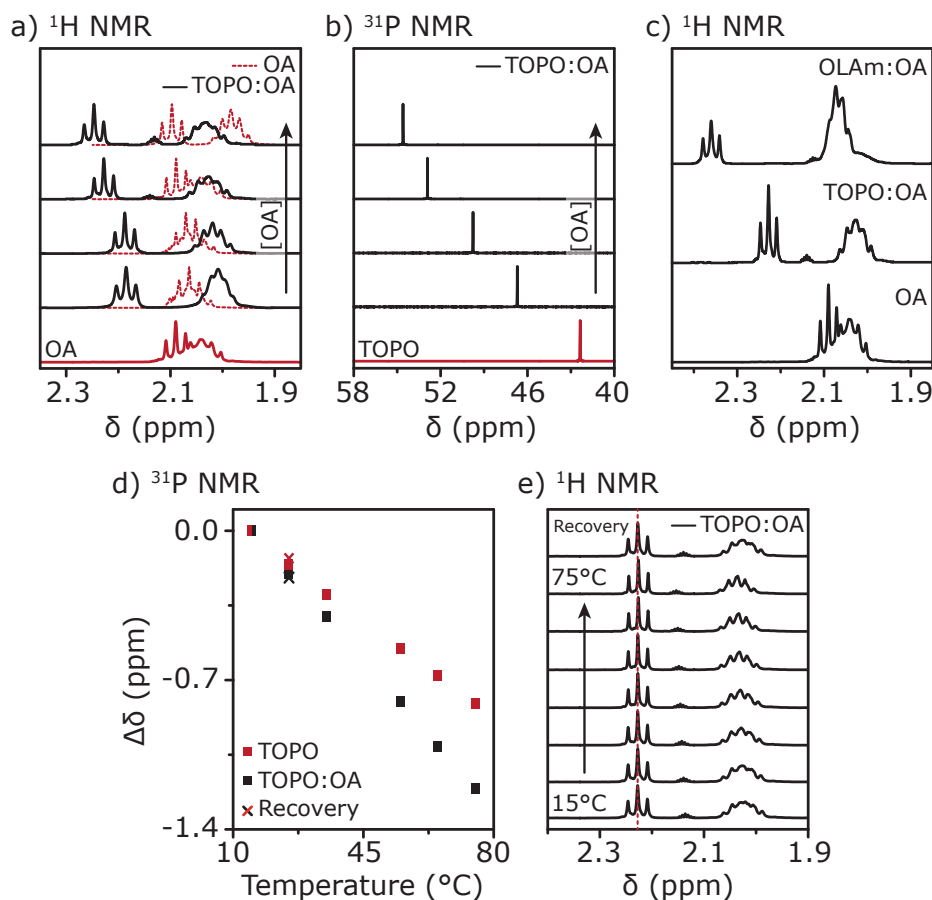


Figure 5.2: a) ¹H NMR spectra of TOPO:OA mixtures (black) and OA alone (red) in d-toluene, selected region observes the splitting in α -CH₂ peaks of OA. b) ³¹P NMR spectra of TOPO:OA mixtures in d-toluene. For both ¹H and ³¹P spectra, the TOPO:OA molar ratios are varied from 1:0.5 to 1:4, see Table 5.1. c) ¹H NMR spectra of OA, TOPO:OA and OLAm:OA in d-toluene at 1:1 molar ratios of acid and base. d) ³¹P NMR signal of TOPO (red) and TOPO:OA (black, 1:1 mol.) in d-toluene over temperature range 15 to 75 °C. e) ¹H NMR spectra of TOPO:OA (1:1 mol.) in d-toluene over temperature range 15 to 75 °C, selected chemical shift range shown is for α -CH₂ in OA

signal is therefore a powerful probe with regard to investigating acid-base equilibria between OA and TOPO. This was particularly evident when the ¹H and ³¹P NMR spectra over a range of temperatures was recorded.

While heating a TOPO:OA (1:1 mol.) solution from 15 to 75 °C only causes a marginal shift to the α -CH₂ resonances of OA, Figure 5.2e, the ³¹P signal of TOPO visibly shifts up-field, Figure 5.2d. Note that even in a solution containing TOPO alone, the ³¹P signal shifts up-field when the temperature is increased, Figure 5.2d, but to a lesser extent than in a TOPO:OA mixture.

Acid-base interactions are exothermic, and upon an increase in temperature a

Chapter 5. Phosphine Oxide Route to Cesium Lead Halide Nanocrystals

TOPO M	OA M	Ratio [TOPO]:[OA]
0.43	0	1 : 0
0.43	0.22	1 : 0.5
0.43	0.43	1 : 1
0.43	0.86	1 : 2
0.43	1.72	1 : 4
0	0.86	0 : 2

Table 5.1: List of TOPO:OA solutions in d-toluene investigated with ^1H and ^{31}P NMR

shift in the equilibrium towards neutral forms of acid and base are expected. These results show that the TOPO and OA interaction follows this behaviour and the greater up-field shift of the ^{31}P signal in the TOPO:OA mixture at higher temperatures is due to the deprotonation of TOPO-H^+ .

5.3 Synthesis and Optimisation

Advantage is taken of this acid-base interaction between TOPO and OA to synthesize CsPbBr_3 NCs via an injection route. Synthetic procedures are carried out in air unless otherwise stated. For synthetic procedure of cesium oleate (Cs-oleate) see Chapter 3.

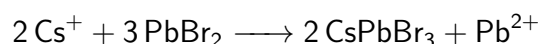
All reactions are performed in vials on a hot plate equipped with a thermocouple and a magnetic stirrer at 800 rpm. In a typical synthesis, PbBr_2 (60 mg, 0.16 mmol), TOPO (1.0 g, 0.88 g/mL, 2.59 mmol) and OA (400 μL , 1.27 mmol) are heated to 75 $^\circ\text{C}$ in ODE (5.0 mL), forming a clear solution. The temperature is set to the desired reaction temperature (25 – 140 $^\circ\text{C}$) and Cs-oleate is injected (1.0 mL), which has been pre-heated to the same temperature. The initially colourless Pb-solution turns immediately green or yellow, depending on the temperature and NC size, upon the injection of Cs-oleate, thus indicating the formation of CsPbBr_3 . After 30 seconds of growth, the vial is plunged into an ice bath to quench the reaction.

The NCs are separated by centrifugation in the absence of an anti-solvent and redispersed in toluene or hexane. To wash the NC dispersion, acetone is added at a volume ratio of 2:1, then the mixture is centrifuged at 3000 rpm for 5 minutes. The supernatant is discarded and the NCs redispersed in toluene or hexane. This process

5.3. Synthesis and Optimisation

is repeated a second time to obtain washed NCs. For best results, 5 μL of OA per 1 mL of NCs is added upon redispersion, obtaining washed + OA NCs. Details of the parameters of optimization experiments are listed in Table 5.2.

The overall reaction can be described by the following equation, which allows a maximum conversion of PbBr_2 into CsPbBr_3 of $\frac{2}{3}$, in terms of Pb:



In order to understand the system and factors governing growth, a series of optimisation experiments are performed investigating the acidity, growth time, temperature and amount of cesium used.

Acidity

To elucidate the role of acidity in the NC synthesis a series of syntheses at a constant temperature (75 °C), and growth time (30 s), but with varying total OA concentration, $[\text{OA}]_{\text{Tot}}$, are performed, Table 5.2 Entries i - vi. $[\text{OA}]_{\text{Tot}}$ is made up of the OA in the Pb solution at the start ($[\text{OA}]_{\text{Pb}}$) and that introduced upon injection of Cs-oleate ($[\text{OA}]_{\text{Cs}}$). As shown in Figure 5.3a, the average NC size decreases from 32.1 to 5.3 nm and the size distribution narrows remarkably from 19.3 nm ($\sigma = 60 \%$) to 0.8 nm ($\sigma = 15 \%$) as $[\text{OA}]_{\text{Tot}}$ increases from 0.04 up to 0.89 M.

A balance between $[\text{OA}]_{\text{Pb}}$ and $[\text{OA}]_{\text{Cs}}$ solutions is critical to achieve monodisperse NCs, Figure 5.3. Note that $[\text{OA}]_{\text{Pb}}$ is limited by the re-precipitation of PbBr_2 , as shown earlier. In Figure 5.3 two samples with an $[\text{OA}]_{\text{Tot}}$ of 0.59 M are presented. Too large a contribution from $[\text{OA}]_{\text{Pb}}$ coupled with a small contribution from $[\text{OA}]_{\text{Cs}}$ results in extremely poly-disperse NCs with weaker optical properties, Figure 5.3e & f. If these contributions are reversed, monodisperse NCs are formed, Figure 5.3b & c. These results highlight the control that acid-base interactions of OA and TOPO have on the reactivity of PbBr_2 and reaction kinetics of forming CsPbBr_3 NCs.

The reaction yields in Pb increases from 17 to 61 % as $[\text{OA}]_{\text{Tot}}$ increases, Figure 5.3d. Yields are determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis of as-synthesised samples. In this case, due to a slight deficiency

Entry	PbBr ₂ (mg)	TOPO (g)	OA (mL)	Cs-oleate in OA		Cs-oleate in ODE		Temp. (°C)	Peak (eV)	PL		Size (nm)
				(mL)	[Cs] (M)	(mL)	[Cs] (M)			FWHM (eV)		
i	60	1	0	0	-	1	0.15	75	2.42	0.10		32 ± 19
ii	60	1	0.4	0	-	1	0.15	75	2.42	0.12		20 ± 15
iii	60	1	0	1	0.15	0	-	75	2.41	0.08		-
iv	60	1	0.4	1	0.15	0	-	75	2.44	0.11		6.8 ± 1.1
v	60	1	0.4	2	0.075	0	-	75	2.45	0.10		5.3 ± 0.8
vi	60	1	1.3	0	-	1	0.15	75	2.49	0.21		-
vii	60	1	0.4	1	0.1	0	-	75	2.42	0.07		9.0 ± 0.9
viii	60	1	0.4	1	0.2	0	-	75	2.44	0.09		7.0 ± 0.6
ix	60	1	0.4	1	0.3	0	-	75	2.46	0.12		7.9 ± 0.8
x	60	1	0.4	1	0.4	0	-	75	2.44	0.12		8.8 ± 0.8
xi	30	0.5	0.2	1	0.15	0	-	25	2.65	0.23		3.4 ± 0.4
xii	60	1	0.4	2	0.075	0	-	50	2.43	0.07		6.0 ± 0.6
xiii	60	1	0.4	2	0.075	0	-	140	2.39	0.08		10.7 ± 1.1
xiv	60	0.72	0.4	1	0.15	0	-	75	2.46	0.11		32 ± 19
xv	60	4	0.4	1	0.15	0	-	75	-	-		-

Table 5.2: Synthesis parameters used in preparation of CsPbBr₃ NCs. Resulting PL peak, full width at half maximum (FWHM) and their size are recorded. The total reaction volume is constant at 7.5 mL using ODE

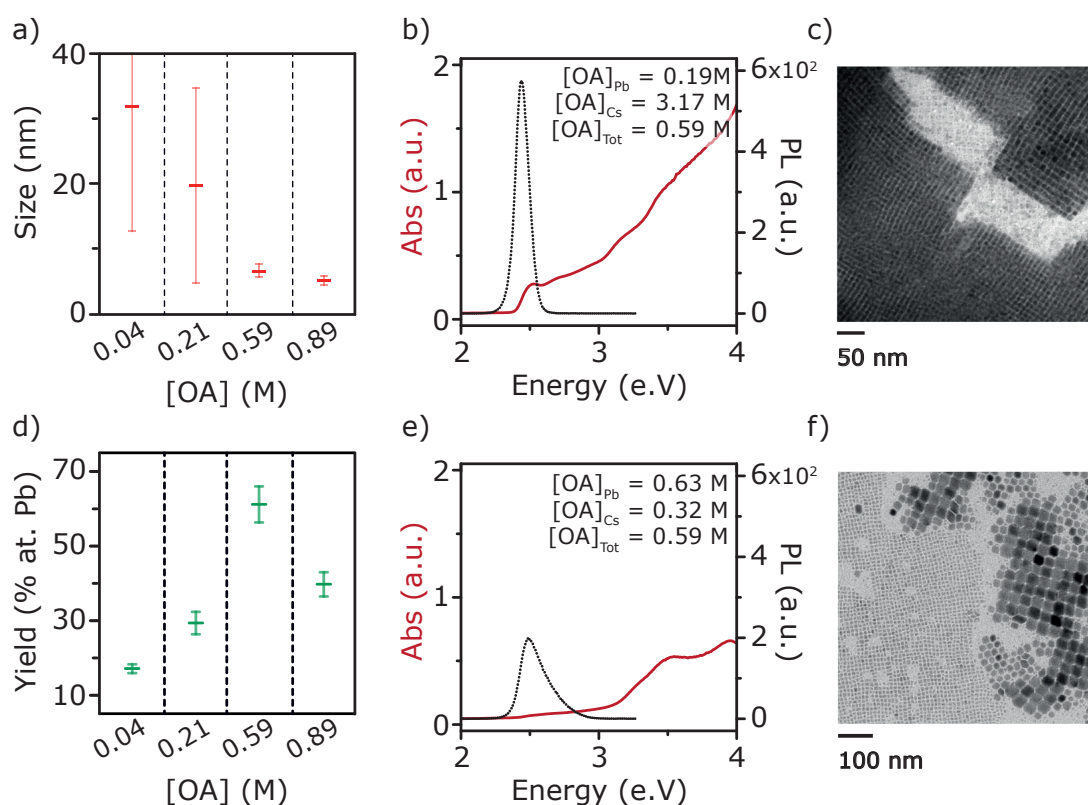
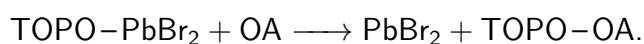


Figure 5.3: a) particle size distribution (PSD) of samples synthesised with various concentrations of OA under otherwise fixed reaction conditions (a reaction temperature of 75 °C, a growth time of 30 seconds, and fixed concentrations of TOPO and PbBr₂; the concentration of OA is the total in the reaction mixture after the injection of Cs-oleate), b) PL (black) and absorption (red) spectra of NCs synthesised at $[OA]_{Tot} = 0.59$ M and c) the corresponding transmission electron microscopy (TEM). d) Reaction yield (% at. Pb) of samples synthesised in a). e) PL (black) and absorption (red) spectra of NCs synthesised at $[OA]_{Tot} = 0.59$ M and f) the corresponding TEM. The contributions of OA from the starting Pb solution, $[OA]_{Pb}$, and that injected with Cs-oleate, $[OA]_{Cs}$, for b-c & e-f are included on the optical data

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in Cs, the theoretical yield in terms of Pb is actually stoichiometrically limited to 62.5 %. Thus the results show that monodisperse CsPbBr₃ NCs are synthesised in yields that are close to the theoretical limit. The reported reaction yield at the highest acid concentration is likely underestimated since a portion of NCs are lost during the separation process due to their reduced dimensions, <5 nm, and this is reflected in Figure 5.3d.

Combining the observations regarding size and yield, it can be concluded that the acid destabilization of the PbBr₂ solution controls both the reactivity of PbBr₂ and the extent of nucleation. The acid destabilization is a result of the competing interaction of OA with TOPO as discussed previously, and can roughly be written in the form:



The [OA]_{Tot} and thus the contributions from [OA]_{Pb} and [OA]_{Cs} are critical for the complete release of PbBr₂ from TOPO and allowing it to form NCs.

Growth Time

An aliquot study is conducted to determine the growth evolution of the NCs by quenching the reaction at a variety of times, from 30 seconds to 10 minutes and observing changes in size and size distribution. This time period between injection and quench is called the growth time. The reaction was conducted at 75 °C with an acidity of [OA]_{Tot} = 0.59 M, where [OA]_{Pb} = 0.19 M and [OA]_{Cs} = 3.17 M. Little to no size variation over the course of 10 minutes growth time is observed as demonstrated by a lack of change in the optical properties of the NCs, Figure 5.4a. Although a small change is seen in the size distribution of NCs in each sample, Figure 5.4b, it is not significant enough to affect the optical properties. The absence of significant size defocusing or Ostwald ripening in this reaction is quite unusual. The monodispersity of NCs prepared via the TOPO route is further attested by their tendency to form three-dimensional cubic superstructures, with coherence lengths of hundreds of nanometers when dropcast on TEM grids from concentrated dispersions, Figure 5.4c.

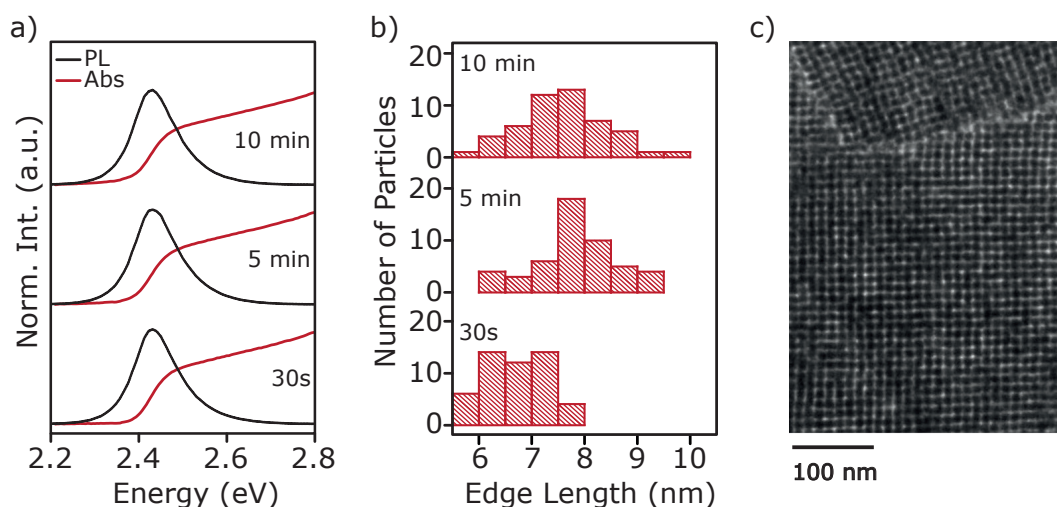


Figure 5.4: a) PL (black) and absorption spectra (red) of NCs and b) PSD of NCs with growth times of 30 seconds, 5 minutes and 10 minutes. c) Example TEM image of a 3D superstructure of CsPbBr₃ NCs with a growth time of 30 seconds. Growth time is defined as the time between the injection of Cs-oleate and the quenching in an ice bath

Temperature

A series of experiments are conducted in which the temperature of reactions are tailored to tune the NC size, Figure 5.5 and Table 5.2 Entries xi - xiii. Under otherwise identical conditions, NCs with edge lengths of 11, 6 and 3 nm are isolated by conducting the synthesis at 140, 50 and 25 °C, respectively. CsPbBr₃ NCs that are synthesised between 140 and 50 °C typically exhibit narrow size distributions ($\sigma = 10\%$), sharp absorption onsets, clear excitonic peaks and a green PL that is characterized by narrow PL full widths at half-maximum (70-80 meV), Figure 5.5b. The NCs prepared at room temperature exhibit a blue emission with broader optical features. Note that the 3 nm NCs are in the strong confinement regime ($\lambda_{PL} = 2.65$ eV), where small size variations lead to strong changes in the electronic structure^{5,44,182}. Furthermore, their isolation is challenging and requires the use of copious amounts of polar solvents, such as acetone, which likely causes the NCs to degrade slightly.

The temperature range in this synthesis is significantly lower than temperatures used in the traditional Hot Injection synthesis, which are 120 °C and above. This is most likely due to the binding strength of TOPO to both PbBr₂ and OA.

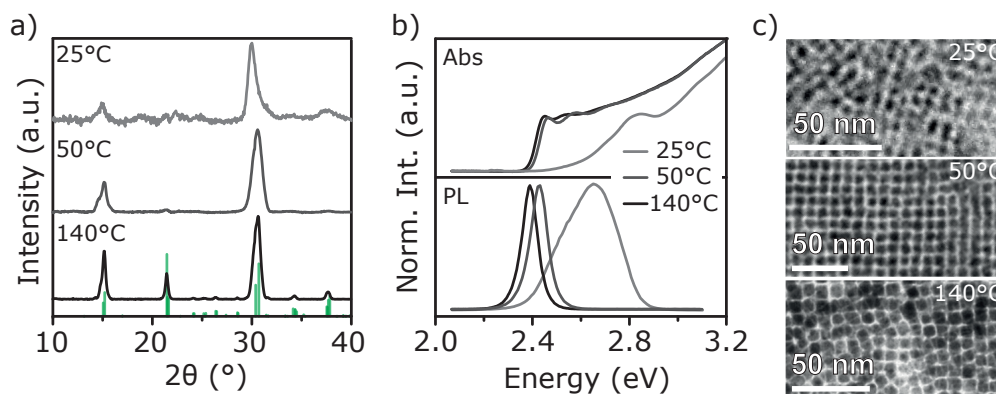


Figure 5.5: a) XRD patterns (reference: COD 4510745), b) absorption and PL spectra and c) TEM images of CsPbBr₃ NCs synthesised with TOPO at reaction temperatures of 25 °C (3 nm), 50 °C (6 nm, $\sigma = 10\%$) and 140 °C (11 nm, $\sigma = 10\%$)

Cs-Oleate

The final synthesis parameter investigated is the concentration of Cs-oleate injected ($[\text{Cs-oleate}]_I$, I stands for Injected), Table 5.2 Entries vii - x. As $[\text{Cs-oleate}]_I$ is increased from 0.1 to 0.4 M little to no change in optical properties and size of the NCs is observed, Figure 5.6a & b. However, photoluminescence quantum yield (PLQY) of as-synthesised NC dispersions increases from 18 to 61 % between 0.1 and 0.3 M, Figure 5.6c. Upon a further increase to 0.4 M, a decrease in the PLQY to 43 % is observed. Given the lack of change in the optical properties and size of the NCs, variations in PLQY are attributed to a change in surface passivation.

Through varying the acidity, growth time, temperature and concentration of Cs an optimal synthesis is established to deliver bright, monodisperse CsPbBr₃ NCs.

5.4 Surface Chemistry and Stability

A series of analyses and calculations are performed which strongly indicate that the surface of these NCs are passivated by Cs-oleate and that TOPO is essentially absent from the ligand shell. Through X-ray photoelectron spectroscopy (XPS) it is revealed that all four samples in this investigation ($[\text{Cs-oleate}]_I = 0.1, 0.2, 0.3, 0.4\text{ M}$) exhibit Br/Pb ratios in the range of 2.3 to 2.5. These numbers are in good agreement with the expected value of 2.7 for PbBr₂ terminated NCs of this size, passivated

5.4. Surface Chemistry and Stability

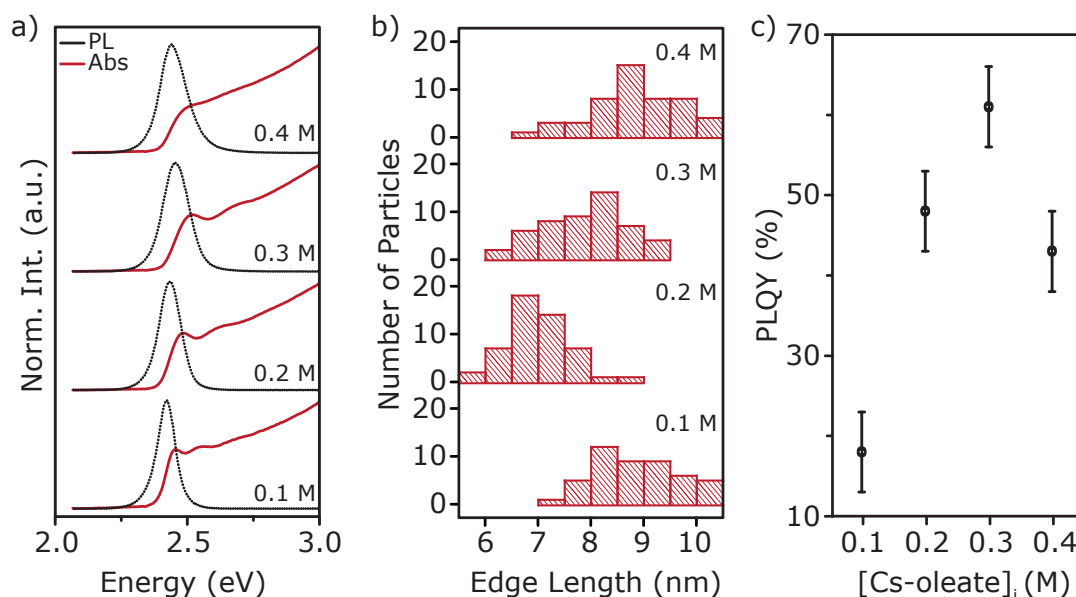


Figure 5.6: a) PL (black) and absorption spectra (red), b) PSD, and c) PLQY of NCs synthesised at different concentrations of cesium in Cs-oleate

with a shell of Cs^+ and a mixture of bromide, oleate, and other anionic species¹¹⁸. The Cs/Pb ratio increases and the Br/Cs ratio decreases as $[Cs-oleate]_I$ is increased confirming that the NC surface becomes richer in Cs, Figure 5.7a. Typically, lead halide perovskite NCs are passivated by pairs of X-type ligands, also named X_2 ligands in the Green's covalent bond classification scheme¹⁸³, such as alkylammonium halides, carboxylates etc¹¹⁴. No phosphorous is observed in XPS measurements of strongly emitting washed samples (i.e. $P/Pb_{surface} \leq 2\%$ at.)¹⁸⁴ suggesting that Cs-oleate is the only compound passivating the NCs.

To further support this, density functional theory is used to compute the adsorption energies of the different ligands that could possibly be passivating these NCs, namely, Cs-oleate, OA and the acid-base salts of TOPO with OA and HBr. To facilitate the calculations, lengths of the aliphatic chains are reduced to one carbon and so acetic acid is used instead of OA. It is considered that each ligand moiety binds onto a $PbBr_2$ terminated (100) surface as a pair of charged species (e.g. acetic acid dissociating into oleate and proton) and a 2.4 nm nanocube was used as a model. The results show that the added ion pairs accommodate on the NC surface, filling the perovskite lattice sites. Negative (i.e. stabilizing) adsorption energies are found for all four ligand

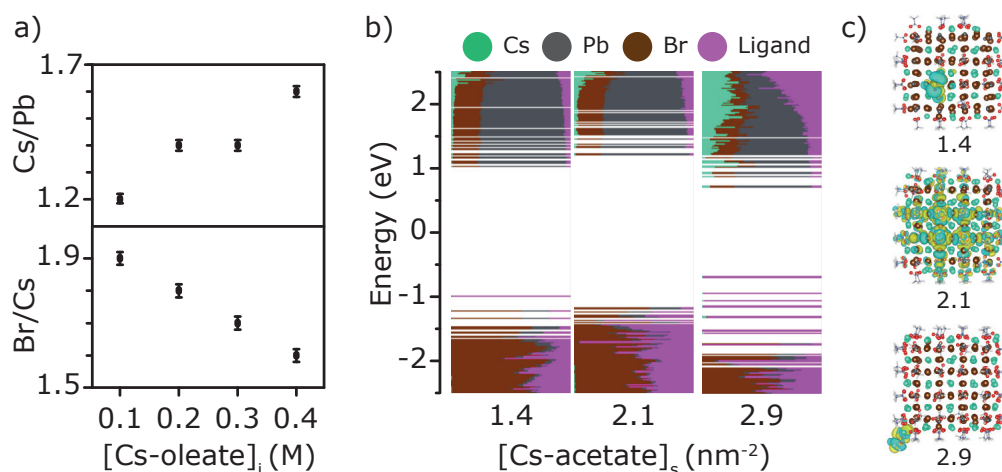


Figure 5.7: a) Cs/Pb and Br/Cs ratios as determined by XPS of NCs synthesised by varying the concentration of Cs-oleate in the injection solution, $[Cs-oleate]_i$. b) Electronic structure of a $CsPbBr_3$ NC ($2.4 \times 2.4 \times 2.4 \text{ nm}^3$) as a function of its surface coverage in Cs-acetate (denoted as $[Cs-acetate]_s$). The contribution of each atom type for a molecular orbital is given with a similar color-code: green (Cs), grey (Pb), brown (Br) and the carboxylate ligand (purple). The isosurface of the highest occupied molecular orbital (i.e. the valence band edge orbital) for each surface passivation is also shown in c) with a counter value of 0.02 $e/Bohr^3$. At low and high surface concentrations of Cs-acetate, surface traps appear as localized states. At intermediate concentrations (2.1 Cs-acetate nm^{-2}), the valence band edge state is delocalised and free of traps

systems under investigation, and Cs-acetate is shown to exhibit the highest affinity towards the NC surface, which is in agreement with the experiments. Additional details of the calculations and examination of results is carried out in Appendix B.

To explain the trend in PLQY, the NC electronic structure as a function of the surface coverage in Cs-acetate is computed, denoted as $[Cs-acetate]$, Figure 5.7b. Here, each molecular orbital is decomposed and color-coded in terms of contributions of a given atom type. Notice that the addition or removal of Cs-acetate ligands from an intermediate passivated trap-free NC with a surface ligand concentration of 2.1 ligands/ nm^2 , leads to the creation of in-gap trap-states that could act as non-radiative recombination centers. The appearance of traps occurs at very high or at very low surface concentration of ligand respectively, Figure 5.7b, and appear as localised surface states as shown in Figure 5.7c. This is in line with the trend that is found in the PLQY as a function of $[Cs-oleate]_i$ reported in Figure 5.6.

To investigate the dynamics of the Cs-oleate capping layer, ^1H NMR on NC dispersions in d-toluene are performed. For this experiment washed NCs are examined.

5.4. Surface Chemistry and Stability

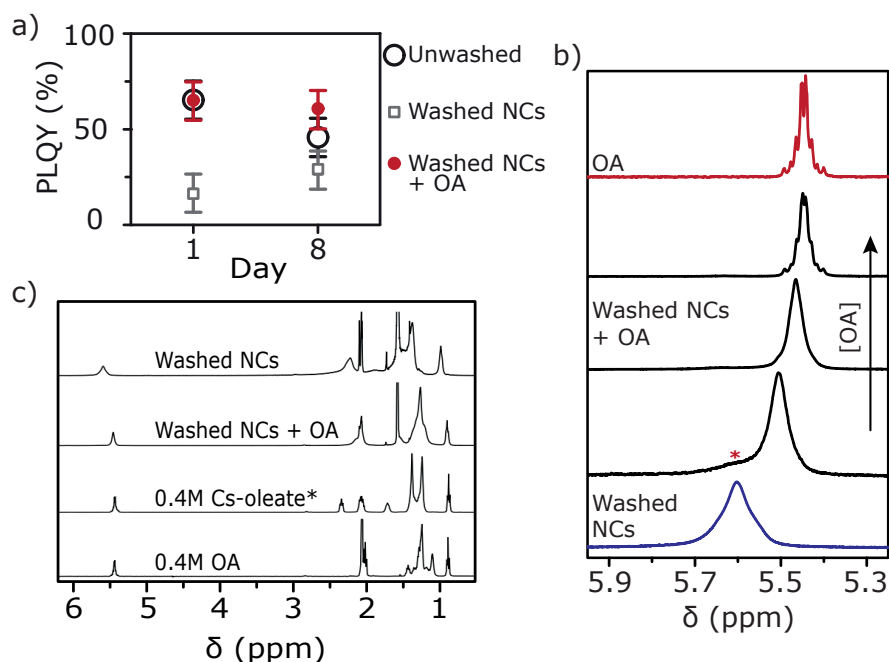


Figure 5.8: a) PLQY of Unwashed (black), Washed (orange), and Washed + OA (green) NCs samples. b) ¹H NMR spectra of washed NC (blue), of washed + OA NC with increasing amounts of OA added (black) and of neat OA (0.22 M, red) in the selected region for the double bond region of OA. c) ¹H NMR spectra of OA, Cs-oleate (*[OA]_{total} = 0.95 M), Washed + OA and Washed NCs. All NMR spectra are of solutions in d-toluene.

As described in detail in section 5.3 of this chapter, Washed NCs employ an anti-solvent and centrifugation process twice and a drop in PLQY is observed, Figure 5.8a. However, the PLQY can be maintained over 60 % by adding small amounts of OA (0.5 % vol. per mL of NCs) after each washing/redispersion cycle, Figure 5.8a, and are denoted as Washed NCs + OA.

The OA resonances can be clearly identified, but are broader and shifted with respect to those of free OA, shown in Figure 5.8c, indicating the presence of tightly bound oleate species, active dynamic processes, or both. This suggests that the presence of free OA can prevent the desorption of bound Cs-oleate and can therefore maintain high PLQY values. In the ¹H spectrum of this sample (Figure 5.8c, second spectrum from the top), two partially overlapped broad peaks are observed in the double bond region which we attribute to bound oleates (OA_{bound}) at 5.60 ppm, and to free OA (OA_{free}) at 5.46 ppm respectively.

This region is highlighted in Figure 5.8b. Here, the ¹H NMR spectra of washed NC dispersions in d-toluene containing increasing amounts of OA in the final suspen-

Chapter 5. Phosphine Oxide Route to Cesium Lead Halide Nanocrystals

sions and of neat OA (0.22 M) are compared. When no additional OA is present (Washed NCs, blue) the right part of the resonance slightly shows a shoulder, which is attributable to the percentage of OA_{free} in exchange with OA_{bound} to NC. When OA is added, the peak of OA_{bound} fractions (indicated by the red asterisk, *) partially overlaps the intense OA_{free} signal. On adding more OA, this shoulder becomes less visible, but is still present and accounts for the line broadening which is affected by the relative populations of the two exchanging sites. These exchange processes are further confirmed by 2D ^1H Nuclear Overhauser effect spectroscopy (NOESY) and diffusion ordered spectroscopy (DOSY) which are discussed in Appendix C. The evidence collected is in line with a rapid exchange mechanism of OA_{bound} and OA_{free} on the surface of NCs¹⁸⁵.

5.5 Comparison to Hot Injection

How the acid-base interactions of OA and OLAm in a traditional Hot Injection synthesis control the morphology of perovskite nanocrystals has been investigated previously¹⁰⁶. It was found that high acidity levels promote the formation of two-dimensional structures and that in order to narrow the size dispersion of $CsPbBr_3$ nanocubes, the concentration of acid and base should be kept to a minimum. Here, using TOPO to solvate $PbBr_2$, it has been shown that two dimensional NCs are not formed at high acidity levels and that they are actually key to obtaining monodisperse $CsPbBr_3$ NCs at reaction yields close to the theoretical limit.

For further comparison with the OLAm route, two batches of ca. 6 nm nanocubes with similar size distribution ($\sigma = 10\%$) are prepared as previously reported¹⁰⁶. In short, 72 mg of $PbBr_2$ (0.2 mmol, 33 mM), 500 μL OLAm, 50 μL OA and 5.45 mL ODE are mixed and degassed for 15 minutes at 100 °C in order to obtain a colourless solution. Thereafter, the temperature is ramped to 140 °C under a dry nitrogen flow and 0.5 mL of a 0.15 M Cs-oleate solution in ODE (previously heated for 10 minutes on a hot-plate set at 200 °C) is swiftly injected. The reaction mixture is immediately cooled after injection with an ice bath and diluted with 5 mL of toluene.

5.5. Comparison to Hot Injection

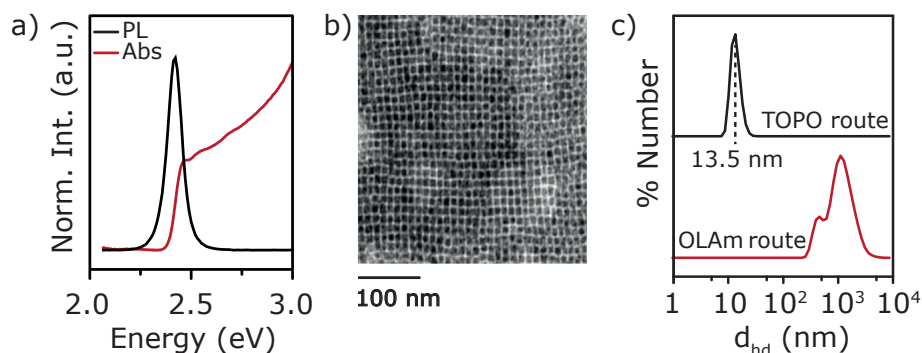


Figure 5.9: a) PL (black) and absorption (red) spectra and b) TEM image of CsPbBr₃ NCs synthesised via the traditional OLAm Hot Injection synthesis. c) DLS spectra of NCs synthesised through the TOPO route (black) and OLAm route (red)

The dispersion is centrifuged at 2500 rpm for 3 minutes and the NCs are redispersed in 2.0 mL of hexane, yielding NCs with both similar optical properties, Figure 5.9a, and size and size distribution, Figure 5.9b, as those made via the TOPO route.

While NCs synthesised via the TOPO route are obtained at a reaction yield in Pb of ca. 60 % at., those synthesised via the OLAm route are obtained at a reaction yield of ca. 8 %. A dynamic light scattering (DLS) analysis on a concentrated toluene dispersion of 6 nm sized CsPbBr₃ NCs synthesised via the TOPO route shows a single narrow peak at ca. 13.5 nm, Figure 5.9. This value is in line with the diameter of a sphere containing one nanocube capped with a monolayer of ligands, and it shows that the NCs are dispersed evenly. Note that NCs of comparable size, size distribution and age, synthesised via the OLAm/OA route employing low [OA] (optimized for a narrow size distribution) tend to aggregate and lose colloidal stability, as is shown in Figure 5.9.

The low reaction yields and poor colloidal stability of these OLAm NCs can be attributed to the low amount of acid used in their preparation. Although a low amount of acid is required to avoid the co-formation of two-dimensional nanostructures and to improve the size dispersion of the nanocubes¹⁰⁶, it is too low to efficiently destabilize the starting lead complexes and to counter the desorption of surface bound oleate species which, in turn, likely lead to NC aggregation.

In both the OLAm and TOPO route, the surface passivation is by pairs of X-ligands which tend to desorb and are in rapid exchange with free ligands¹¹⁴. However, the

Chapter 5. Phosphine Oxide Route to Cesium Lead Halide Nanocrystals

absence of an alkylammonium cation (e.g. oleylammonium) and the poor affinity of phosphine oxide ligands towards the NC surface, allows NCs passivated with a simpler ligand shell comprising of only one type of ligand to be obtained in the TOPO route.

A final note regards the absence of Ostwald ripening effect in the TOPO route. Under the strong acidic conditions of the synthesis, all TOPO molecules are hydrogen bonded, hence they are unable to stabilize any PbBr_2 species that would most likely be extracted from the NCs in case of Ostwald ripening. This is different from the standard syntheses of nanocubes, in the presence of primary amines, in which strongly acidic environments are carefully avoided, forcing the synthesis to be conducted in an acid base regime (low [acid], high [primary amine]) propitious to the extraction of PbBr_2 ¹⁰⁶. On the other hand, when strongly acidic conditions are employed in the amine route, they lead to nanosheets/nanoplatelets with narrow thickness distributions, suggesting that Ostwald ripening does not occur in this case either.

5.6 Expansion to Similar Systems

Synthesis and Transformation to Cs_4PbBr_6

An excess of TOPO causes Cs_4PbBr_6 NCs to be formed instead of CsPbBr_3 . The same procedure is used as described in Section 5.3, but with 4.0 g TOPO (10.36 mmol) and 2.36 mL ODE instead. To separate the NCs, toluene is added to the reaction mixture prior to centrifuging to avoid the excess TOPO from solidifying. The formation of Cs_4PbBr_6 is confirmed through optical and structural characterisation, Figure 5.10a.

This material can also be formed by converting CsPbBr_3 to Cs_4PbBr_6 through the addition of TOPO post synthesis, in the same way that an excess of amine also causes the phase change as previously reported^{106,173,174}. The phase change occurs through a similar dissolution and recrystallization process as for the amine case¹⁷⁴, and can be monitored through UV-Vis spectroscopy and XRD, Figure 5.10b & c.

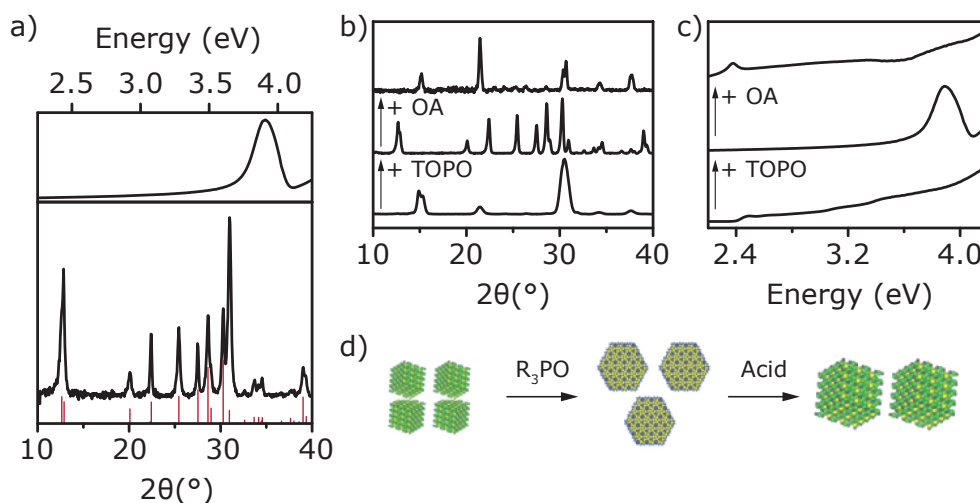


Figure 5.10: a) Optical absorption (top) and XRD patterns (bottom) of Cs_4PbBr_6 NCs (Table 5.2, Entry iv), XRD reference pattern in red is ICSD 98-009-7851. b) XRD spectra and c) absorption spectra of CsPbBr_3 NCs being transformed to Cs_4PbBr_6 via the addition of TOPO and then back to CsPbBr_3 via the addition of OA. Back transformed CsPbBr_3 NCs exhibit narrower XRD peaks with respect to the starting ones, indicative of larger grain size. d) Schematic for the quasi-reversible CsPbBr_3 to Cs_4PbBr_6 transformation

In this transformation, 100 μL of a NC dispersion ($[\text{Pb}] = 0.025\text{mM}$, as measured by ICP-OES) is mixed with 100 μL of toluene and stirred at room temperature. A 0.96 M TOPO in toluene solution is added, 10 μL at a time with stirring intervals, until the solution turns from a bright green suspension to white, indicating the formation of Cs_4PbBr_6 . The total added was 150 μL over 30 minutes. The same transformation can be achieved by adding 50 μL of NCs to a 0.58 M TOPO solution in toluene and stirring for 15 minutes. The transformation does not occur in the presence of oleic acid. To reverse the previous transformation, 100 μL of oleic acid is added to the white Cs_4PbBr_6 solution with stirring, and a yellow-green solution forms. This colour change indicates the formation of CsPbBr_3 but note the loss in confinement of the NCs, as shown by the colour change and absorption spectroscopy, and therefore the transformation is denoted as quasi-reversible, Figure 5.10d.

Employing Different Acids

The TOPO route can also form NCs using both phosphonic and phosphinic acids instead of carboxylic acids. The acidity of di-isooctyl phosphinic acid (DOPA) and

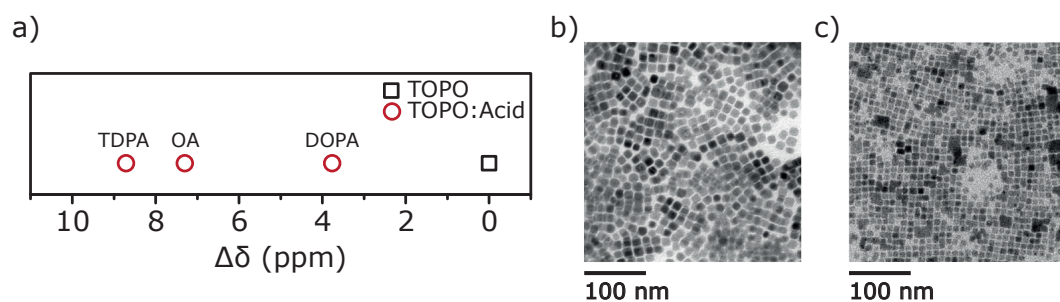


Figure 5.11: a) Differences of ^{31}P chemical shift of TOPO (black square) with OA, n-tetradecyl phosphonic acid (TDPA) and di-isooctyl phosphinic acid (DOPA) (red circles) all in a 1:1 molar ratio with TOPO, b) TEM image of NCs made with TDPA instead of OA (10 nm, $\sigma = 10\%$), c) TEM image of NCs made with DOPA instead of OA (7 nm, $\sigma = 28\%$).

n-tetradecyl phosphonic acid (TDPA) towards TOPO are determined through ^{31}P NMR. TDPA causes the largest downfield shift, and thus has the strongest affinity towards TOPO, Figure 5.11a. At equimolar conditions, NCs of controlled shape and size are prepared (10 nm, $\sigma = 10\%$), similar to those obtained with OA, Figure 5.11b. However, DOPA, which has the weakest affinity towards TOPO, produces larger and more polydisperse NCs (57 nm, $\sigma = 35\%$). Nevertheless, by increasing the concentration of DOPA in the synthesis, smaller NCs with narrower size distributions can be obtained (7 nm, $\sigma = 28\%$), Figure 5.11c. These results are in line with previous studies observing that acidic environments increase the crystallization rate of millimeter sized lead halide perovskite crystals in carbonyl and thionyl dipolar solvents¹⁸⁶.

Chloride and Iodide Systems

TOPO is also able to solubilise PbCl_2 and PbI_2 . As with PbBr_2 , by adding acid to dilute solutions of $\text{TOPO}:\text{PbX}_2$, the corresponding lead salts are precipitated as confirmed by XRD, Figure 5.12a & d.

Monodisperse NCs of CsPbCl_3 are readily formed at 75°C , with bright emission at 3.07 eV, Figure 5.12b & c. However, the corresponding iodide nanocrystals are harder to obtain in a controlled manner, with a loss of shape and size control seen by the growth of nanorods instead, Figure 5.12e & f. This loss of control could be

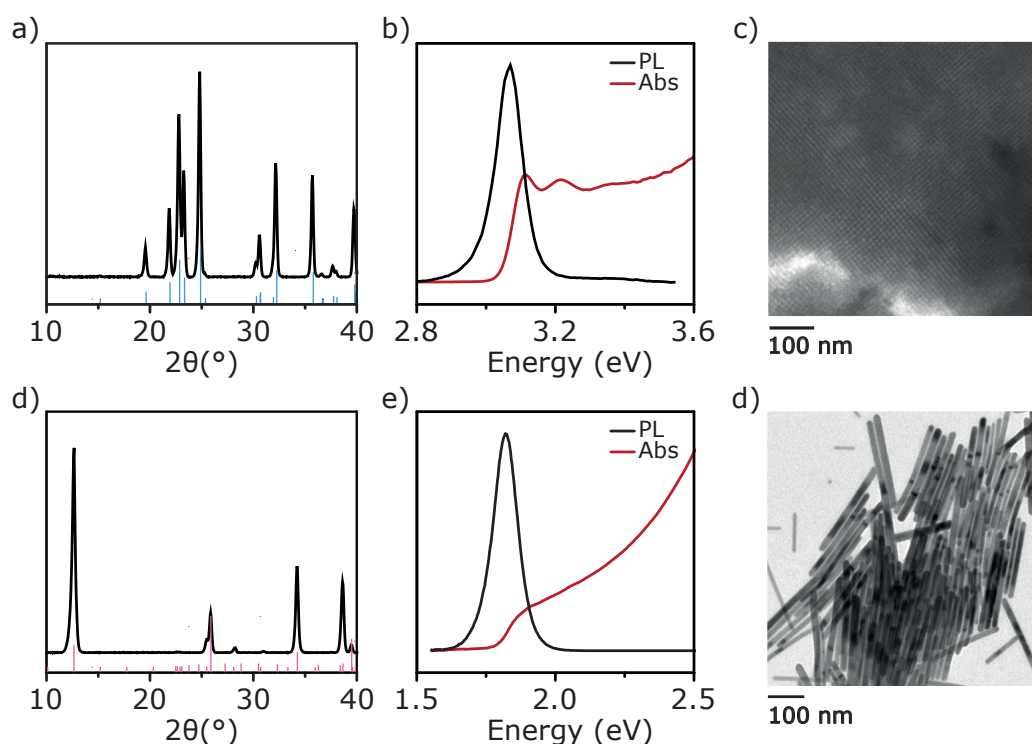


Figure 5.12: a) XRD spectra (reference: COD 96-900-9196, blue), b) optical properties and c) TEM image of CsPbCl₃ NCs made via the TOPO route. d) XRD spectra (reference: ICSD 98-002-3762, red), e) optical properties and f) TEM image of CsPbI₃ NCs made via the TOPO route.

attributed to a difference in the binding strength of TOPO to PbI₂, and thus further optimisation of the synthetic parameters would be required.

5.7 Conclusion

A new method for synthesizing lead halide perovskite NCs that utilises TOPO to dissolve the lead halide precursor has been presented. There are several advantages that this new procedure has over the traditional Hot Injection synthesis that employs primary amines (OLAm route). In particular, it is possible to obtain monodisperse NCs in yields close to theoretical limits with bright emission and at low temperatures. The resulting NCs have a simple and dynamic oleate-only ligand shell, and the system can be readily expanded to form NCs with different ligand shells through employing different acids.

Contributions

This work was conducted at Istituto Italiano Di Tecnologia (IIT) Central Research Laboratory, Italy, and was a joint project with Dr Guilherme Almeida under the supervision of Dr Liberato Manna. Dr Luca Goldoni (IIT, Italy) collected the NMR spectra with aid from Dr Daniela Maggioni for the 2D NMR (DOSY and NOESY) experiments at Università degli Studi di Milano, Italy. The computational work was conducted by Urko Petralanda, (IIT, Italy) and Dr Ivan Infante (Vrije Universiteit Amsterdam, The Netherlands). XPS and DLS measurements were collected by Dr Mirko Prato and Lea Pasquale (IIT, Italy). ICP-OES was conducted by Filippo Drago (IIT, Italy). This work was published in The Journal of the American Chemical Society in October 2018 (*J. Am. Chem. Soc.* 2018, 140, 14878-14886). Permission was granted to reproduce the data in this thesis, Appendix E.

Phosphine Oxide Route to Formamidinium Lead Halide Nanocrystals

In this chapter, the synthesis of FAPbBr_3 nanocrystals (NCs) using the phosphine oxide synthesis is attempted. Bright nanoparticles are made with emission tunability but with distinct differences in their shape, size, and interactions with ligands compared to their CsPbBr_3 counterpart.

Firstly, optimisation parameters such as temperature and growth time are discussed. This is followed by an examination of the influence of the trioctylphosphine oxide (TOPO):oleic acid (OA) ratio on the properties of FAPbBr_3 . Thirdly, the effect of washing the material is presented for device applications. Finally, the interactions of TOPO, OA, and formamidinium (FA) are investigated using nuclear magnetic resonance spectroscopy (NMR), and discussion of the synthetic results within this context is presented.

Chapter 6. Phosphine Oxide Route to Formamidinium Lead Halide Nanocrystals

Key Findings

- Photoluminescence quantum yields of 70 % achieved
- Reactions carried out at room temperature
- Reactions conducted in air
- Phosphine oxide interacts with the ammonium protons on FA

6.1 Motivation

Following the successes of synthesizing CsPbBr₃ NCs via an injection route with TOPO, the same synthesis is applied to FAPbBr₃. The motivation for this synthesis is largely the same as it was for CsPbBr₃ but there are some additional factors. FAPbX₃ has been synthesised through traditional Hot Injection and ligand assisted reprecipitation routes in recent literature^{89,90,187,188}. In all cases, there is a complex ligand shell comprised of typical X-type ligand pairs. It has been noted in these studies that FA is particularly susceptible to oleylamine (OLAm)^{89,90}. It is speculated that this is due to a deprotonation of FA, although in the literature there is a lack of data to directly show this. Given the lower proton affinity of phosphine oxides in comparison to amines¹⁷⁹, TOPO may have added benefit of circumventing this issue.

The optimisation of a phosphine oxide synthesis for FAPbX₃ would open up the investigation into mixed cation NCs once again. With oleate-only capping, there would be less surface instability of the FA, and a greater scope for miscibility of the two cations.

6.2 Synthesis and Optimisation

The synthetic procedures in this chapter are carried out in air, unless otherwise stated. For synthetic procedure of formamidinium oleate (FA-oleate) see Chapter 3. All reactions are performed in vials on a hot plate equipped with a thermocouple and a magnetic stirrer at 800 rpm. In a typical synthesis, PbBr₂ (60 mg, 0.16 mmol),

6.2. Synthesis and Optimisation

TOPO (1.0 g, 0.88 g/mL, 2.59 mmol) and OA (400 μ L, 1.27 mmol) are heated to 75 °C in 1-octadecene (ODE) (5.0 mL), providing a clear solution. The temperature is set to the desired reaction temperature (between room temperature (rT) and 75 °C) and FA-oleate is injected (0.4 M, 1.0 mL), which has been pre-heated to the desired temperature. Depending on the chosen temperature, the injection of FA-oleate immediately turns the initially colourless Pb-solution green or yellow, indicating the formation of FAPbBr₃. After 30 seconds of growth, the vial is plunged into an ice bath to quench the reaction. In the absence of an anti-solvent NCs are separated by centrifugation at 5,000 rpm for 10 minutes and redispersed in toluene or hexane. The yield of the reaction is determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) and is 15.3 % at. in Pb.

Temperature

The synthesis is carried out at temperatures ranging from rT to 75 °C, where rT is in the range 19-23 °C. These temperatures are significantly lower than previous reports of FAPbBr₃ nanocrystals synthesised by an injection method, which were conducted between 80 and 130 °C⁸⁹. Instead, the reaction temperatures used here are of a similar range to those used in the phosphine oxide synthesis of CsPbBr₃¹⁸⁹, Chapter 5. For CsPbBr₃ a reaction temperature below 50 °C was unfavourable, due to purification issues.

A blue shift in photoluminescence (PL) is observed with decreasing reaction temperature, from 2.31 eV to 2.40 eV, Figure 6.1a & b. This is a narrow shift in PL for a 50 °C range with only a 0.10 eV difference in peak maxima from 23 to 75 °C. In the Hot Injection synthesis of FAPbBr₃, a 0.35 eV shift is reported for a 50 °C range (80 - 130 °C)⁸⁹. Similar narrower shifts are reported over large temperature ranges when the synthesis is OLAm free and attributed to fast reaction kinetics⁸⁹.

An increase in full width at half maximum (FWHM) and photoluminescence quantum yield (PLQY) is evident with decreasing temperature. The highest PLQY is obtained with a synthesis at rT, Figure 6.1c & d. Interestingly, the trends observed

Chapter 6. Phosphine Oxide Route to Formamidinium Lead Halide Nanocrystals

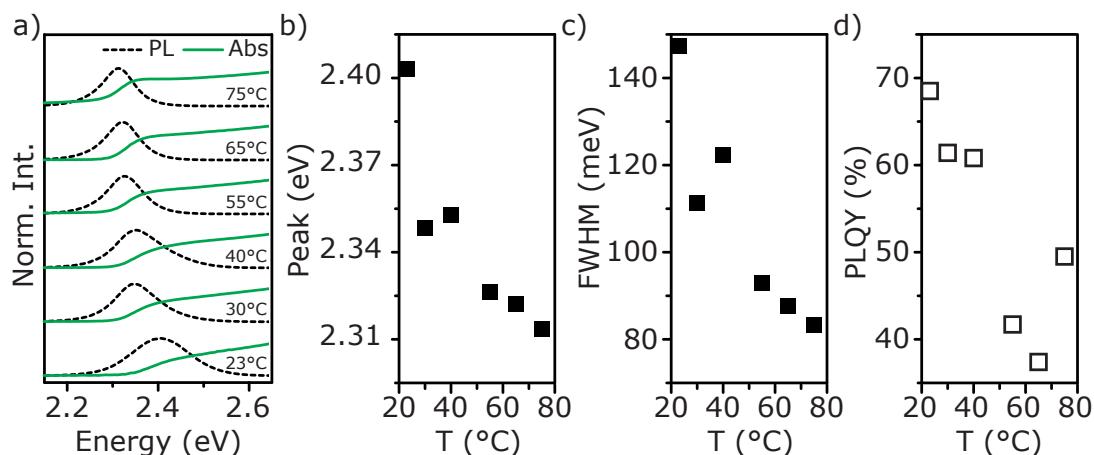


Figure 6.1: a) PL and absorption spectra of FAPbBr₃ synthesised at temperatures from 23 to 75 °C, with the corresponding b) peak position, c) FWHM and d) PLQY

for the emission peak position, FWHM, and PLQY are the same, Figure 6.1. This is unexpected, and may relate to the ligand coverage on the surface of the NCs and the resulting effect on their size and shape. Alternatively, it could be a product of the separation process from the reaction mixture, but both of these insights are speculative.

Although a lower temperature range for FAPbBr₃ is expected when compared with CsPbBr₃^{5,89}, this reaction does not form nanoparticles with extreme quantum confinement at rT. Given that wider band gap FAPbBr₃ is achievable at 2.64 eV⁸⁹, it highlights a limitation of this synthesis, and leaves scope for other synthetic parameters to be manipulated in order to further decrease the size of the FAPbBr₃ NCs.

Growth Time

An aliquot study is conducted to determine the effect of time on the growth evolution of the nanoparticles. A small shift is seen in both the PL peak position and absorption onset, Figure 6.2a. The pattern in PLQY and FWHM suggest that over the first two minutes there is little change in the surface passivation and size distribution of nanoparticles, but after 10 minutes there may be deviations, Figure 6.2b. Growth time appears to have little effect on the optical properties of the nanoparticles, and is indicative of fast nucleation and growth with no further ripening^{69,88}.

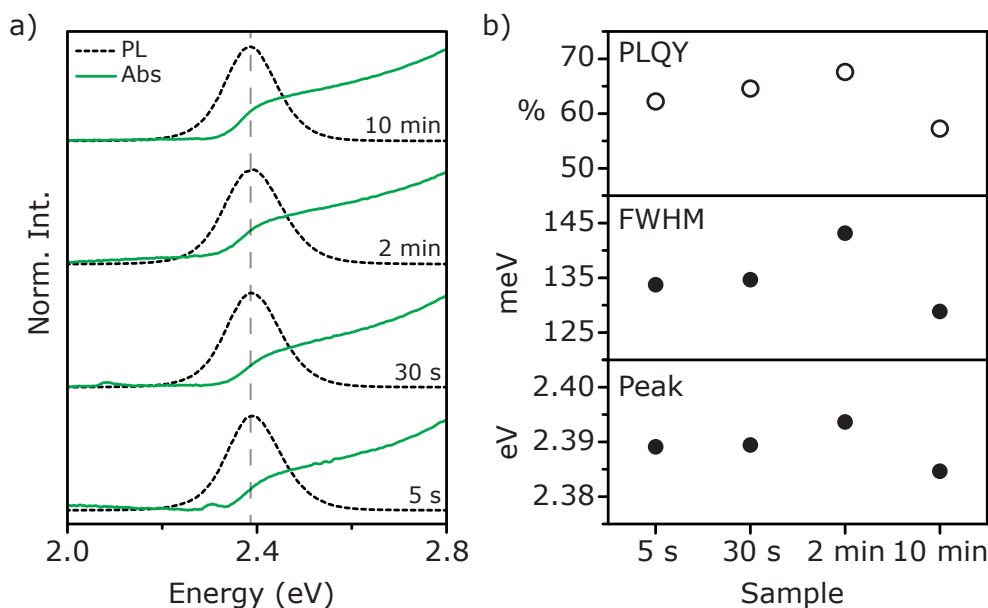


Figure 6.2: a) PL and absorption spectra of FAPbBr₃ synthesised with growth times from 5 seconds to 10 minutes, with the corresponding b) peak position, FWHM and PLQY (bottom to top)

FA-Oleate

FA-oleate concentration is varied at two different reaction temperatures, Figure 6.3, and the impact on the PLQY and also PL peak position and FWHM is visible. This is not a linear relationship, with a minima in peak position and FWHM at 0.2 M FA-oleate.

For CsPbBr₃ NCs, changes in cesium oleate (Cs-oleate) concentration were attributed to the oleate coverage of the NC surface. CsPbBr₃ NCs had a distinct maxima at 0.3 M Cs-oleate, and little effect on the PL peak and FWHM. Here the PLQY trend is inconsistent across two temperatures, and there is an obvious effect on the other optical parameters. This indicates that in the case of FAPbBr₃, the injection of FA-oleate does not only affect the amount of surface coverage on the NC, but that further interactions with the reactants are occurring to change the growth dynamics of these nanoparticles. The change in concentration of FA-oleate also has a larger effect at lower temperatures than at higher temperatures.

The optical results for the optimisation experiments thus far do not reflect the same trends seen for CsPbBr₃ NCs. Over the same temperature range, a much larger shift in PL peak is seen for CsPbBr₃ at 0.21 eV, in comparison to the 0.10 eV for

Chapter 6. Phosphine Oxide Route to Formamidinium Lead Halide Nanocrystals

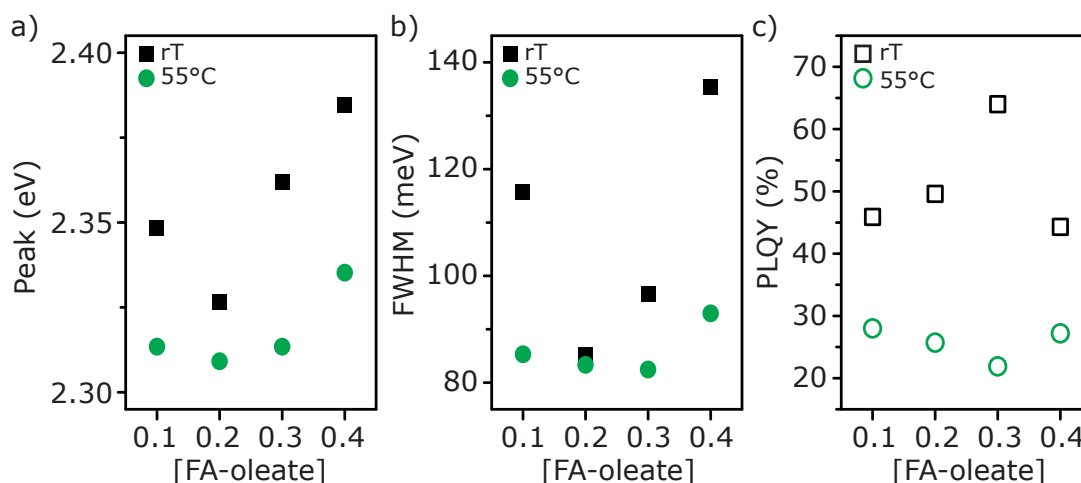


Figure 6.3: a) PL Peak position, b) FWHM and c) PLQY of FAPbBr₃ synthesised at 55 °C and room temperature (rT) with varying concentrations of FA-oleate injected

FAPbBr₃. The FWHM are consistently broader for comparable reaction conditions and the PLQY trends are notably different, and dependent on temperature more so than oleate concentration.

The starting reaction mixture is the same for both CsPbBr₃ and FAPbBr₃: PbBr₂ dissolved in TOPO with OA in ODE. Therefore the disparity in optical results and trends must be associated with the addition of FA-oleate and the effect this has on the acid-base relationship of TOPO and OA.

Acid-Base Effects

The effect of OA:TOPO ratio on the FAPbBr₃ nanoparticles is investigated. For CsPbBr₃, the acid content was seen to control the monodispersity of NCs. Here, both the OA and TOPO content are varied, and the molar ratio of the two is considered as opposed to an exact amount of each. For the ratios stated, the TOPO value is always set to one, e.g. a ratio of 0.8 is 0.8:1 OA:TOPO. In all cases, the OA content includes that introduced by the injection of FA-oleate in OA. Reactions are carried out at three temperatures: rT (19-23 °C), 40 °C and 55 °C.

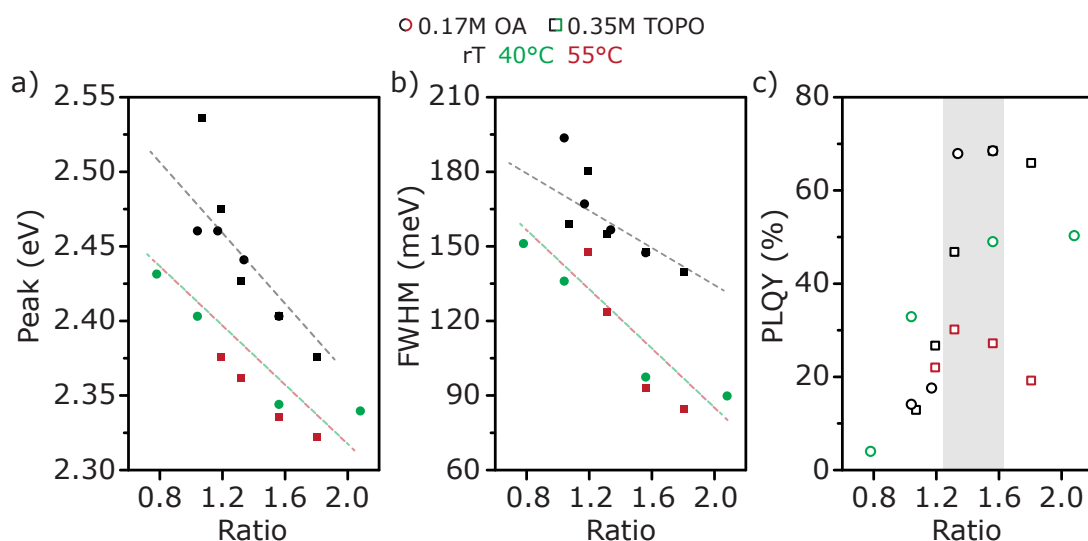


Figure 6.4: Optical properties of FAPbBr₃ synthesised at either room temperature (rT) or at higher temperature (40 or 55 °C) with varying ratio of OA:TOPO. Desired ratios are achieved by fixing either the TOPO or OA content. a) PL peak position, b) FWHM and c) PLQY. Regions of interest are reflected in the dashed lines or grey box

Optical Properties

The PL peak, FWHM, and the PLQY are shown in Figure 6.4. A distinct decrease in energy, or red shift, in the PL emission is seen for an increasing ratio of OA:TOPO. The FWHM also narrows as the ratio is increased from 0.8 to 2. In both cases, this relationship appears to be linear, with the temperature of the reaction affecting the rate of change, Figure 6.4a, b.

The PLQY also increases with an increasing ratio, but in this case it also goes through a maxima. At OA:TOPO ratios between 1.2 and 1.6 the highest PLQY values are obtained and this region is highlighted in Figure 6.4c. An increase in temperature causes a significant decrease in the PLQY, dropping from 70 % at rT to 30 % at 55 °C. Outside of this highlighted region, the PLQY is significantly lower, and the decrease is especially pronounced at higher temperatures.

Bumps in the absorption spectra from 2.75 eV onwards are clear, as can be seen in Figure 6.5. As the ratio decreases, these features are more prominent and there is a loss of a clear absorption onset at 2.4 eV for the lowest ratio of 1.04. A lower reaction temperature also increases the prominence of these bumps. At higher temperatures the onset of absorption has a steeper gradient, and is coupled with a narrower PL

Chapter 6. Phosphine Oxide Route to Formamidinium Lead Halide Nanocrystals

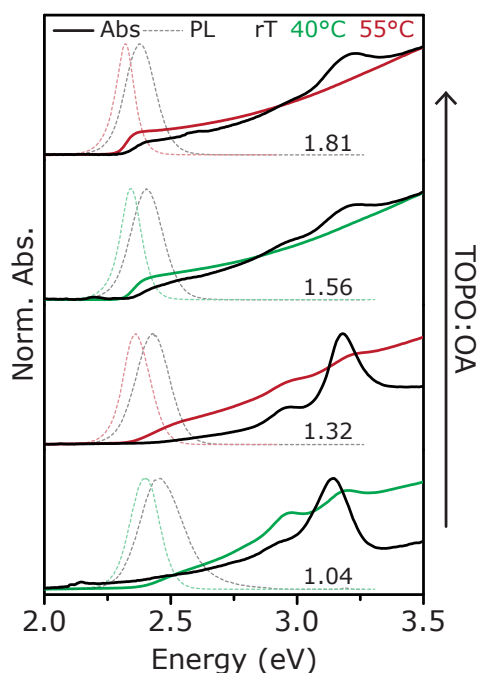


Figure 6.5: Absorption and PL spectra of FAPbBr₃ synthesised at either room temperature (rT) or at higher temperature (40 or 55 °C) with varying ratio of OA:TOPO. Desired ratios are achieved by fixing either the TOPO or OA content

peak. Even when there is no onset, or a shallow onset, at 2.4 eV, the PL emission does not reflect such a drastic change. For the lower ratio and temperature cases, there is a clear lack of overlap between the PL and absorption, which is not expected for a 3D lead halide perovskite structure, such as FAPbBr₃. Similar absorption and emission spectra have been shown for Cs₄PbBr₆, known as a 0D perovskite structure^{190–192}.

In a typical NC system, temperature is expected to play a large role in the size of the NC and thus the PL peak. For FAPbBr₃ synthesised here, the temperature has a larger effect on FWHM and PLQY than would be expected. It has also been shown to be critical factor for the OA:TOPO ratio.

Structural Properties

To assess the size and shape of the NCs transmission electron microscopy (TEM) is conducted, Figure 6.6. For perovskite NCs, an array of cubes would be expected, with varying sizes for wide PL FWHM. From the images shown in Figure 6.6, it is clear that the expected NCs of FAPbBr₃ have not formed.

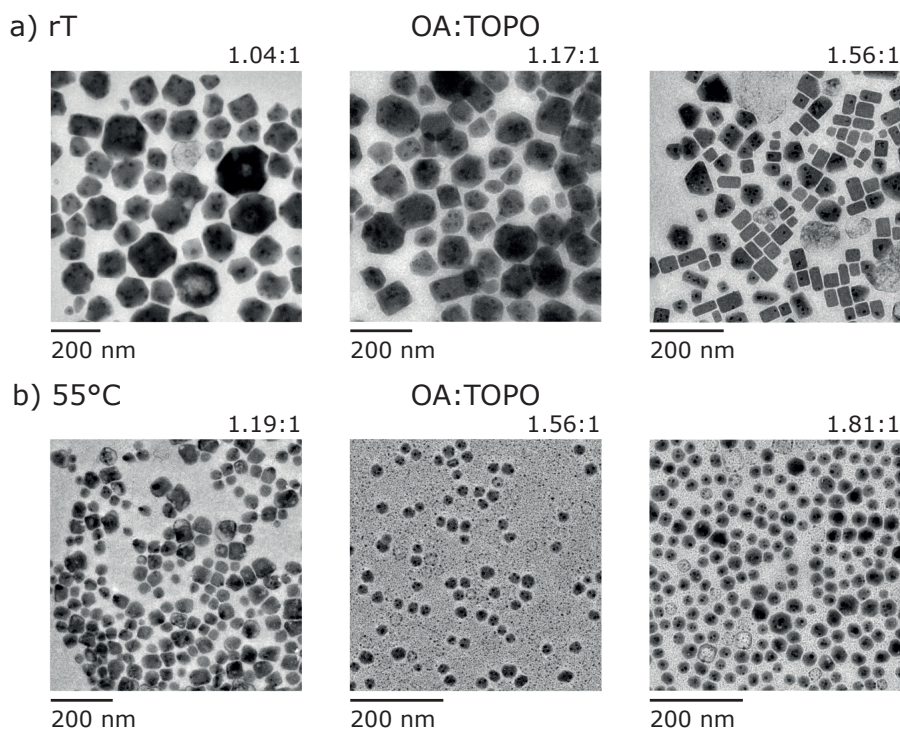


Figure 6.6: TEM of FAPbBr₃ synthesised at a) room temperature (rT) and b) 55 °C with varying ratio of OA:TOPO. Desired ratios are achieved by fixing either the TOPO or OA content.

Large particles form at rT, with a lack of shape control at low OA:TOPO ratios. More cubic or rectangular particles are formed at 1.56:1, but there is little uniformity across the sample as a whole, Figure 6.6a. At 55 °C, smaller particles are formed that are more spherical in shape, Figure 6.6b. The increase in ratio from 1.19 to 1.81 does not yield distinct differences.

Assessing the TEM images alongside the absorption data shown in Figure 6.5, it is plausible that a lower dimension perovskite has been formed instead. More spherical or hexagonal particles are expected for 0D perovskite^{190–192}. For all samples no lattice fringes are observed, nor diffraction rings or spots in the fast Fourier transform (FFT), indicating a non-crystalline material.

To determine if a different phase is formed, X-Ray Diffraction (XRD) is conducted. Samples for XRD are prepared as follows. Reactions are conducted at rT at four ratios of OA:TOPO: 1.19, 1.32, 1.56, 1.81. When the reaction mixture is centrifuged, a solid pellet is collected at the bottom of the centrifuge tube and a green oily substance coats the rest of the tube. For XRD, the solid pellet at the bottom of the centrifuge

Chapter 6. Phosphine Oxide Route to Formamidinium Lead Halide Nanocrystals

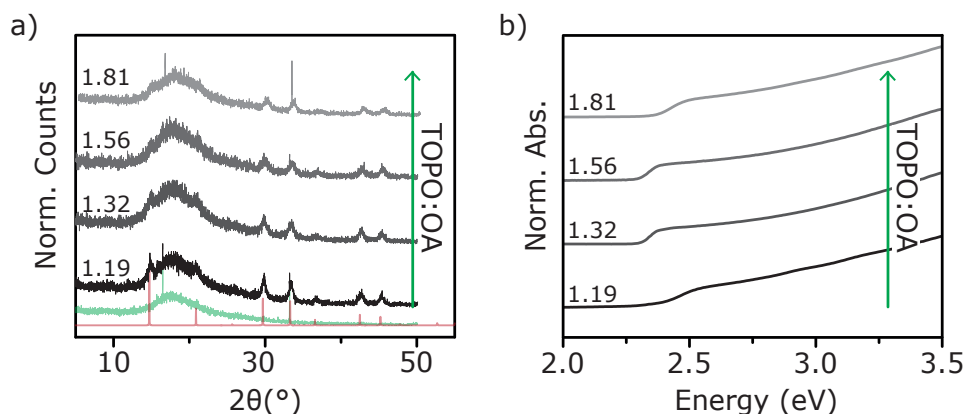


Figure 6.7: a) XRD and b) absorption spectra of FAPbBr₃ synthesised at room temperature (rT) with varying ratio of OA:TOPO. Desired ratios are achieved by fixing either the TOPO or OA content. The XRD is measured under air-free conditions using a dome holder, with reference pattern for the dome shown in green and a simulated XRD pattern for FAPbBr₃ shown in red

tube is smeared onto a quartz disc in a glove box. The oily material is disregarded. Air-free XRD is conducted using domes sealed in a glovebox to avoid any moisture in the air interacting with the material. After the XRD is taken, the solid on the quartz disc is dispersed in hexane and the absorption spectra are collected. This is conducted for four ratios of OA:TOPO.

In all cases, the XRD signal is very weak, and there is a clear decrease in intensity with an increasing ratio, Figure 6.7a. This matches the TEM observation that the material formed is not wholly crystalline. There are no obvious shifts or additional peaks with an increasing ratio. The observed peaks match the simulated spectra for 3D cubic FAPbBr₃, Figure 6.7a shown in red. In the absorption spectra there are no bumps above 2.75 eV.

Together, this data indicates that the presence of a lower dimensionality perovskite is unlikely. One explanation for the discrepancy between TEM and previous absorption spectra presented, Figure 6.5, with the XRD and associated absorption spectra is the part of the product used. Only the pellet in the centrifuge tube was examined, and it may be that the green oily substance on the inside of the centrifuge tube contains lower phase materials. However as this is only a fraction of the product, it would be surprising that no cubes are observed in the TEM if they were formed at all.

6.3 Washing and Films

Despite the aberrant structural data, high PLQY is obtained with these nanoparticles centred at 2.33 eV. This is the optimal band gap for a green light emitting diode (LED)⁸. However, films of the materials are particularly wet and unable to be characterised. When drop cast onto glass or spin coated they do not dry, and remain incredibly oily, due to the retention of excess long chain ligands. Washing of the nanoparticles is needed to alleviate this. Washing procedures could also be beneficial to the structural properties of the nanoparticles and reduce the large FWHM.

Three washing treatments are used for the nanoparticles. The resulting nanoparticles are drop cast on to glass from hexane:octane (9:1) and left to dry without annealing.

Sep The nanoparticles are separated from the reaction mixture by adding an equal volume of toluene and half volume of acetonitrile with respect to the reaction mixture volume. The nanoparticles are then centrifuged at 5,000 rpm for 10 minutes. The supernatant is discarded, and the nanoparticles are redispersed in octane or a hexane:octane mix.

Wash The nanoparticles are separated from the solution as before, using toluene and acetonitrile. The nanoparticles are redispersed in toluene, and acetonitrile is added at a 2:1 volume ratio. The mixture is then centrifuged at 3,000 rpm for 5 minutes. The supernatant is discarded, and the nanoparticles are redispersed in octane or a hexane:octane mix.

Wash + OA The nanoparticles are washed as for the previous case, but upon redispersal in toluene after the initial separation, a small amount of oleic acid is added back to the nanoparticles. Acetonitrile is then added before centrifuging and redispersing again.

From the optical properties, we see that in all cases there are no bumps in the absorption spectra above 2.75 eV, and that the onset of absorption becomes sharper with an added washing step, Figure 6.8a. When the nanoparticle solutions are made into films differences are observed in the PL spectra. In solution, washing the

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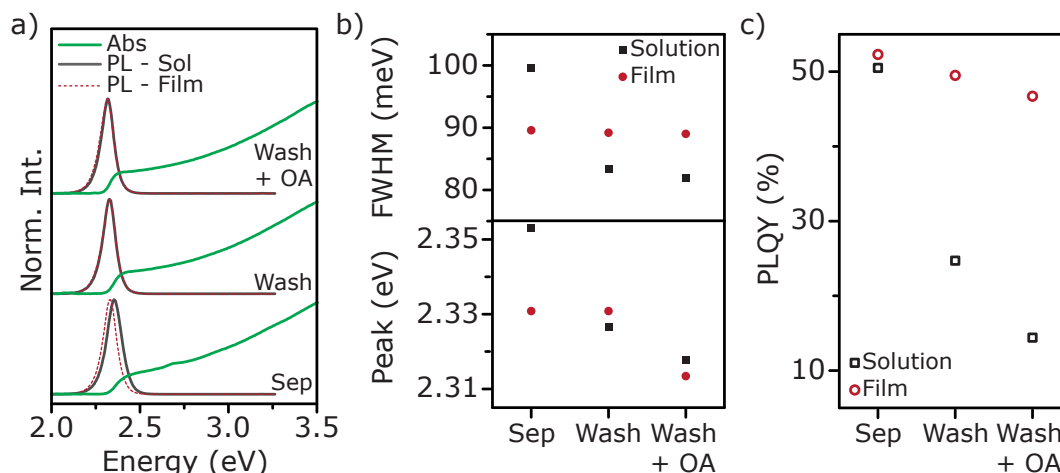


Figure 6.8: a) PL and absorption spectra, b) corresponding PL peak position and FWHM and c) PLQY of FAPbBr₃ nanoparticles separated (Sep) and washed in different ways with toluene and acetonitrile in solution and drop cast films

nanoparticles induces a red shift and narrowing of the PL which is further enhanced with the addition of OA. However in the films there is little difference in the FWHM across all three samples, Figure 6.8b, and only the addition of OA causes the PL of the film to be red shifted.

The PLQY of the nanoparticle solution suffers greatly through the separation and washing steps, Figure 6.8c. Previously, the addition of OA maintained a high PLQY for CsPbBr₃ NCs, whereas here it only causes a further decrease in the PLQY. However when drop cast into films there is very little difference in the PLQY. Surprisingly, a solution lower than 20 % can still yield a film of roughly 50 %. This is encouraging behaviour for LED device applications; when washed there are less ligands around to disrupt the charge transfer, but a high PLQY is maintained to boost the external quantum efficiency (EQE) of the device.

LED devices are made in the architecture ITO/Poly-TPD/FAPbBr₃/TPBi/Li-F/Al. FAPbBr₃ nanoparticles are spin coated from octane in a glovebox, and the electron injection layer and electrical contacts are deposited using a glovebox evaporator. The devices are then measured in a nitrogen filled holder. As expected, the most efficient device has the least amount of ligands, **Wash**, Figure 6.9. When not enough ligands are washed away, **Sep**, then the device does not turn on. Where additional OA is added, **Wash + OA**, the device performance is again impeded. The poorer performance is

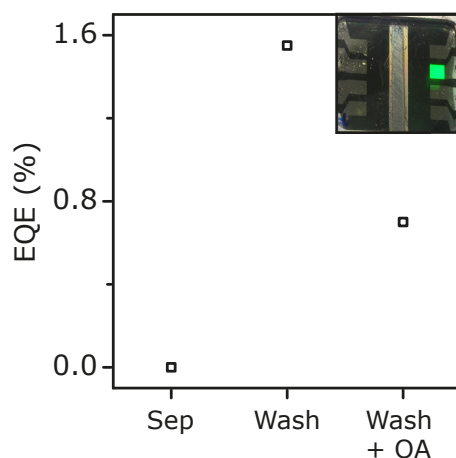


Figure 6.9: EQE of LED devices made with FAPbBr₃ nanoparticles separated or washed with Toluene and Acetonitrile with inset picture of operational pixel for the "Wash" sample

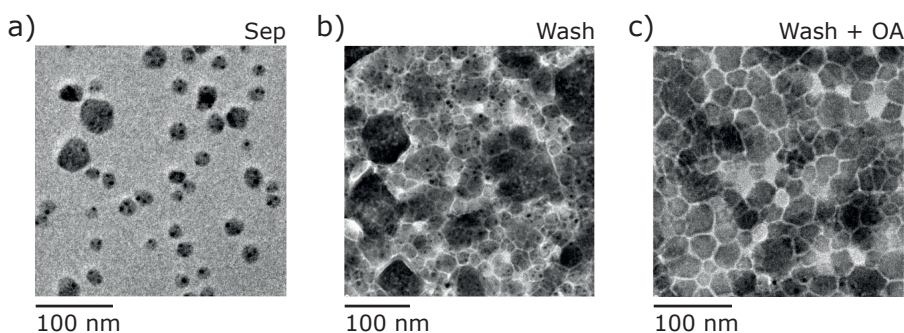


Figure 6.10: TEM images of FAPbBr₃ nanoparticles that have been a) separated (Sep), b) washed or c) washed with additional OA in solution

most likely as a result of poor charge transfer due to an excess of long ligands in the film.

TEM is conducted to assess if the washing processes affects the structure of the nanoparticles, Figure 6.10. When the nanoparticles are washed they pack closer together on the grid and have a more defined hexagonal shape, albeit it an irregular hexagon. The darker shadows on top can be attributed to organic matter, i.e. the ligands left in solution. As seen above, the optical properties of the FAPbBr₃ nanoparticles appear to converge when made into a film. This questions whether what is seen in TEM for these materials is a true reflection of what is in the solution. Regardless, there is no dramatic difference in the TEM when the nanoparticles are washed or not, and no ideally cubic NCs are observed.

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Sample	[TOPO] M	[OA] M	[A-oleate] M
TOPO	0.43	0	0
OA	0	0.53	0
TOPO:OA	0.43	0.53	0
FA-oleate	0	0.46	0.07
TOPO:FA-oleate	0.43	0.46	0.07
Cs-oleate	0	0.48	0.05
TOPO:Cs-oleate	0.43	0.48	0.05

Table 6.1: List of solutions in d-toluene investigated with ^1H and ^{31}P NMR

6.4 TOPO interactions with FA

To further understand the interaction of FA with TOPO and OA, a series of NMR experiments are conducted. The concentration of TOPO, OA and the A-cation oleate (A-oleate) can be found in Table 6.1. All samples are in d-toluene with triethyl phosphate (TEP) as an external standard for ^{31}P NMR. Residual toluene peaks are used to calibrate the ^1H NMR spectra. Full spectra for all samples can be found in Appendix D.

First the impact on TOPO is investigated by looking at ^{31}P NMR, Figure 6.11. The addition of OA causes a downfield shift, the extent of which is dictated by the concentration of OA. It was previously shown in Chapter 5 that when an equimolar amount of OA is added to PbX_2 dissolved in TOPO, it causes the PbX_2 to crash out of solution due to a more favourable interaction of TOPO and OA. From the NMR data, it can be seen that the shift in TOPO caused by interaction with OA only begins to plateau at a ratio of 1:4, Figure 6.11a. Therefore, TOPO continues to be affected by the presence of OA past the equimolar point. This is unexpected, and could suggest that the overall acidity of the solution is affecting the TOPO as opposed to a molecular interaction, or a combination of the two.

When neat OA is replaced with either 0.3 M Cs-oleate or 0.4 M FA-oleate in OA there are differences in the signal behaviour, Figure 6.11b. In both cases, the signal isn't as upfield shifted as for neat OA at the same concentration, indicating

6.4. TOPO interactions with FA

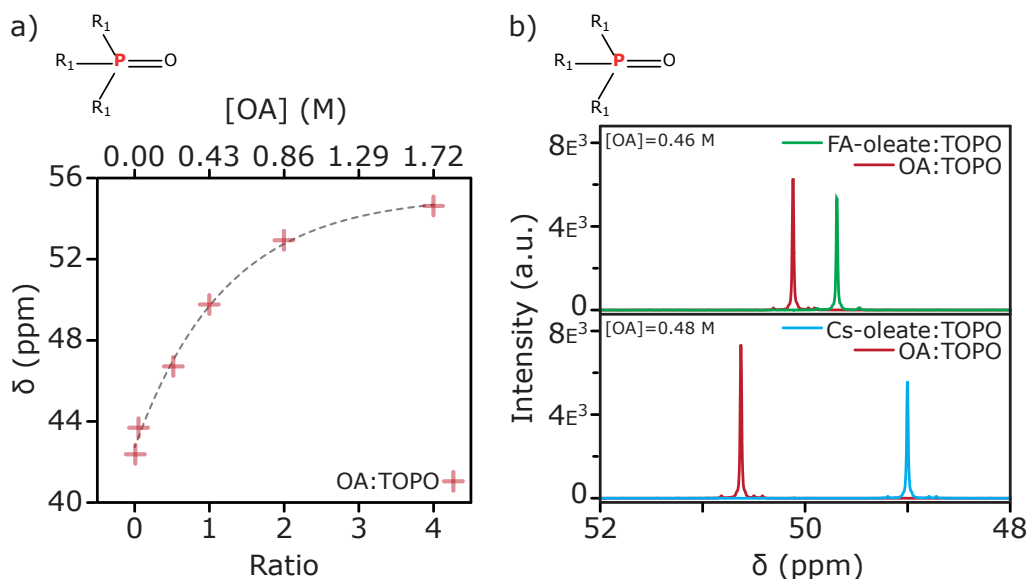


Figure 6.11: a) Peak position of TOPO P (highlighted in red, $\text{R}_1 = \text{CH}_3(\text{CH}_2)_7$) in ^{31}P NMR with OA at varying concentrations and b) peak position of TOPO P (highlighted in red, $\text{R}_1 = \text{CH}_3(\text{CH}_2)_7$) in ^{31}P NMR with OA at varying concentrations, Cs-oleate and FA-oleate. In both cases, the concentration of OA is given on the top, and the ratio of OA:TOPO is given on the bottom, with TOPO set to 1

that the OA present isn't interacting with TOPO to the same extent as expected. For Cs-oleate this is significant, with a difference of 1.63 ppm, whereas for FA-oleate it is less pronounced and only 0.43 ppm. The ^{31}P shift of TOPO with Cs-oleate is distinctly more similar to a lower concentration of OA being present. Therefore in the case of Cs-oleate, more OA is strongly interacting with the cesium (Cs).

The narrower difference for FA-oleate could be a result of a weaker interaction with OA by FA-oleate or the FA itself also interacting with TOPO and adding to the deshielding. Regardless of the reason, TOPO is clearly interacting with the Cs-oleate and FA-oleate differently, and thus points towards Cs-based syntheses not being directly translatable to FA ones.

The acidic proton on OA also gives a large insight to these interactions. In Figure 6.12a & b (bottom panel), a downfield shift is seen for this proton on the addition of TOPO to OA. This is to be expected due to the acid-base equilibria, where a level of bonding character is established between this proton and the phosphine oxide. The downfield shift is a result of the deshielding of the proton due to attraction of the electron density to the TOPO. The drop in intensity of the signal seen from OA

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to OA:TOPO (Figure 6.12 bottom panels) is consistent with the associated drop in concentration of OA.

Comparing FA-oleate to OA, there is an upfield shift of the acidic proton and slight broadening. For Cs-oleate, there is significant sharpening of the peak alongside a downfield shift. This indicates that the acidic proton is less labile and has a more well defined bond. For both, the addition of TOPO induces a small downfield shift with broadening. This shift is larger for Cs-oleate at 0.15 ppm, and 0.09 ppm for FA-oleate.

Two conclusions can be drawn from this data. Firstly, that TOPO is interacting with the acidic proton on OA in a similar way for neat OA, Cs-oleate and FA-oleate. The extent or strength of this interaction may differ due to the difference in the extent of the shift and broadening seen. Secondly, that FA and Cs have opposite effects on the acidic proton of OA. This is largely attributable to the introduction of labile protons on FA which are not present for Cs. This follows the observations for the ^{31}P NMR that the synthetic mechanisms for Cs systems are not directly applicable to FA systems with these precursors.

The presence of TOPO induces a downfield shift in the methine proton NMR of FA, Figure 6.13. Interestingly, the labile amine protons can be seen in the FA-oleate alone (bottom panel, marked with *), as the broad peak centred around 8.3 ppm. This broad peak is lost to baseline noise on the addition of TOPO. Amine protons (NH) are extremely labile, and their NMR signal moves around significantly depending upon the concentration, solvent, acidity, and temperature of the solution. Hydrogen bonding also has a large effect on where these protons appear, and the breadth of their peak. Given that they are observable without TOPO, it indicates that there is an extent of interaction between these protons with TOPO, and results in a loss in intensity of the signal. Further, as the methine proton on FA is also affected, it demonstrates that the electronic environment around this proton has been altered.

From the data presented thus far, it is clear that FA interacts with TOPO and OA. In order to establish the nature of this interaction, temperature dependent NMR experiments are conducted. First ^{31}P NMR is considered, Figure 6.14a. As seen

6.4. TOPO interactions with FA

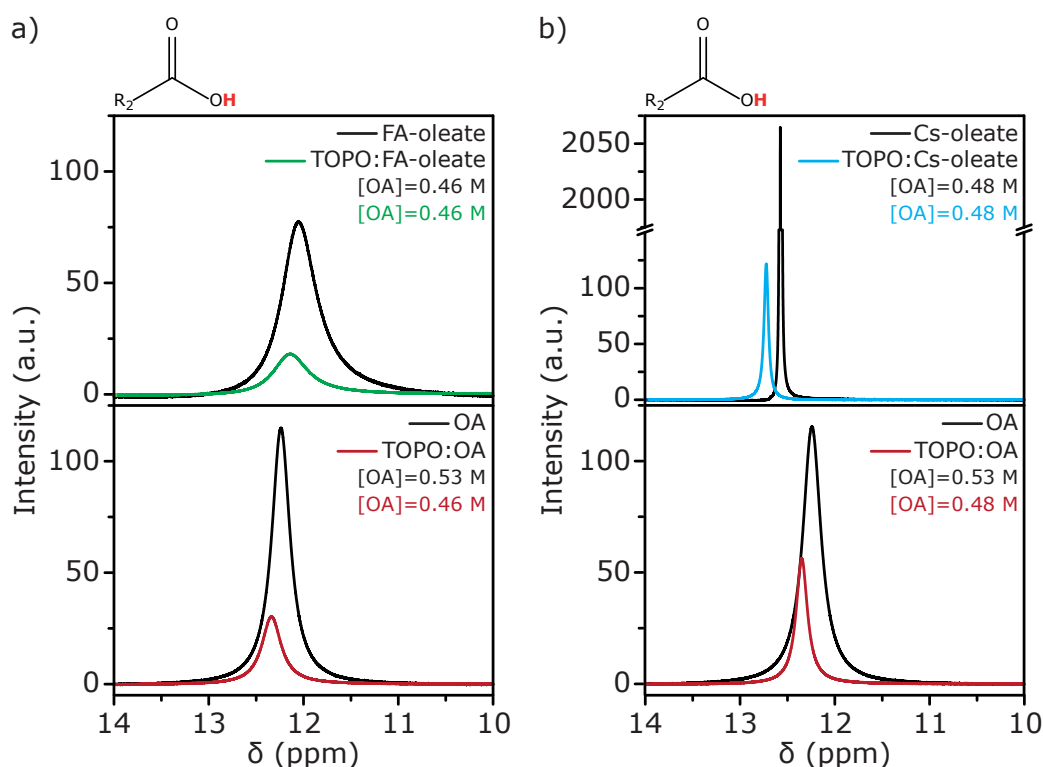


Figure 6.12: ^1H NMR spectra of the region for the acidic proton on OA (highlighted in red, $\text{R}_2 = \text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7$). a) FA-oleate, TOPO:FA-oleate (top) and OA, TOPO:OA (bottom) at specified concentrations of OA and b) Cs-oleate, TOPO:Cs-oleate (top) and OA, TOPO:OA (bottom) at specified concentrations of OA

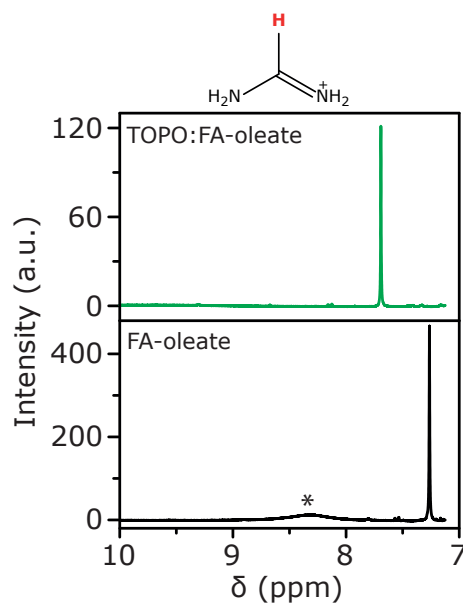


Figure 6.13: ^1H NMR spectra of the region for the methine proton on FA (highlighted in red) for TOPO:FA-oleate (top) and FA-oleate (bottom). The broad peak marked with an asterisk (*) in the bottom panel is assigned to the labile amine protons

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previously, over increasing temperature there is an upfield shift in the position of neat TOPO. On the addition of OA this shift is intensified, and attributed to the acid-base interaction of TOPO:OA, see Chapter 5. When TOPO and FA-oleate in OA are evaluated over this temperature range, the relative shift sits between that of neat TOPO and TOPO:OA. This indicates that the FA is impacting OA and TOPO's acid-base interaction.

For FA alone, there is little variation over the temperature range for the methine hydrogen, Figure 6.14b. When TOPO is present there is a significant upfield shift, indicating an increase in the electron density around the hydrogen. At higher temperatures, there is more neutral TOPO present due to the exothermic TOPO:OA interaction. If the FA-oleate shifts when TOPO is present, then the neutral TOPO must be interacting with FA to cause this shift.

Then consider the acidic proton on OA, Figure 6.14c. For the TOPO:OA mixture, a downfield shift and narrowing of the peak are observed as the acidic proton goes back on to OA, as can be seen in the bottom spectra of Figure 6.14c. This is due to the neutral form of TOPO and OA forming and is inline with ^{31}P NMR observations. For FA-oleate alone, there is significant sharpening and shift across the temperature range, as observed in the middle spectra. At higher temperatures, the acidic proton will be exchanging between OA molecules faster due to a higher energy, and the molecules will be tumbling quicker. This results in a more defined position of the acidic proton on the NMR timescale, and thus a sharper peak.

With the addition of TOPO the same trend is observed, as seen in the top spectra of Figure 6.14c. The lack of difference in these trends could be due to the fact that TOPO is preferentially interacting with FA over OA. In that case, the acidic proton on OA is free to continue to exchange between different OA molecules, as it was in the FA-oleate case. If there was a more favourable interaction between OA and TOPO in the TOPO:FA-oleate mixture, then a broader peak for the acidic proton would be expected, reflecting the TOPO:OA character.

This data infers that neutral TOPO interacts with the labile amine protons on FA. This is a competing interaction to that of the acidic OA proton and TOPO. The

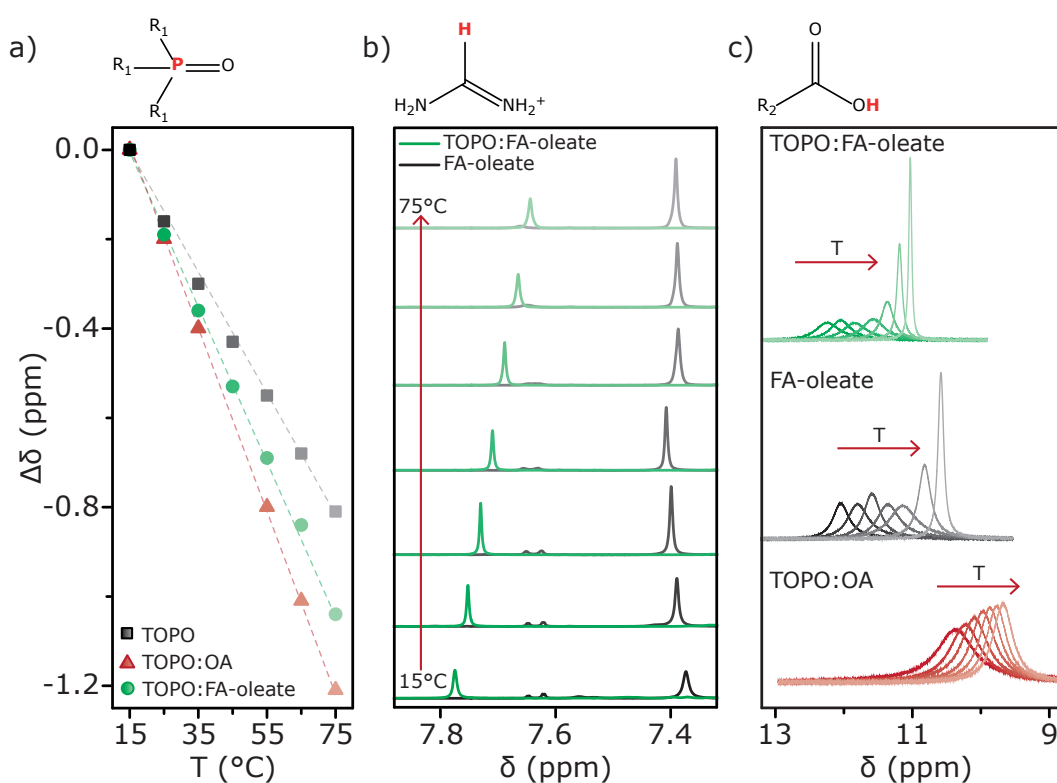


Figure 6.14: a) Shift of peak position of TOPO P (highlighted in red, $\text{R}_1=\text{CH}_3(\text{CH}_2)_7$) in ^{31}P NMR for TOPO, TOPO:OA and TOPO:FA-oleate over temperature range 15-75 °C. b) ^1H NMR spectra of the region for the proton on FA (highlighted in red) for TOPO:FA-oleate and FA-oleate over temperature range 15 - 75 °C. c) ^1H NMR spectra of the region for the acidic proton on OA (highlighted in red, $\text{R}_2=\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7$) for TOPO:FA-oleate, FA-oleate and TOPO:OA (top to bottom) over temperature range 15-75 °C

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concentration of FA is considerably lower than that of OA in all cases, Table 6.1. As differences in the peaks associated with TOPO and FA are notable, with little change noted for OA, it supports the notion that it is more preferable for TOPO to be interacting with FA over OA.

Discussion

From the NMR data there are clearly two main interactions to consider to understand the experimental results in the FAPbBr₃ NCs phosphine-oxide synthesis. The first is acid-base equilibria of OA and TOPO, the same as seen for the CsPbBr₃ synthesis, Figure 6.15a. At high temperatures this reaction is pushed in favour of the neutral forms of the acid and base, Figure 6.15b. The hypothesis for the success of the phosphine oxide route for CsPbBr₃ NCs relies on this interaction. When enough OA is added to the precursor solution, the TOPO releases the PbBr₂ and is bound up by interacting with OA. This leaves the Cs-oleate to freely react with PbBr₂ and form monodisperse NCs. The second interaction is that of TOPO and FA, Figure 6.15c. From the NMR data this interaction is clearly preferential.

The pK_a values for OA¹⁹³ and FA¹⁹⁴ are used to calculate the corresponding pK_b . The pK_b value for TOPO is an approximation based on a similar alkyl phosphonic acid¹⁹⁵ and is used to calculate the corresponding pK_a , using Equation 6.1. In both cases, the reaction going from a stronger acid (lower pK_a) to a weaker acid (higher pK_a) is in accordance with an exothermic acid-base interaction.

$$pK_b \approx 14 - pK_a \quad (6.1)$$

Given the difference in pK_a values from Figure 6.15a-c, it is more likely that the OA and TOPO interaction goes closer to completion, or complete dissociation of the proton from OA, than for FA and TOPO. This is reflected in the structures drawn for these two equilibria.

The interaction of FA and TOPO will have two main impacts on the synthesis. Firstly, the proportion of FA interacting with TOPO is unlikely to be able to react

6.4. TOPO interactions with FA

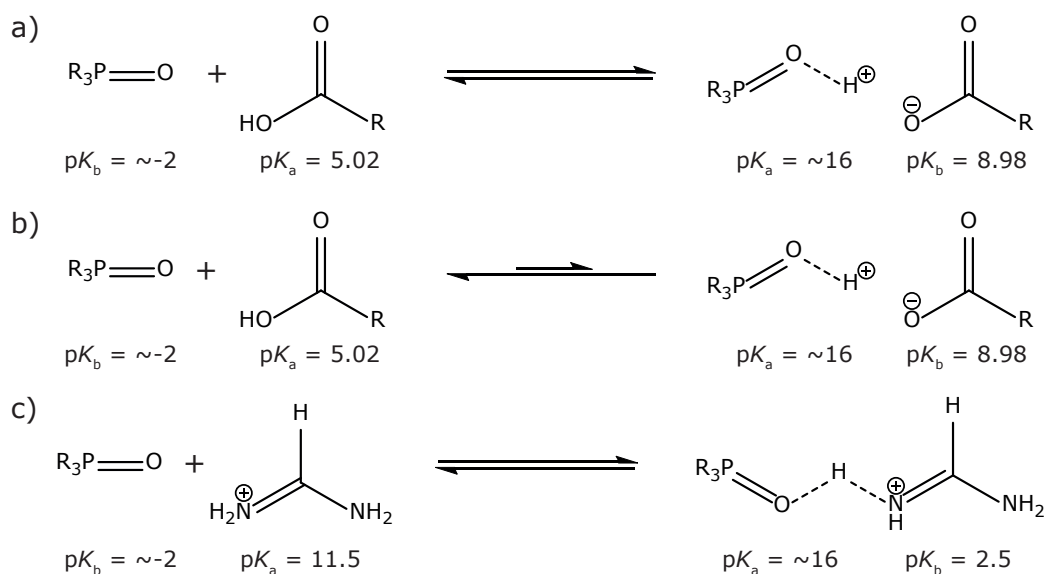


Figure 6.15: Generalised equilibrium equations between TOPO and OA under a) standard conditions and b) high temperature and between c) TOPO and FA

with the lead halide to form the perovskite. The phosphine oxide synthesis gave record yields for CsPbBr₃ NCs but is not replicated here. This is confirmed by the ICP-OES results where only a 15.3 % at. Pb is yielded.

Secondly, the ligand coverage on the surface of the nanoparticles will be impacted, and the interaction may promote TOPO to be on the surface of FAPbBr₃. Having such a large molecule on the surface could easily disrupt ligand packing and the shape of the nanoparticles. Intercalation of TOPO between layers of FAPbBr₃ is another potential cause for the optical and structural properties observed for these nanoparticles. It has previously been shown experimentally and computationally that dimethyl sulfoxide (DMSO) can intercalate into polycrystalline FAPbBr₃¹⁹⁶. This causes an increase in the PLQY of the films and further band gap tunability due to a mixing of 3D and 2D perovskite phases. Similar features below 2.75 eV are also observed in the absorption spectra of these films. Due to similarities between TOPO and DMSO, the mechanism for intercalation here is plausible. However, for DMSO structural differences were noted through XRD which are not emulated here.

The optical and structural data for the washed FAPbBr₃ nanoparticles supports the hypothesis of a more complex ligand shell being present than just oleate-only, as seen for CsPbBr₃ NCs. Adding back OA would have increased the PLQY of oleate-only

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capped nanoparticles through manipulation of the ligand equilibria between the surface and solution. This was seen for CsPbBr₃ NCs¹⁸⁹. As the addition of OA in the washing steps induces a further decrease in PLQY instead, there is a disruption in the surface coverage by the ligand shell. This is potentially due to OA interacting with any TOPO on the surface of the NC in a competing pathway. This would draw TOPO away from the surface, leaving dangling bonds to act as trap-states for charge carriers and quenching the PLQY.

The TOPO:OA ratio has been shown to play a pivotal role in the optical properties of FAPbBr₃ nanoparticles in this synthesis. Ratios between 1.2 and 1.6 give rise to higher PLQYs and less pronounced bumps above 2.75 eV in the absorption spectra. At higher amounts of OA there is less neutral TOPO available to interact with FA.

Lower temperatures enhance these properties further, with the highest PLQY of 70 % record for a rT synthesis. Due to the exothermic acid-base equilibria of FA and TOPO, a lower temperature promotes their interaction and formation of a complex, Figure 6.15c.

These two arguments deliver conflicting conclusions. On balance, it would appear that the FA-TOPO interaction is not wholly detrimental to the formation of FAPbBr₃ nanoparticles of some form. This relationship must be balanced in order to form highly luminescent material.

6.5 Conclusion

It has been demonstrated that the labile amine protons on FA interact with TOPO and that FA-oleate and Cs-oleate have very different effects on OA. These two factors combined lead to a lack of translation of the successful synthesis of monodisperse CsPbBr₃ NCs to FAPbBr₃.

Despite this, the phosphine oxide assisted synthesis of FAPbBr₃ nanoparticles can be conducted at room temperature, and LED devices from the material can be made at the industrially desired wavelength of 2.34 eV (530 nm). A lack of control over the size and shape of these nanoparticles highlights a complicated ligand shell and

equilibria in solution. Overall, highly luminescent FAPbBr₃ nanoparticles have been formed through a phosphine oxide synthesis.

Contributions

ICP-OES was conducted by Filippo Drago (Istituto Italiano Di Tecnologia (IIT), Italy). Device fabrication was conducted with Dr Ashley Marshall and Jonathan Warby. Device characterisation was measured with Dr Bernard Wenger. Temperature dependent NMR measurements of FA-oleate and TOPO:FA-oleate were conducted by Dr Nader Amin (Chemistry, University of Oxford). Temperature dependent NMR measurements of TOPO and TOPO:OA were conducted by Dr Luca Goldoni (IIT, Italy). This set of NMR data from IIT was published in The Journal of the American Chemical Society in October 2018 (*J. Am. Chem. Soc.* 2018, 140, 14878-14886). Permission was granted to reproduce the data in this thesis, Appendix E.

CHAPTER 7

Conclusion

This thesis has shown the challenges of a synthesis for mixed cation perovskite nanocrystals (NCs), and the development of a phosphine oxide assisted synthesis for perovskite NCs. Controlling the miscibility of incorporation of cations cesium (Cs) and formamidinium (FA) in the perovskite structure, whilst maintaining control over size, shape, and ligand shell, was problematic. The nature of interaction of the two different cations, one inorganic and one organic, with the ligands oleylamine (OLAm) and oleic acid (OA) was deemed to be central to finding a solution.

Utilising a phosphine oxide in the synthesis of CsPbX_3 NCs allowed for a dynamic, oleate-only ligand shell, as opposed to an oleylammonium-oleate based shell. By harnessing and manipulating the acid-base equilibria between OA and trioctylphosphine oxide (TOPO), bright and monodisperse NC were synthesised at temperatures lower than a traditional Hot Injection synthesis. The interaction of cesium oleate (Cs-oleate) with the surface of the NCs was investigated with nuclear magnetic resonance spectroscopy (NMR), and the lack of phosphine in the X-ray photoelectron spectroscopy (XPS) data confirmed a phosphine free surface. These NCs showed stability

Chapter 7. Conclusion

to washing with anti-solvents by adding back small amounts of OA, maintaining a photoluminescence quantum yield (PLQY) of $\sim 70\%$.

These developments showcase the ability to synthesise bright and monodisperse CsPbX_3 NCs through a much more scalable process, avoiding laborious degassing steps. The high yield of perovskite NC obtained through this method, at $\sim 60\%$ at. in lead, is also key in the scalability of this process for applications.

An attempt to replicate this simpler ligand shell and facile synthesis technique was trialled for FAPbBr_3 NCs. In this case, although a bright material at a commercially relevant wavelength was achieved, the size and shape of these nanostructures diverged from the expected cubes for a perovskite NC. To understand the reason behind the divergence, NMR was used to investigate the interaction of FA with both OA and TOPO. The results showed that the labile protons on FA introduced a competing pathway for the acid-base equilibria of OA and TOPO, and thus disrupted the synthesis of FAPbBr_3 nanocubes.

Moving forward, the investigation into FAPbX_3 through a phosphine oxide route forms two strands of research. Firstly, the bright nanoparticle-like material formed can be further investigated for device applications, with the light emitting diodes (LEDs) presented providing a starting point for device optimisation. Secondly, the synthesis can be further investigated to establish a route to cube-like NCs of FAPbX_3 , with an emphasis on expansion to different halides. This could be achieved through trialling different acids, such as phosphonic acids, or changing the FA precursor.

It has been demonstrated that the nature of the ligand shell of a perovskite NC is a key factor in determining not only the size and shape of the NC, but also is a factor controlling the composition. The stark molecular differences between Cs and FA are emphasised through their interactions with acidic and basic ligands, and by the stability of the surface of the perovskite that they form. In order to achieve full miscibility between these two cations in monodisperse perovskite nanocubes, further investigations into appropriate ligands and synthetic conditions for an injection-style synthesis are required. The labile protons on FA are arguably the first, and largest, barrier to achieving this. By tackling the precursors and ligand choices in the synthesis,



Figure 7.1: Photograph of blue, green and red emitting lead halide perovskite NCs under UV illumination. Photograph courtesy of Helio Display Materials Ltd.

and investigating their interactions using NMR and other techniques, there is still scope to achieve bright and monodisperse $\text{FA}_x\text{Cs}_{1-x}\text{PbX}_3$ NCs.

More broadly, with the tremendous research effort and vast number of publications on perovskite NCs, it is plausible to see this family of materials making a large impact on the optoelectronic industry in the near future. As research into perovskite NCs becomes focused on their stability and ligand shells, advances to commercialisation are strengthened. The research presented in this thesis aids understanding on the miscibility of cations, the effects of the ligand shell and surface passivation, and on how to optimise a synthesis to achieve monodisperse perovskite NCs with high PLQY under ambient conditions. The phosphine oxide route to perovskite NCs presents an opportunity for scalability, owing to the reaction being conducted in air, at low temperatures and the high yields achievable. This thesis forms part of a wider effort to understand more of the fundamental factors governing the synthesis of perovskite NCs and what can be done to harness this wonder material.

Stretched Exponential Fit Code

This appendix documents the MatLab Code for the stretched exponential fit of the time resolved photoluminescence spectroscopy (TRPL) data for $\text{FA}_x\text{Cs}_{1-x}\text{PbI}_y\text{Br}_{3-y}$ nanocrystals (NCs), Chapter 4.

```
function[Z] = TRPLv2(file)
%%\% Import Data

data_folder = '(input folder extension)';
Z = importdata([data_folder, file], '\t', 75);
x = Z.data(:,1);
y = Z.data(:,2);

range = [5 900];
yfit = y(find(x>range(1),1):find(x>range(2),1));
xfit = x(find(x>range(1),1):find(x>range(2),1));
```

Appendix A. Stretched Exponential Fit Code

```
[xData, yData] = prepareCurveData( xfit, yfit );

%%%% Set up fittype and options.

ft = fittype(
'a*exp(-(x/tau)^beta)+b''', 'independent', 'x', 'dependent', 'y'
);

opts = fitoptions( 'Method', 'NonlinearLeastSquares' );
opts.Display = 'Off';
opts.Lower = [100 0 0 0];
opts.Robust = 'LAR';
opts.StartPoint = [100000 0 0.5 10];
opts.Upper = [100000000 75 1 200];

%%%% Fit model to data.

[fitresult, ~] = fit( xData, yData, ft, opts );
f = fit( xData, yData, ft, opts);

%%%% Average Lifetime
%%The average lifetime is given by <tau>=(tau/beta)*gamma(1/beta)
%% <tau>=expectation/average of tau
%% gamma function - in MatLab already

Coeff = coeffvalues(f);
tau = Coeff(4);
beta = Coeff(3);
Av_tau = (tau/beta)*gamma(1/beta);
TauText = [num2str(Av_tau,3), 'ns'];
disp(TauText)
```

```
display(beta)
```

```
\%\% Export Function
```

```
fileID = fopen('AvTau.txt', 'a');  
fwrite(fileID,[13 10],'char');  
fprintf(fileID,[file char(9)]);  
fprintf(fileID,TauText);  
fclose(fileID);
```

```
\%\% Plotting
```

```
figure( 'Name', 'Stretch Exp' );  
clf;  
h = plot( fitresult, xData, yData );  
set(gca,'YScale','log')  
legend(h, 'Raw Data', 'Stretch Exp Fit', 'Location', 'NorthEast');  
xlabel('Time (ns)');  
ylabel('Counts');  
title(file);  
dim1 = [.2 .5 .3 .3];  
str1=['Average Lifetime =' TauText];  
annotation('textbox',dim1,'String',str1,'FitBoxToText','on');  
dim2 = [.2 .4 .3 .3];  
str2=['Beta =' beta];  
annotation('textbox',dim2,'String',str2,'FitBoxToText','on');  
dim3 = [.3 .4 .3 .3];  
str2=beta;  
annotation('textbox',dim3,'String',str2,'FitBoxToText','on');  
filesave = strcat(file);
```

Appendix A. Stretched Exponential Fit Code

```
saveas(gcf, strcat(data_folder, filesave, '.jpg'));
\\%% Export processed data

RawExport = [x';y'];

yFit = feval(fitresult, xData);
fitExport = [xData';yFit'];

fid = fopen([data_folder, file 'Raw.dat'], 'w');
fprintf(fid, '\\%s \\%s\\n', 'Time(ns)', 'RawData');
fprintf(fid, '\\%f \\%f\\n', RawExport);
fclose(fid);

fid = fopen([data_folder, file 'Fit.dat'], 'w');
fprintf(fid, '\\%s \\%s\\n', 'FitTime(ns)', 'StretchExpFit');
fprintf(fid, '\\%g \\%f\\n', Av_tau, beta);
fprintf(fid, '\\%f \\%f\\n', fitExport);
fclose(fid);
end
```

APPENDIX B

Computational Details

This appendix relates to the computational studies of ligands on the surface of CsPbBr₃ nanocrystals (NCs) synthesised through the phosphine oxide synthesis, Chapter 5.

A model of a CsPbBr₃ NC with edge size of about 2.4 nm was built by cutting a cubic bulk structure along the (100) facets, leaving cesium (Cs) and bromine (Br) on the surface. This NC presents a stoichiometry of Cs₁₂₅Pb₆₄Br₂₄₀, with an excess positive charge when each ion is considered in its more stable thermodynamic electronic configuration (i.e. Cs⁺, Pb²⁺ and Br⁻). This excess was compensated by randomly removing 13 Cs ions from the surface, resulting in the following stoichiometry Cs₁₁₂Pb₆₄Br₂₄₀. Four reactions are modelled to calculate the stability of the ligands proposed. Each ligand is formed of a cation and an anion, and is considered to replace a CsBr pair of adjacent atoms on a facet of the NC:

1. NC(o)-Br-TOPOH $\rightleftharpoons$ NC(o) + TOPO + HBr
2. NC(o)-oleate-TOPOH $\rightleftharpoons$ NC(o) + TOPO + OA
3. NC(o)-oleate-Cs $\rightleftharpoons$ NC(o) + Cs-oleate

Appendix B. Computational Details

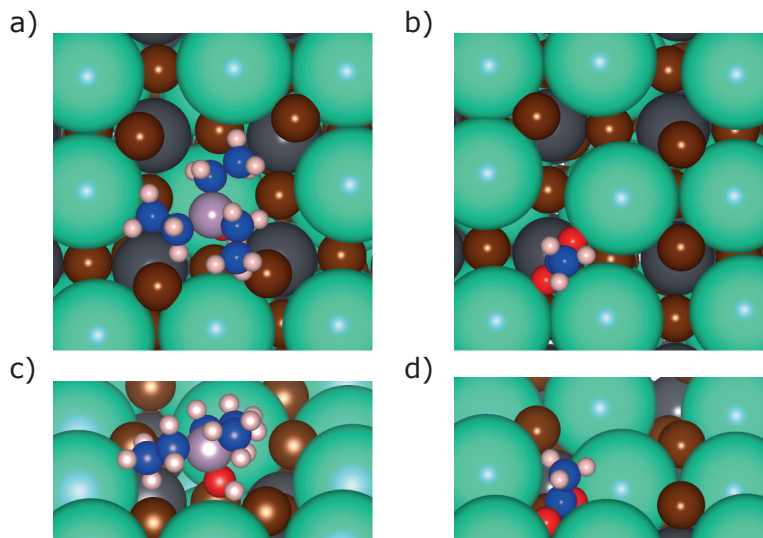
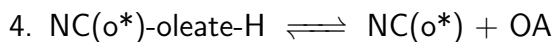


Figure B.1: Relaxed structures with the Cs-oleate and TOPOH..Br attached to the NC surface. TOPOH⁺ substitutes Cs⁺ and Br⁻ occupies a Br⁻ site shown in a) birds-eye view and c) side view. Cs⁺ enters a Cs⁺ site and the oleate anion substitutes Br⁻ shown in b) birds-eye view and d) side view



Here the dash before the ion indicates that it is bound to the NC surface, and NC(o) and NC(o*) refer to the NC described above but with one and five CsBr pairs of atoms extracted from its surface respectively. The energies -21.34, -9.72, -26.24 and -2.54 kcal/mol are found respectively, for the four reactions. The negative number indicating a more stable configuration of the left side of the equilibrium.

To study the electronic properties of the NC at different Cs concentrations, different degrees of surface passivation of the NC with cesium oleate (Cs-oleate) ligands are considered. The starting point is from an ideal fully passivated NC, with oleate ions substituting all Br⁻ on the surface, yielding 16 Cs-oleate ligands per face. From this point Cs-oleate ligands are added and subtracted, in order to see effects on the density of states. Adding two Cs-oleate ligands on the surface is enough to induce two clear trap levels localized at the added extra ligands.

To study the removal of Cs-oleate ligands from the surface of the initial NC, the most stable ligand removal sequence is calculated first. Vertex ligands are found in the structure, where a Pb²⁺ cation is bound to three oleate anions; edge ligands, where a Pb²⁺ cation is bound to two oleate anions; and finally facet ligands, where a Pb²⁺

cation is bound to an oleate anion. The higher the oleate coordination around Pb, the easier it is to remove a Cs-oleate ligand. Hence, this order for ligand removal is respected. Here, when about 55 % of the ligands are removed, trap states localized at ligands start to reduce the band gap. This last structure presents the stoichiometry of $\text{Cs}_{65}\text{Pb}_{64}\text{Br}_{144}$.

APPENDIX C

2D NMR

This appendix relates to the nuclear magnetic resonance spectroscopy (NMR) studies of ligands on the surface of CsPbBr₃ nanocrystals (NCs) synthesised through the phosphine oxide synthesis, Chapter 5.

Method

Acid-base interactions A Bruker Avance III 400 MHz spectrometer is used, equipped with a Broad Band Inverse probe (BBI)

Nanocrystal Samples A Bruker DRX400 spectrometer 400.13 MHz equipped with a Bruker 5 mm BBI Z-gradient probe head affording a maximum gradient strength of 53.5 G/cm is used. After an automatic 90° calculation on each sample-tube, ¹H NMR spectra are accumulated, at 300 K, as follows: 1 transient and 64k data points, no steady state scans, over a spectral width of 20.55 ppm (offset at 6.18 ppm), at a fixed receiver gain (1). Inverse gated ¹H decoupled ³¹P NMR spectra are acquired, at 300 K, as follows: 1 transient and 64k data points, no steady scans, over a spectral width of 200.45 ppm, (offset at 0.00 ppm), at a fixed receiver gain (1820).

Appendix C. 2D NMR

Temperature Dependent NMR, 288 - 354 K Temperature is actively monitored and the samples are left to equilibrate for at least 5 minutes inside the probe before the acquisition. The ^1H NMR spectra are performed with 4 transients and an inter-pulse delay of 30 seconds, while the ^{31}P spectra are performed with 1 transient and an inter-pulses delay of 60 seconds.

All ^1H NMR chemical shifts are referred to a 0.049 M tetramethylsilane (TMS) internal reference solution, at 0.0 ppm and a triethyl phosphate (TEP) 0.049 M external reference solution, at 0.00 ppm for ^{31}P .

2D Diffusion Ordered Spectroscopy (DOSY) Experiments are acquired at 297 K using a ledbp pulse sequence (ledbpgp2s of the Bruker library), with a diffusion time (Δ) of 300 ms and a total gradient pulse duration (δ) of 4 ms. The gradient strength (G) was linearly incremented in 32 steps from 5 to 95 % of its maximum value.

Equation C.1 describes the intensity decay. I is the observed intensity, I_0 is the non-attenuated signal intensity, D_t is the diffusion translational coefficient, γ is the gyromagnetic ratio of ^1H and τ is the time between bipolar gradients. Diffusion coefficients are obtained by analyzing the signal intensity decay as a function of the gradient strength G of at least three different resonances by using a least square linear fitting.

$$\ln \frac{I}{I_0} = -(\gamma\delta)^2 D_t \left(\Delta - \frac{\delta}{3} - \frac{\tau}{2} \right) G^2 \quad (\text{C.1})$$

2D Nuclear Overhauser effect spectroscopy (^1H - ^1H NOESY) Experiments (noesygp2d of the Bruker library) are performed with a mixing time of 300 ms, 2048 data points in the direct dimension for 256 data points in the indirect dimension, accumulating 32 transients each. The chemical shifts of the DOSY and NOESY NMR spectra are referred to the non deuterated residual peak of d-toluene at 7.09 ppm.

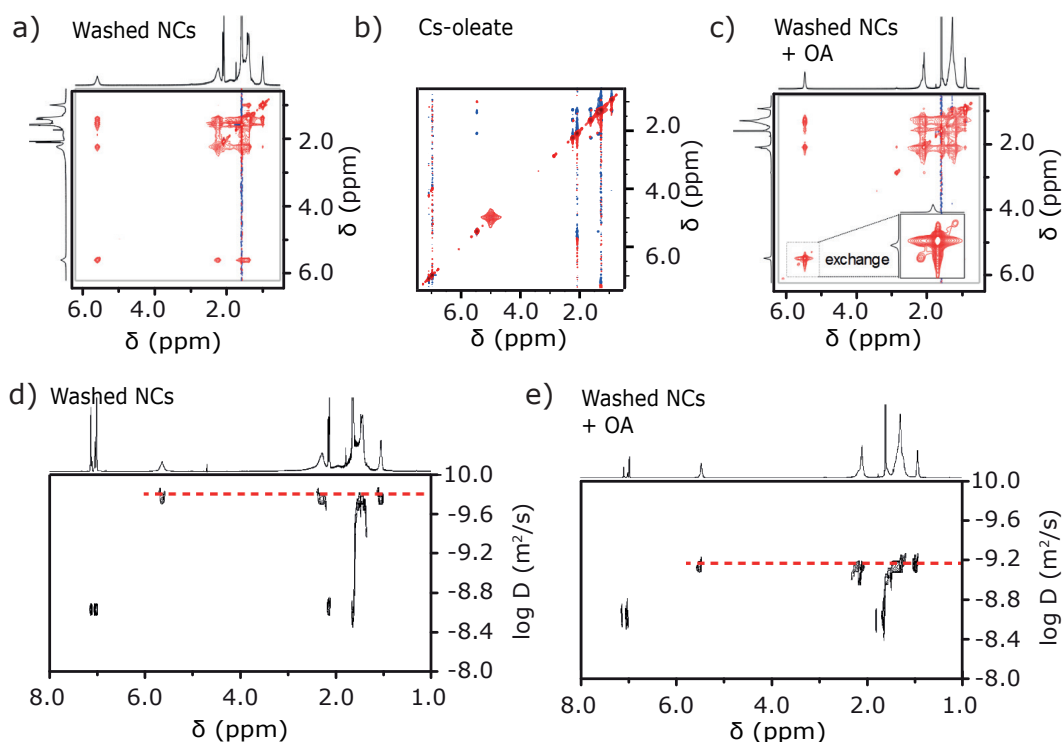


Figure C.1: ^1H NOESY of a) Washed NC, b) Cs-oleate and c) Washed NC + OA and ^1H DOSY of d) Washed NC and e) Washed NC + OA

2D NMR Results

Confirmation of the interaction of oleate species with the NC surface is inferred through the 2D NMR experiments. Firstly, a negative (red) NOE cross peak is observable in the NC sample, whereas positive NOE cross peaks are observed on free ligands, cesium oleate (Cs-oleate) in oleic acid (OA), Figure C.1a & b. The negative cross peak is characteristic of species with long correlation times (τ_c) that move more slowly in solution compared to small free molecules. These findings are supported by diffusion ordered spectroscopy, Figure C.1d, where a diffusion coefficient of $242 \mu\text{m}^2/\text{s}$ is found, which is considerably smaller than that of free OA or Cs-oleate in d-toluene (725 and $726 \mu\text{m}^2/\text{s}$, respectively, 0.2 M solutions)¹⁸⁹. From this, the bound fraction of oleate species is calculated to be ca. 76 % following the method of de Roo et al¹¹⁴.

The free OA signal exhibits a line broadening that is indicative of exchange processes, and this is confirmed by the cross peak between the two double bond signals in a 2D ^1H NOESY, along with negative NOE cross peaks, Figure C.1c. The

Appendix C. 2D NMR

^1H DOSY experiment instead shows a considerable increase of the weighted average diffusion coefficient ($624\ \mu\text{m}^2/\text{s}$) of the free and bound states, tending to the value of free OA, Figure C.1e. Such evidence is in line with a rapid exchange mechanism¹⁸⁵.

APPENDIX D

NMR Spectra

This appendix relates to the nuclear magnetic resonance spectroscopy (NMR) studies in Chapter 6, and includes the full NMR spectra of the different ligand combinations.

Appendix D. NMR Spectra

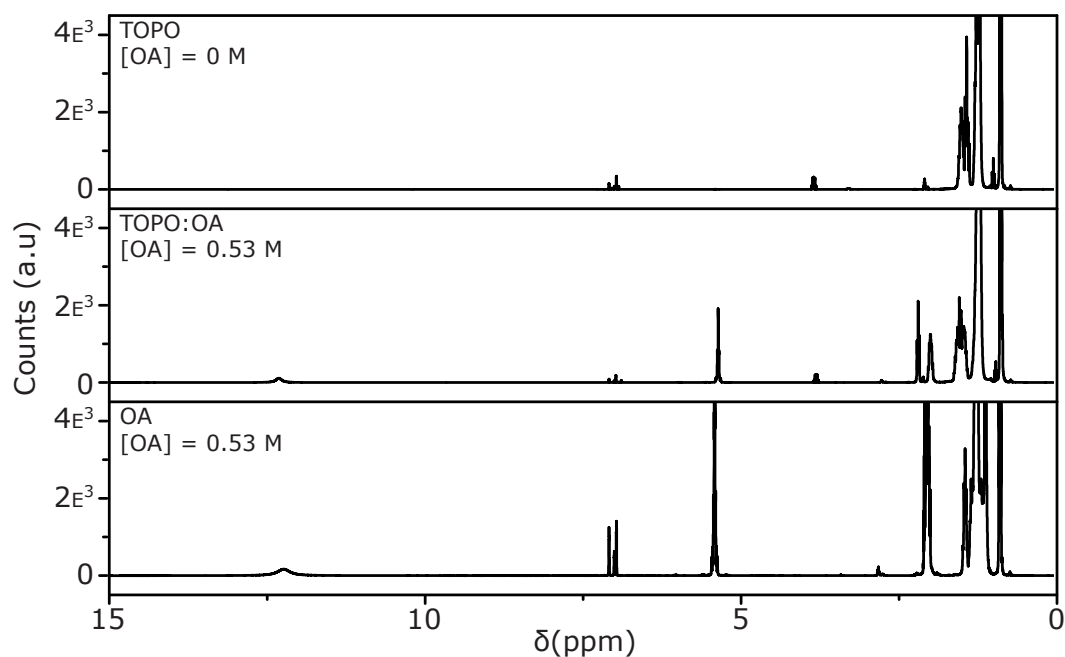


Figure D.1: ^1H NMR spectra from 0 - 15 ppm of trioctylphosphine oxide (TOPO), TOPO:oleic acid (OA) and OA at given concentrations (top to bottom)

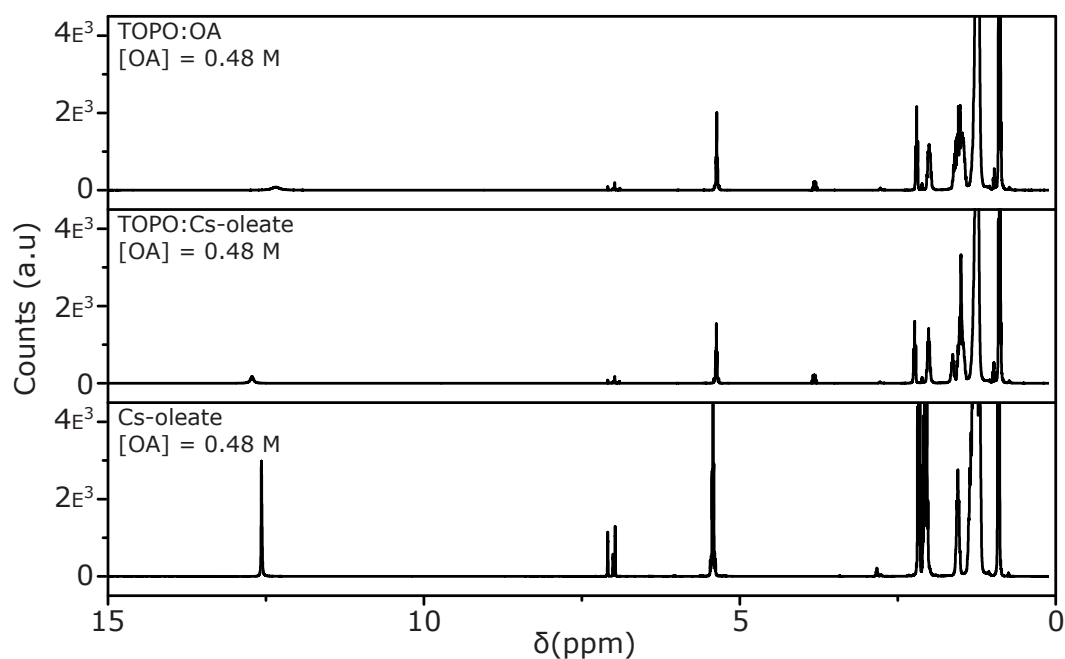


Figure D.2: ^1H NMR spectra from 0 - 15 ppm of cesium oleate (Cs-oleate), TOPO:Cs-oleate and TOPO:OA at given concentrations (top to bottom)

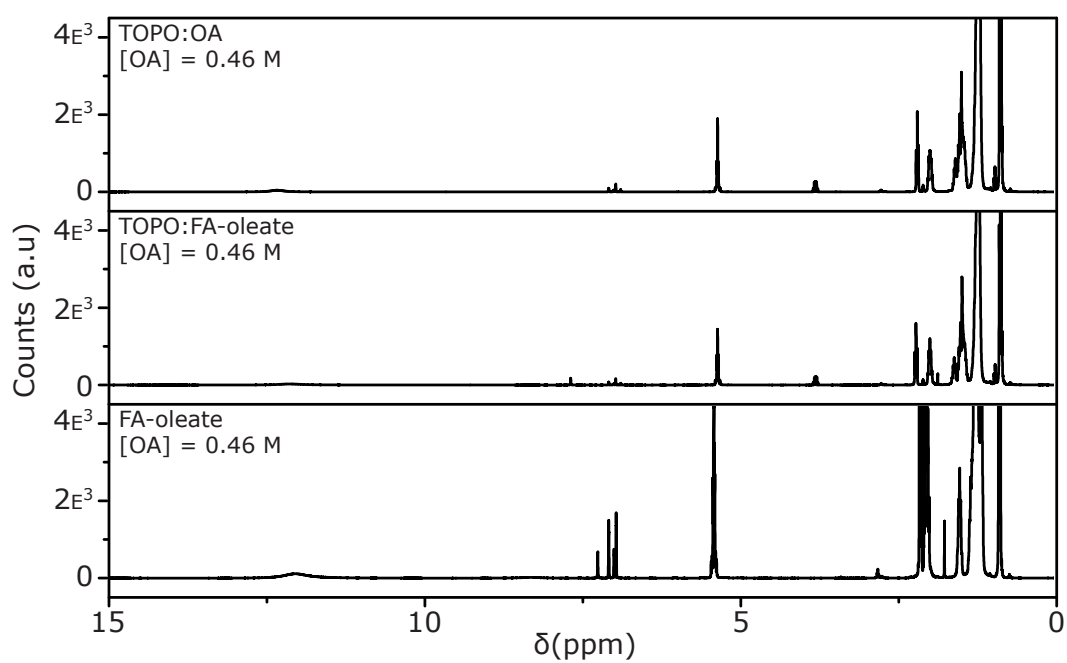


Figure D.3: ^1H NMR spectra from 0 - 15 ppm of formamidine oleate (FA-oleate), TOPO:FA-oleate and TOPO:OA at given concentrations (top to bottom)

APPENDIX E

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Bibliography

1. Samsung Newsroom South Africa, "QLED TV vs. OLED TV," 2018.
2. M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, and H. J. Snaith, "Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites," *Science*, vol. 338, pp. 643–647, nov 2012.
3. NREL (Date Accessed 2019-08-29), "Best Research-Cell Efficiency Chart."
4. L. C. Schmidt, A. Pertegás, S. González-Carrero, O. Malinkiewicz, S. Agouram, G. Mínguez Espallargas, H. J. Bolink, R. E. Galian, and J. Pérez-Prieto, "Non-template Synthesis of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Perovskite Nanoparticles," *Journal of the American Chemical Society*, vol. 136, pp. 850–853, jan 2014.
5. L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh, and M. V. Kovalenko, "Nanocrystals of Cesium Lead Halide Perovskites (CsPbX_3 , $\text{X} = \text{Cl}, \text{Br}, \text{and I}$): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut," *Nano Letters*, vol. 15, pp. 3692–3696, jun 2015.

Bibliography

6. L. Polavarapu, Q. Zhang, and R. Krahne, "Nanoscale & Nanoscale Advances joint themed collection on halide perovskite nanocrystals," *Nanoscale*, vol. 11, no. 18, pp. 8648–8650, 2019.
7. A. Swarnkar, A. R. Marshall, E. M. Sanhira, B. D. Chernomordik, D. T. Moore, J. A. Christians, T. Chakrabarti, and J. M. Luther, "Quantum dot-induced phase stabilization of α -CsPbI₃ perovskite for high-efficiency photovoltaics," *Science*, vol. 354, pp. 92–95, oct 2016.
8. R. I.-r. Bt and B. T. S. Broadcasting, "Image parameter values for high dynamic range television for use in production and international programme exchange," tech. rep., 2018.
9. J. Shamsi, A. S. Urban, M. Imran, L. De Trizio, and L. Manna, "Metal Halide Perovskite Nanocrystals: Synthesis, Post-Synthesis Modifications, and Their Optical Properties," *Chemical Reviews*, vol. 119, pp. 3296–3348, mar 2019.
10. M. Prato and F. Di Stasio, "Lead Halide Perovskite Nanocrystals - A New Promise for Light Emitting Devices," *LED Professional*, pp. 46 – 53, may 2017.
11. Y. Zhou, J. Chen, O. M. Bakr, and H.-T. Sun, "Metal-Doped Lead Halide Perovskites: Synthesis, Properties, and Optoelectronic Applications," *Chemistry of Materials*, vol. 30, pp. 6589–6613, oct 2018.
12. M. Saliba, T. Matsui, K. Domanski, J.-Y. Seo, A. Ummadisingu, S. M. Zakeeruddin, J.-P. Correa-Baena, W. R. Tress, A. Abate, A. Hagfeldt, and M. Gratzel, "Incorporation of rubidium cations into perovskite solar cells improves photovoltaic performance," *Science*, vol. 354, pp. 206–209, oct 2016.
13. A. D. Jodlowski, C. Roldán-Carmona, G. Grancini, M. Salado, M. Ralaifarisoa, S. Ahmad, N. Koch, L. Camacho, G. de Miguel, and M. K. Nazeeruddin, "Large guanidinium cation mixed with methylammonium in lead iodide perovskites for 19% efficient solar cells," *Nature Energy*, vol. 2, pp. 972–979, dec 2017.

14. G. E. Eperon, C. E. Beck, and H. J. Snaith, "Cation exchange for thin film lead iodide perovskite interconversion," *Materials Horizons*, vol. 3, no. 1, pp. 63–71, 2016.
15. Y.-M. Xie, B. Yu, C. Ma, X. Xu, Y. Cheng, S. Yuan, Z.-K. Wang, H. T. Chandran, C.-S. Lee, L.-S. Liao, and S.-W. Tsang, "Direct observation of cation-exchange in liquid-to-solid phase transformation in $\text{FA}_{1-x}\text{MA}_x\text{PbI}_3$ based perovskite solar cells," *Journal of Materials Chemistry A*, vol. 6, no. 19, pp. 9081–9088, 2018.
16. G. Nedelcu, L. Protesescu, S. Yakunin, M. I. Bodnarchuk, M. J. Grotevent, and M. V. Kovalenko, "Fast Anion-Exchange in Highly Luminescent Nanocrystals of Cesium Lead Halide Perovskites (CsPbX_3 , $X = \text{Cl, Br, I}$)," *Nano Letters*, vol. 15, pp. 5635–5640, aug 2015.
17. Q. A. Akkerman, V. D'Innocenzo, S. Accornero, A. Scarpellini, A. Petrozza, M. Prato, and L. Manna, "Tuning the Optical Properties of Cesium Lead Halide Perovskite Nanocrystals by Anion Exchange Reactions," *Journal of the American Chemical Society*, vol. 137, pp. 10276–10281, aug 2015.
18. T. Zhang, G. Li, Y. Chang, X. Wang, B. Zhang, H. Mou, and Y. Jiang, "Full-spectra hyperfluorescence cesium lead halide perovskite nanocrystals obtained by efficient halogen anion exchange using zinc halogenide salts," *CrystEngComm*, vol. 19, no. 8, pp. 1165–1171, 2017.
19. S. Fang, G. Li, Y. Lu, and L. Li, "Highly Luminescent CsPbX_3 ($X=\text{Cl, Br, I}$) Nanocrystals Achieved by a Rapid Anion Exchange at Room Temperature," *Chemistry - A European Journal*, vol. 24, pp. 1898–1904, feb 2018.
20. L. De Trizio and L. Manna, "Forging Colloidal Nanostructures via Cation Exchange Reactions," *Chemical Reviews*, vol. 116, pp. 10852–10887, sep 2016.
21. V. K. Ravi, R. A. Scheidt, A. Nag, M. Kuno, and P. V. Kamat, "To Exchange or Not to Exchange . Suppressing Anion Exchange in Cesium Lead Halide Perovskites

Bibliography

- with PbSO_4 –Oleate Capping,” *ACS Energy Letters*, vol. 3, pp. 1049–1055, apr 2018.
22. J. S. Manser, J. A. Christians, and P. V. Kamat, “Intriguing Optoelectronic Properties of Metal Halide Perovskites,” *Chemical Reviews*, vol. 116, pp. 12956–13008, nov 2016.
23. W. Li, Z. Wang, F. Deschler, S. Gao, R. H. Friend, and A. K. Cheetham, “Chemically diverse and multifunctional hybrid organic–inorganic perovskites,” *Nature Reviews Materials*, vol. 2, p. 16099, mar 2017.
24. Q. A. Akkerman, G. Rainò, M. V. Kovalenko, and L. Manna, “Genesis, challenges and opportunities for colloidal lead halide perovskite nanocrystals,” *Nature Materials*, vol. 17, pp. 394–405, may 2018.
25. L. Polavarapu, B. Nickel, J. Feldmann, and A. S. Urban, “Advances in Quantum-Confinement Perovskite Nanocrystals for Optoelectronics,” *Adv. Energy Mater.*, vol. 7, p. 1700267, 2017.
26. N. Wang, W. Liu, and Q. Zhang, “Perovskite-Based Nanocrystals: Perovskite-Based Nanocrystals: Synthesis and Applications beyond Solar Cells,” *Small Methods*, vol. 2, p. 1800035, jun 2018.
27. H.-C. Wang, Z. Bao, H.-Y. Tsai, A.-C. Tang, and R.-S. Liu, “Perovskite Quantum Dots and Their Application in Light-Emitting Diodes,” *Small*, vol. 14, p. 1702433, jan 2018.
28. Y. Wang and H. Sun, “All-Inorganic Metal Halide Perovskite Nanostructures: From Photophysics to Light-Emitting Applications,” *Small Methods*, vol. 2, p. 1700252, jan 2018.
29. D. Yang, X. Li, and H. Zeng, “Surface Chemistry of All Inorganic Halide Perovskite Nanocrystals: Passivation Mechanism and Stability,” *Advanced Materials Interfaces*, vol. 5, p. 1701662, apr 2018.

30. Q. Zhang and Y. Yin, "All-Inorganic Metal Halide Perovskite Nanocrystals: Opportunities and Challenges," *ACS Central Science*, vol. 4, pp. 668–679, jun 2018.
31. P. A. Cox, *The electronic structure and chemistry of solids*, vol. 231. Oxford University Press, 1987.
32. P. W. Atkins, T. Overton, J. Rourke, M. Weller, and F. Armstrong, *Shriver & Atkins' inorganic chemistry*. Oxford; New York: Oxford University Press, 5 ed., 2010.
33. L. M. Herz, "Charge-Carrier Dynamics in Organic-Inorganic Metal Halide Perovskites," *Annual Review of Physical Chemistry*, vol. 67, pp. 65–89, may 2016.
34. Y. Fang, H. Wei, Q. Dong, and J. Huang, "Quantification of re-absorption and re-emission processes to determine photon recycling efficiency in perovskite single crystals," *Nature Communications*, vol. 8, p. 14417, apr 2017.
35. Q. Wei, B. Du, B. Wu, J. Guo, M. jie Li, J. Fu, Z. Zhang, J. Yu, T. Hou, G. Xing, T. C. Sum, and W. Huang, "Two-Photon Optical Properties in Individual Organic-Inorganic Perovskite Microplates," *Advanced Optical Materials*, vol. 5, p. 1700809, dec 2017.
36. T. Yamada, Y. Yamada, Y. Nakaike, A. Wakamiya, and Y. Kanemitsu, "Photon Emission and Reabsorption Processes in $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Single Crystals Revealed by Time-Resolved Two-Photon-Excitation Photoluminescence Microscopy," *Physical Review Applied*, vol. 7, p. 014001, jan 2017.
37. J. M. Richter, M. Abdi-Jalebi, A. Sadhanala, M. Tabachnyk, J. P. Rivett, L. M. Pazos-Outón, K. C. Gödel, M. Price, F. Deschler, and R. H. Friend, "Enhancing photoluminescence yields in lead halide perovskites by photon recycling and light out-coupling," *Nature Communications*, vol. 7, p. 13941, dec 2016.

Bibliography

38. B. Wenger, P. K. Nayak, X. Wen, S. V. Kesava, N. K. Noel, and H. J. Snaith, "Consolidation of the optoelectronic properties of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite single crystals," *Nature Communications*, vol. 8, p. 590, dec 2017.
39. H. Diab, C. Arnold, F. Lédée, G. Trippé-Allard, G. Delport, C. Vilar, F. Bretenaker, J. Barjon, J.-S. Lauret, E. Deleporte, and D. Garrot, "Impact of Reabsorption on the Emission Spectra and Recombination Dynamics of Hybrid Perovskite Single Crystals," *The Journal of Physical Chemistry Letters*, vol. 8, pp. 2977–2983, jul 2017.
40. Y. Yamada, T. Yamada, L. Q. Phuong, N. Maruyama, H. Nishimura, A. Wakamiya, Y. Murata, and Y. Kanemitsu, "Dynamic Optical Properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$ Single Crystals As Revealed by One- and Two-Photon Excited Photoluminescence Measurements," *Journal of the American Chemical Society*, vol. 137, pp. 10456–10459, aug 2015.
41. T. Yamada, Y. Yamada, H. Nishimura, Y. Nakaike, A. Wakamiya, Y. Murata, and Y. Kanemitsu, "Fast Free-Carrier Diffusion in $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Single Crystals Revealed by Time-Resolved One- and Two-Photon Excitation Photoluminescence Spectroscopy," *Advanced Electronic Materials*, vol. 2, p. 1500290, mar 2016.
42. T. W. Crothers, R. L. Milot, J. B. Patel, E. S. Parrott, J. Schlipf, P. Müller-Buschbaum, M. B. Johnston, and L. M. Herz, "Photon Reabsorption Masks Intrinsic Bimolecular Charge-Carrier Recombination in $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite," *Nano Letters*, vol. 17, pp. 5782–5789, sep 2017.
43. A. P. Alivisatos, "Perspectives on the Physical Chemistry of Semiconductor Nanocrystals," *The Journal of Physical Chemistry*, vol. 100, pp. 13226–13239, jan 1996.
44. A. L. Efros and M. Rosen, "The Electronic Structure of Semiconductor Nanocrystals," *Annual Review of Materials Science*, vol. 30, pp. 475–521, aug 2000.

45. P. Kambhampati, "Fundamentals of the Quantum Confinement Effect," in *Handbook of Luminescent Semiconductor Materials* (L. Bergman and J. L. McHale, eds.), pp. 279–306, CRC Press, 2011.
46. F. T. Rabouw and C. de Mello Donega, "Excited-State Dynamics in Colloidal Semiconductor Nanocrystals," *Topics in Current Chemistry*, vol. 374, p. 58, aug 2016.
47. Z. Yang, A. Surrente, K. Galkowski, N. Bruyant, D. K. Maude, A. A. Haghighirad, H. J. Snaith, P. Plochocka, and R. J. Nicholas, "Unraveling the Exciton Binding Energy and the Dielectric Constant in Single-Crystal Methylammonium Lead Triiodide Perovskite," *The Journal of Physical Chemistry Letters*, vol. 8, pp. 1851–1855, apr 2017.
48. J. Butkus, P. Vashishtha, K. Chen, J. K. Gallaher, S. K. K. Prasad, D. Z. Metin, G. Laufersky, N. Gaston, J. E. Halpert, and J. M. Hodgkiss, "The Evolution of Quantum Confinement in CsPbBr₃ Perovskite Nanocrystals," *Chemistry of Materials*, vol. 29, pp. 3644–3652, apr 2017.
49. P. Cottingham and R. L. Brutchey, "On the crystal structure of colloiddally prepared CsPbBr₃ quantum dots," *Chemical Communications*, vol. 52, no. 30, pp. 5246–5249, 2016.
50. D. Norris, "Electronic Structure in Semiconductor Nanocrystals," in *Nanocrystal Quantum Dots, Second Edition*, pp. 63–96, CRC Press, apr 2010.
51. A. L. Efros, M. Rosen, M. Kuno, M. Nirmal, D. J. Norris, and M. Bawendi, "Band-edge exciton in quantum dots of semiconductors with a degenerate valence band: Dark and bright exciton states," *Physical Review B*, vol. 54, pp. 4843–4856, aug 1996.
52. D. J. Norris, A. L. Efros, M. Rosen, and M. G. Bawendi, "Size dependence of exciton fine structure in CdSe quantum dots," *Physical Review B*, vol. 53, pp. 16347–16354, jun 1996.

Bibliography

53. D. J. Norris and M. G. Bawendi, "Measurement and assignment of the size-dependent optical spectrum in CdSe quantum dots," *Physical Review B*, vol. 53, pp. 16338–16346, jun 1996.
54. D. A. B. Miller, "Optical physics of quantum wells," " *Quantum Dynamics of Simple Systems*," ed. G.-L. Oppo, SM Barnett, E. Riis, and M. Wilkinson (Institute of Physics, London, 1996), pp. 239–266, 1994.
55. J. Maes, L. Balcaen, E. Drijvers, Q. Zhao, J. De Roo, A. Vantomme, F. Vanhaecke, P. Geiregat, and Z. Hens, "Light Absorption Coefficient of CsPbBr₃ Perovskite Nanocrystals," *The Journal of Physical Chemistry Letters*, vol. 9, pp. 3093–3097, jun 2018.
56. E. M. Hutter, R. J. Sutton, S. Chandrashekar, M. Abdi-Jalebi, S. D. Stranks, H. J. Snaith, and T. J. Savenije, "Vapour-Deposited Cesium Lead Iodide Perovskites: Microsecond Charge Carrier Lifetimes and Enhanced Photovoltaic Performance," *ACS Energy Letters*, vol. 2, pp. 1901–1908, aug 2017.
57. H.-H. Fang, L. Protesescu, D. M. Balazs, S. Adjokatse, M. V. Kovalenko, and M. A. Loi, "Exciton Recombination in Formamidinium Lead Triiodide: Nanocrystals versus Thin Films," *Small*, vol. 13, p. 1700673, aug 2017.
58. M. C. Brennan, J. E. Herr, T. S. Nguyen-Beck, J. Zinna, S. Draguta, S. Rouvimov, J. Parkhill, and M. Kuno, "Origin of the Size-Dependent Stokes Shift in CsPbBr₃ Perovskite Nanocrystals," *Journal of the American Chemical Society*, vol. 139, pp. 12201–12208, sep 2017.
59. Z. Gan, W. Chen, L. Yuan, G. Cao, C. Zhou, S. Huang, X. Wen, and B. Jia, "External stokes shift of perovskite nanocrystals enlarged by photon recycling," *Applied Physics Letters*, vol. 114, p. 011906, jan 2019.
60. N. J. Davis, F. J. De La Peña, M. Tabachnyk, J. M. Richter, R. D. Lamboll, E. P. Booker, F. Wisnivesky Rocca Rivarola, J. T. Griffiths, C. Ducati, S. M. Menke, F. Deschler, and N. C. Greenham, "Photon Reabsorption in Mixed

- CsPbCl₃:CsPbI₃ Perovskite Nanocrystal Films for Light-Emitting Diodes," *Journal of Physical Chemistry C*, vol. 121, pp. 3790–3796, feb 2017.
61. H. Huang, M. I. Bodnarchuk, S. V. Kershaw, M. V. Kovalenko, and A. L. Rogach, "Lead Halide Perovskite Nanocrystals in the Research Spotlight: Stability and Defect Tolerance," *ACS Energy Letters*, vol. 2, pp. 2071–2083, sep 2017.
62. H. Zhu, K. Miyata, Y. Fu, J. Wang, P. P. Joshi, D. Niesner, K. W. Williams, S. Jin, and X.-Y. Zhu, "Screening in crystalline liquids protects energetic carriers in hybrid perovskites," *Science*, vol. 353, pp. 1409–1413, sep 2016.
63. A. A. Bakulin, O. Selig, H. J. Bakker, Y. L. Rezus, C. Müller, T. Glaser, R. Lovrincic, Z. Sun, Z. Chen, A. Walsh, J. M. Frost, and T. L. C. Jansen, "Real-Time Observation of Organic Cation Reorientation in Methylammonium Lead Iodide Perovskites," *The Journal of Physical Chemistry Letters*, vol. 6, pp. 3663–3669, sep 2015.
64. J. Kang and L.-W. Wang, "High Defect Tolerance in Lead Halide Perovskite CsPbBr₃," *The Journal of Physical Chemistry Letters*, vol. 8, pp. 489–493, jan 2017.
65. R. E. Brandt, V. Stevanović, D. S. Ginley, and T. Buonassisi, "Identifying defect-tolerant semiconductors with high minority-carrier lifetimes: beyond hybrid lead halide perovskites," *MRS Communications*, vol. 5, pp. 265–275, jun 2015.
66. N.-G. Park, "Perovskite solar cells: an emerging photovoltaic technology," *Mater. Today (Oxford, U. K.)*, vol. 18, no. 2, pp. 65–72, 2015.
67. S. P. Senanayak, B. Yang, T. H. Thomas, N. Giesbrecht, W. Huang, E. Gann, B. Nair, K. Goedel, S. Guha, X. Moya, C. R. McNeill, P. Docampo, A. Sadhanala, R. H. Friend, and H. Sirringhaus, "Understanding charge transport in lead iodide perovskite thin-film field-effect transistors," *Science Advances*, vol. 3, p. e1601935, jan 2017.

Bibliography

68. C. Gehrman and D. A. Egger, "Dynamic shortening of disorder potentials in anharmonic halide perovskites," *Nature Communications*, vol. 10, p. 3141, dec 2019.
69. J. Chang and E. R. Waclawik, "Colloidal semiconductor nanocrystals: Controlled synthesis and surface chemistry in organic media," *RSC Advances*, vol. 4, no. 45, pp. 23505–23527, 2014.
70. L. Protesescu, S. Yakunin, O. Nazarenko, D. N. Dirin, and M. V. Kovalenko, "Low-Cost Synthesis of Highly Luminescent Colloidal Lead Halide Perovskite Nanocrystals by Wet Ball Milling," *ACS Applied Nano Materials*, vol. 1, pp. 1300–1308, mar 2018.
71. D. Yang, M. Cao, Q. Zhong, P. Li, X. Zhang, and Q. Zhang, "All-inorganic cesium lead halide perovskite nanocrystals: synthesis, surface engineering and applications," *Journal of Materials Chemistry C*, vol. 7, no. 4, pp. 757–789, 2019.
72. H. Huang, L. Polavarapu, J. A. Sichert, A. S. Susa, A. S. Urban, and A. L. Rogach, "Colloidal lead halide perovskite nanocrystals: synthesis, optical properties and applications," *NPG Asia Materials*, vol. 8, pp. e328–e328, nov 2016.
73. H. Kasai, H. S. Nalwa, H. Oikawa, S. Okada, H. Matsuda, N. Minami, A. Kakuta, K. Ono, A. Mukoh, and H. Nakanishi, "A Novel Preparation Method of Organic Microcrystals," *Japanese Journal of Applied Physics*, vol. 31, pp. L1132–L1134, aug 1992.
74. G. C. Papavassiliou, G. Pagona, N. Karousis, G. A. Mousdis, I. Koutselas, and A. Vassilakopoulou, "Nanocrystalline/microcrystalline materials based on lead-halide units," *Journal of Materials Chemistry*, vol. 22, no. 17, p. 8271, 2012.

-
75. Y. Zhao, X. Xu, and X. You, "Colloidal Organometal Halide Perovskite ($\text{MAPbBr}_x\text{I}_{3-x}$, $0 \leq x \leq 3$) Quantum Dots: Controllable Synthesis and Tunable Photoluminescence," *Scientific Reports*, vol. 6, p. 35931, dec 2016.
76. I. Levchuk, P. Herre, M. Brandl, A. Osvet, R. Hock, W. Peukert, P. Schweizer, E. Spiecker, M. Batentschuk, and C. J. Brabec, "Ligand-assisted thickness tailoring of highly luminescent colloidal $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{Br}$ and I) perovskite nanoplatelets," *Chemical Communications*, vol. 53, no. 1, pp. 244–247, 2017.
77. M. C. Weidman, M. Seitz, S. D. Stranks, and W. A. Tisdale, "Highly Tunable Colloidal Perovskite Nanoplatelets through Variable Cation, Metal, and Halide Composition," *ACS Nano*, vol. 10, pp. 7830–7839, aug 2016.
78. I. Levchuk, A. Osvet, X. Tang, M. Brandl, J. D. Perea, F. Hoegl, G. J. Matt, R. Hock, M. Batentschuk, and C. J. Brabec, "Brightly Luminescent and Color-Tunable Formamidinium Lead Halide Perovskite FAPbX_3 ($\text{X} = \text{Cl}$, Br , I) Colloidal Nanocrystals," *Nano Letters*, vol. 17, pp. 2765–2770, may 2017.
79. D. N. Minh, J. Kim, J. Hyon, J. H. Sim, H. H. Sowlih, C. Seo, J. Nam, S. Eom, S. Suk, S. Lee, E. Kim, and Y. Kang, "Room-Temperature Synthesis of Widely Tunable Formamidinium Lead Halide Perovskite Nanocrystals," *Chemistry of Materials*, vol. 29, pp. 5713–5719, jul 2017.
80. X. Li, Y. Wu, S. Zhang, B. Cai, Y. Gu, J. Song, and H. Zeng, " CsPbX_3 Quantum Dots for Lighting and Displays: Room-Temperature Synthesis, Photoluminescence Superiorities, Underlying Origins and White Light-Emitting Diodes," *Advanced Functional Materials*, vol. 26, pp. 2435–2445, apr 2016.
81. S. Seth and A. Samanta, "A Facile Methodology for Engineering the Morphology of CsPbX_3 Perovskite Nanocrystals under Ambient Condition," *Scientific Reports*, vol. 6, p. 37693, dec 2016.
-

Bibliography

82. J. Shamsi, P. Rastogi, V. Caligiuri, A. L. Abdelhady, D. Spirito, L. Manna, and R. Krahne, "Bright-Emitting Perovskite Films by Large-Scale Synthesis and Photoinduced Solid-State Transformation of CsPbBr₃ Nanoplatelets," *ACS Nano*, vol. 11, pp. 10206–10213, oct 2017.
83. S. Wei, Y. Yang, X. Kang, L. Wang, L. Huang, and D. Pan, "Room-temperature and gram-scale synthesis of CsPbX₃ (X = Cl, Br, I) perovskite nanocrystals with 50–85 % photoluminescence quantum yields," *Chemical Communications*, vol. 52, no. 45, pp. 7265–7268, 2016.
84. C. B. Murray, D. J. Norris, and M. G. Bawendi, "Synthesis and characterization of nearly monodisperse CdE (E = sulfur, selenium, tellurium) semiconductor nanocrystallites," *Journal of the American Chemical Society*, vol. 115, pp. 8706–8715, sep 1993.
85. Y. Yin and A. P. Alivisatos, "Colloidal nanocrystal synthesis and the organic–inorganic interface," *Nature*, vol. 437, pp. 664–670, sep 2005.
86. G. H. Carey, A. L. Abdelhady, Z. Ning, S. M. Thon, O. M. Bakr, and E. H. Sargent, "Colloidal Quantum Dot Solar Cells," *Chemical Reviews*, vol. 115, pp. 12732–12763, dec 2015.
87. V. K. LaMer and R. H. Dinegar, "Theory, Production and Mechanism of Formation of Monodispersed Hydrosols," *Journal of the American Chemical Society*, vol. 72, pp. 4847–4854, nov 1950.
88. N. T. K. Thanh, N. Maclean, and S. Mahiddine, "Mechanisms of Nucleation and Growth of Nanoparticles in Solution," *Chemical Reviews*, vol. 114, pp. 7610–7630, aug 2014.
89. L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Bertolotti, N. Masciocchi, A. Guagliardi, and M. V. Kovalenko, "Monodisperse Formamidinium Lead Bromide Nanocrystals with Bright and Stable Green Photoluminescence," *Journal of the American Chemical Society*, vol. 138, pp. 14202–14205, nov 2016.

90. L. Protesescu, S. Yakunin, S. Kumar, J. Bär, F. Bertolotti, N. Masciocchi, A. Guagliardi, M. Grotevent, I. Shorubalko, M. I. Bodnarchuk, C.-J. Shih, and M. V. Kovalenko, "Dismantling the "Red Wall" of Colloidal Perovskites: Highly Luminescent Formamidinium and Formamidinium–Cesium Lead Iodide Nanocrystals," *ACS Nano*, vol. 11, pp. 3119–3134, mar 2017.
91. A. Wang, Y. Guo, F. Muhammad, and Z. Deng, "Controlled Synthesis of Lead-Free Cesium Tin Halide Perovskite Cubic Nanocages with High Stability," *Chemistry of Materials*, vol. 29, pp. 6493–6501, aug 2017.
92. O. Vybornyi, S. Yakunin, and M. V. Kovalenko, "Polar-solvent-free colloidal synthesis of highly luminescent alkylammonium lead halide perovskite nanocrystals," *Nanoscale*, vol. 8, no. 12, pp. 6278–6283, 2016.
93. C. B. Murray, C. R. Kagan, and M. G. Bawendi, "Synthesis and Characterization of Monodisperse Nanocrystals and Close-Packed Nanocrystal Assemblies," *Annual Review of Materials Science*, vol. 30, pp. 545–610, aug 2000.
94. I. Lignos, S. Stavrakis, G. Nedelcu, L. Protesescu, A. J. DeMello, and M. V. Kovalenko, "Synthesis of Cesium Lead Halide Perovskite Nanocrystals in a Droplet-Based Microfluidic Platform: Fast Parametric Space Mapping," *Nano Letters*, vol. 16, pp. 1869–1877, mar 2016.
95. R. M. Maceiczky, K. Dümbgen, I. Lignos, L. Protesescu, M. V. Kovalenko, and A. J. DeMello, "Microfluidic Reactors Provide Preparative and Mechanistic Insights into the Synthesis of Formamidinium Lead Halide Perovskite Nanocrystals," *Chemistry of Materials*, vol. 29, pp. 8433–8439, oct 2017.
96. M. Koolyk, D. Amgar, S. Aharon, and L. Etgar, "Kinetics of cesium lead halide perovskite nanoparticle growth; focusing and de-focusing of size distribution," *Nanoscale*, vol. 8, no. 12, pp. 6403–6409, 2016.

Bibliography

97. T. Udayabhaskararao, M. Kazes, L. Houben, H. Lin, and D. Oron, "Nucleation, Growth, and Structural Transformations of Perovskite Nanocrystals," *Chemistry of Materials*, vol. 29, pp. 1302–1308, feb 2017.
98. Z. Dang, J. Shamsi, Q. A. Akkerman, M. Imran, G. Bertoni, R. Brescia, and L. Manna, "Low-Temperature Electron Beam-Induced Transformations of Cesium Lead Halide Perovskite Nanocrystals," *ACS Omega*, vol. 2, pp. 5660–5665, sep 2017.
99. J. W. Mullin, *Crystallization*. Elsevier, 2001.
100. X. Peng, "Mechanisms for the Shape-Control and Shape-Evolution of Colloidal Semiconductor Nanocrystals," *Advanced Materials*, vol. 15, pp. 459–463, mar 2003.
101. J. H. Yu, J. Joo, H. M. Park, S.-I. Baik, Y. W. Kim, S. C. Kim, and T. Hyeon, "Synthesis of Quantum-Sized Cubic ZnS Nanorods by the Oriented Attachment Mechanism," *Journal of the American Chemical Society*, vol. 127, pp. 5662–5670, apr 2005.
102. K.-S. Cho, D. V. Talapin, W. Gaschler, and C. B. Murray, "Designing PbSe Nanowires and Nanorings through Oriented Attachment of Nanoparticles," *Journal of the American Chemical Society*, vol. 127, pp. 7140–7147, may 2005.
103. Y. Bekenstein, B. A. Koscher, S. W. Eaton, P. Yang, and A. P. Alivisatos, "Highly Luminescent Colloidal Nanoplates of Perovskite Cesium Lead Halide and Their Oriented Assemblies," *Journal of the American Chemical Society*, vol. 137, pp. 16008–16011, dec 2015.
104. D. Zhang, S. W. Eaton, Y. Yu, L. Dou, and P. Yang, "Solution-Phase Synthesis of Cesium Lead Halide Perovskite Nanowires," *Journal of the American Chemical Society*, vol. 137, pp. 9230–9233, jul 2015.

105. A. Pan, B. He, X. Fan, Z. Liu, J. J. Urban, A. P. Alivisatos, L. He, and Y. Liu, "Insight into the Ligand-Mediated Synthesis of Colloidal CsPbBr₃ Perovskite Nanocrystals: The Role of Organic Acid, Base, and Cesium Precursors," *ACS Nano*, vol. 10, pp. 7943–7954, aug 2016.
106. G. Almeida, L. Goldoni, Q. Akkerman, Z. Dang, A. H. Khan, S. Marras, I. Moreels, and L. Manna, "Role of Acid–Base Equilibria in the Size, Shape, and Phase Control of Cesium Lead Bromide Nanocrystals," *ACS Nano*, vol. 12, pp. 1704–1711, feb 2018.
107. S. Sun, D. Yuan, Y. Xu, A. Wang, and Z. Deng, "Ligand-Mediated Synthesis of Shape-Controlled Cesium Lead Halide Perovskite Nanocrystals via Reprecipitation Process at Room Temperature," *ACS Nano*, vol. 10, pp. 3648–3657, mar 2016.
108. J. A. Sichert, Y. Tong, N. Mutz, M. Vollmer, S. Fischer, K. Z. Milowska, R. García Cortadella, B. Nickel, C. Cardenas-Daw, J. K. Stolarczyk, A. S. Urban, and J. Feldmann, "Quantum Size Effect in Organometal Halide Perovskite Nanoplatelets," *Nano Letters*, vol. 15, pp. 6521–6527, oct 2015.
109. S. Kumar, J. Jagielski, S. Yakunin, P. Rice, Y.-C. Chiu, M. Wang, G. Nedelcu, Y. Kim, S. Lin, E. J. G. Santos, M. V. Kovalenko, and C.-J. Shih, "Efficient Blue Electroluminescence Using Quantum-Confined Two-Dimensional Perovskites," *ACS Nano*, vol. 10, pp. 9720–9729, oct 2016.
110. B. Luo, Y.-C. Pu, S. A. Lindley, Y. Yang, L. Lu, Y. Li, X. Li, and J. Z. Zhang, "Organolead Halide Perovskite Nanocrystals: Branched Capping Ligands Control Crystal Size and Stability," *Angewandte Chemie International Edition*, vol. 55, pp. 8864–8868, jul 2016.
111. J. Cho, Y.-H. Choi, T. E. O'Loughlin, L. De Jesus, and S. Banerjee, "Ligand-Mediated Modulation of Layer Thicknesses of Perovskite Methylammonium Lead Bromide Nanoplatelets," *Chemistry of Materials*, vol. 28, pp. 6909–6916, oct 2016.

Bibliography

112. A. Kirakosyan, J. Kim, S. W. Lee, I. Swathi, S.-G. Yoon, and J. Choi, "Optical Properties of Colloidal $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Nanocrystals by Controlled Growth of Lateral Dimension," *Crystal Growth & Design*, vol. 17, pp. 794–799, feb 2017.
113. M. A. Boles, D. Ling, T. Hyeon, and D. V. Talapin, "The surface science of nanocrystals," *Nature Materials*, vol. 15, pp. 141–153, feb 2016.
114. J. De Roo, M. Ibáñez, P. Geiregat, G. Nedelcu, W. Walravens, J. Maes, J. C. Martins, I. Van Driessche, M. V. Kovalenko, and Z. Hens, "Highly Dynamic Ligand Binding and Light Absorption Coefficient of Cesium Lead Bromide Perovskite Nanocrystals," *ACS Nano*, vol. 10, pp. 2071–2081, feb 2016.
115. J. De Roo, K. De Keukeleere, Z. Hens, and I. Van Driessche, "From ligands to binding motifs and beyond; The enhanced versatility of nanocrystal surfaces," *Dalton Transactions*, vol. 45, no. 34, pp. 13277–13283, 2016.
116. C. Giansante and I. Infante, "Surface Traps in Colloidal Quantum Dots: A Combined Experimental and Theoretical Perspective," *The Journal of Physical Chemistry Letters*, vol. 8, pp. 5209–5215, oct 2017.
117. S. ten Brinck and I. Infante, "Surface Termination, Morphology, and Bright Photoluminescence of Cesium Lead Halide Perovskite Nanocrystals," *ACS Energy Letters*, vol. 1, pp. 1266–1272, dec 2016.
118. M. I. Bodnarchuk, S. C. Boehme, S. ten Brinck, C. Bernasconi, Y. Shynkarenko, F. Krieg, R. Widmer, B. Aeschlimann, D. Günther, M. V. Kovalenko, and I. Infante, "Rationalizing and Controlling the Surface Structure and Electronic Passivation of Cesium Lead Halide Nanocrystals," *ACS Energy Letters*, vol. 4, pp. 63–74, jan 2019.
119. F. Krieg, S. T. Ochsenbein, S. Yakunin, S. ten Brinck, P. Aellen, A. Süess, B. Clerc, D. Guggisberg, O. Nazarenko, Y. Shynkarenko, S. Kumar, C.-J. Shih, I. Infante, and M. V. Kovalenko, "Colloidal CsPbX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) Nanocrystals

- 2.0: Zwitterionic Capping Ligands for Improved Durability and Stability," *ACS Energy Letters*, vol. 3, pp. 641–646, mar 2018.
120. B. A. Koscher, J. K. Swabeck, N. D. Bronstein, and A. P. Alivisatos, "Essentially Trap-Free CsPbBr₃ Colloidal Nanocrystals by Postsynthetic Thiocyanate Surface Treatment," *Journal of the American Chemical Society*, vol. 139, pp. 6566–6569, may 2017.
121. J. Y. Woo, Y. Kim, J. Bae, T. G. Kim, J. W. Kim, D. C. Lee, and S. Jeong, "Highly Stable Cesium Lead Halide Perovskite Nanocrystals through in Situ Lead Halide Inorganic Passivation," *Chemistry of Materials*, vol. 29, pp. 7088–7092, sep 2017.
122. D. P. Nenon, K. Pressler, J. Kang, B. A. Koscher, J. H. Olshansky, W. T. Osowiecki, M. A. Koc, L.-W. Wang, and A. P. Alivisatos, "Design Principles for Trap-Free CsPbX₃ Nanocrystals: Enumerating and Eliminating Surface Halide Vacancies with Softer Lewis Bases," *Journal of the American Chemical Society*, vol. 140, pp. 17760–17772, dec 2018.
123. S. Masi, S. Colella, A. Listorti, V. Roiati, A. Liscio, V. Palermo, A. Rizzo, and G. Gigli, "Growing perovskite into polymers for easy-processable optoelectronic devices," *Scientific Reports*, vol. 5, p. 7725, jul 2015.
124. H. C. Wang, S. Y. Lin, A. C. Tang, B. P. Singh, H. C. Tong, C. Y. Chen, Y. C. Lee, T. L. Tsai, and R. S. Liu, "Mesoporous Silica Particles Integrated with All-Inorganic CsPbBr₃ Perovskite Quantum-Dot Nanocomposites (MP-PQDs) with High Stability and Wide Color Gamut Used for Backlight Display," *Angewandte Chemie - International Edition*, vol. 55, no. 28, pp. 7924–7929, 2016.
125. H. Huang, B. Chen, Z. Wang, T. F. Hung, A. S. Susa, H. Zhong, and A. L. Rogach, "Water resistant CsPbX₃ nanocrystals coated with polyhedral oligomeric silsesquioxane and their use as solid state luminophores in all-perovskite white light-emitting devices," *Chemical Science*, vol. 7, no. 9, pp. 5699–5703, 2016.

Bibliography

126. S. Huang, Z. Li, L. Kong, N. Zhu, A. Shan, and L. Li, "Enhancing the Stability of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Quantum Dots by Embedding in Silica Spheres Derived from Tetramethyl Orthosilicate in "Waterless" Toluene," *Journal of the American Chemical Society*, vol. 138, pp. 5749–5752, may 2016.
127. A. Loiudice, S. Saris, E. Oveisi, D. T. L. Alexander, and R. Buonsanti, "CsPbBr₃ QD/ AlO_x Inorganic Nanocomposites with Exceptional Stability in Water, Light, and Heat," *Angewandte Chemie International Edition*, vol. 56, pp. 10696–10701, aug 2017.
128. J. Pan, Y. Shang, J. Yin, M. De Bastiani, W. Peng, I. Dursun, L. Sinatra, A. M. El-Zohry, M. N. Hedhili, A.-H. Emwas, O. F. Mohammed, Z. Ning, and O. M. Bakr, "Bidentate Ligand-Passivated CsPbI₃ Perovskite Nanocrystals for Stable Near-Unity Photoluminescence Quantum Yield and Efficient Red Light-Emitting Diodes," *Journal of the American Chemical Society*, vol. 140, pp. 562–565, jan 2018.
129. Y.-H. Suh, T. Kim, J. W. Choi, C.-L. Lee, and J. Park, "High-Performance CsPbX₃ Perovskite Quantum-Dot Light-Emitting Devices via Solid-State Ligand Exchange," *ACS Applied Nano Materials*, vol. 1, pp. 488–496, feb 2018.
130. F. Palazon, G. Almeida, Q. A. Akkerman, L. De Trizio, Z. Dang, M. Prato, and L. Manna, "Changing the Dimensionality of Cesium Lead Bromide Nanocrystals by Reversible Post-Synthesis Transformations with Amines," *Chemistry of Materials*, vol. 29, no. 10, p. acs.chemmater.7b00895, 2017.
131. T. Udayabhaskararao, L. Houben, H. Cohen, M. Menahem, I. Pinkas, L. Avram, T. Wolf, A. Teitelboim, M. Leskes, O. Yaffe, D. Oron, and M. Kazes, "A Mechanistic Study of Phase Transformation in Perovskite Nanocrystals Driven by Ligand Passivation," *Chemistry of Materials*, vol. 30, pp. 84–93, jan 2018.

-
132. X. Chen, D. Chen, J. Li, G. Fang, H. Sheng, and J. Zhong, "Tunable CsPbBr₃/Cs₄PbBr₆ phase transformation and their optical spectroscopic properties," *Dalton Transactions*, vol. 47, no. 16, pp. 5670–5678, 2018.
133. Z. Liu, Y. Bekenstein, X. Ye, S. C. Nguyen, J. Swabeck, D. Zhang, S.-T. Lee, P. Yang, W. Ma, and A. P. Alivisatos, "Ligand Mediated Transformation of Cesium Lead Bromide Perovskite Nanocrystals to Lead Depleted Cs₄PbBr₆ Nanocrystals," *Journal of the American Chemical Society*, vol. 139, pp. 5309–5312, apr 2017.
134. J. Li, H. Zhang, S. Wang, D. Long, M. Li, D. Wang, and T. Zhang, "Inter-Conversion between Different Compounds of Ternary Cs-Pb-Br System," *Materials*, vol. 11, p. 717, 2018.
135. J. Pan, L. N. Quan, Y. Zhao, W. Peng, B. Murali, S. P. Sarmah, M. Yuan, L. Sinatra, N. M. Alyami, J. Liu, E. Yassitepe, Z. Yang, O. Voznyy, R. Comin, M. N. Hedhili, O. F. Mohammed, Z. H. Lu, D. H. Kim, E. H. Sargent, and O. M. Bakr, "Highly Efficient Perovskite-Quantum-Dot Light-Emitting Diodes by Surface Engineering," *Advanced Materials*, vol. 28, pp. 8718–8725, oct 2016.
136. N. Yarita, H. Tahara, M. Saruyama, T. Kawawaki, R. Sato, T. Teranishi, and Y. Kanemitsu, "Impact of Postsynthetic Surface Modification on Photoluminescence Intermittency in Formamidinium Lead Bromide Perovskite Nanocrystals," *The Journal of Physical Chemistry Letters*, vol. 8, pp. 6041–6047, dec 2017.
137. X. Zhang, C. Sun, Y. Zhang, H. Wu, C. Ji, Y. Chuai, P. Wang, S. Wen, C. Zhang, and W. W. Yu, "Bright Perovskite Nanocrystal Films for Efficient Light-Emitting Devices," *The Journal of Physical Chemistry Letters*, vol. 7, pp. 4602–4610, nov 2016.
138. R. Wang, Y. Shang, P. Kanjanaboos, W. Zhou, Z. Ning, and E. H. Sargent, "Colloidal quantum dot ligand engineering for high performance solar cells," *Energy & Environmental Science*, vol. 9, no. 4, pp. 1130–1143, 2016.
-

Bibliography

139. L. M. Wheeler, E. M. Sanehira, A. R. Marshall, P. Schulz, M. Suri, N. C. Anderson, J. A. Christians, D. Nordlund, D. Sokaras, T. Kroll, S. P. Harvey, J. J. Berry, L. Y. Lin, and J. M. Luther, "Targeted Ligand-Exchange Chemistry on Cesium Lead Halide Perovskite Quantum Dots for High-Efficiency Photovoltaics," *Journal of the American Chemical Society*, vol. 140, pp. 10504–10513, aug 2018.
140. J. Song, J. Li, X. Li, L. Xu, Y. Dong, and H. Zeng, "Quantum Dot Light-Emitting Diodes Based on Inorganic Perovskite Cesium Lead Halides (CsPbX_3)," *Advanced Materials*, vol. 27, pp. 7162–7167, nov 2015.
141. W. Deng, X. Xu, X. Zhang, Y. Zhang, X. Jin, L. Wang, S.-T. Lee, and J. Jie, "Organometal Halide Perovskite Quantum Dot Light-Emitting Diodes," *Advanced Functional Materials*, pp. 1–6, 2016.
142. A. Hazarika, Q. Zhao, E. A. Gaulding, J. A. Christians, B. Dou, A. R. Marshall, T. Moot, J. J. Berry, J. C. Johnson, and J. M. Luther, "Perovskite Quantum Dot Photovoltaic Materials beyond the Reach of Thin Films: Full-Range Tuning of A-Site Cation Composition," *ACS Nano*, vol. 12, pp. 10327–10337, oct 2018.
143. Q. A. Akkerman, M. Gandini, F. Di Stasio, P. Rastogi, F. Palazon, G. Bertoni, J. M. Ball, M. Prato, A. Petrozza, and L. Manna, "Strongly emissive perovskite nanocrystal inks for high-voltage solar cells," *Nat. Energy*, vol. 2, p. 16194, 2017.
144. B. Li, Y. Zhang, L. Fu, T. Yu, S. Zhou, L. Zhang, and L. Yin, "Surface passivation engineering strategy to fully-inorganic cubic CsPbI_3 perovskites for high-performance solar cells," *Nature Communications*, vol. 9, p. 1076, dec 2018.
145. P. Liu, X. He, J. Ren, Q. Liao, J. Yao, and H. Fu, "Organic–Inorganic Hybrid Perovskite Nanowire Laser Arrays," *ACS Nano*, vol. 11, pp. 5766–5773, jun 2017.

-
146. J. Zhang, Q. Wang, X. Zhang, J. Jiang, Z. Gao, Z. Jin, and S. F. Liu, "High-performance transparent ultraviolet photodetectors based on inorganic perovskite CsPbCl₃ nanocrystals," *RSC Advances*, vol. 7, no. 58, pp. 36722–36727, 2017.
147. G. Gao, Q. Xi, H. Zhou, Y. Zhao, C. Wu, L. Wang, P. Guo, and J. Xu, "Novel inorganic perovskite quantum dots for photocatalysis," *Nanoscale*, vol. 9, no. 33, pp. 12032–12038, 2017.
148. Y. Hassan, O. J. Ashton, J. H. Park, G. Li, N. Sakai, B. Wenger, A.-A. Haghighi-irad, N. K. Noel, M. H. Song, B. R. Lee, R. H. Friend, and H. J. Snaith, "Facile Synthesis of Stable and Highly Luminescent Methylammonium Lead Halide Nanocrystals for Efficient Light Emitting Devices," *Journal of the American Chemical Society*, vol. 141, pp. 1269–1279, jan 2019.
149. D. Han, M. Imran, M. Zhang, S. Chang, X.-g. Wu, X. Zhang, J. Tang, M. Wang, S. Ali, X. Li, G. Yu, J. Han, L. Wang, B. Zou, and H. Zhong, "Efficient Light-Emitting Diodes Based on in Situ Fabricated FAPbBr₃ Nanocrystals: The Enhancing Role of the Ligand-Assisted Reprecipitation Process," *ACS Nano*, vol. 12, pp. 8808–8816, aug 2018.
150. S. T. Ochsenbein, F. Krieg, Y. Shynkarenko, G. Rainò, and M. V. Kovalenko, "Engineering Color-Stable Blue Light-Emitting Diodes with Lead Halide Perovskite Nanocrystals," *ACS Applied Materials & Interfaces*, vol. 11, pp. 21655–21660, jun 2019.
151. D. Aldakov and P. Reiss, "Safer-by-Design Fluorescent Nanocrystals: Metal Halide Perovskites vs Semiconductor Quantum Dots," *The Journal of Physical Chemistry C*, vol. 123, p. acs.jpcc.8b12228, feb 2019.
152. C. Lu, M. W. Wright, X. Ma, H. Li, D. S. Itanze, J. A. Carter, C. A. Hewitt, G. L. Donati, D. L. Carroll, P. M. Lundin, and S. M. Geyer, "Cesium Oleate Precursor Preparation for Lead Halide Perovskite Nanocrystal Synthesis: The Influence

Bibliography

- of Excess Oleic Acid on Achieving Solubility, Conversion, and Reproducibility," *Chemistry of Materials*, vol. 31, pp. 62–67, jan 2019.
153. J. C. de Mello, H. F. Wittmann, and R. H. Friend, "An improved experimental determination of external photoluminescence quantum efficiency," *Advanced Materials*, vol. 9, pp. 230–232, mar 1997.
154. D. P. McMeekin, G. Sadoughi, W. Rehman, G. E. Eperon, M. Saliba, M. T. Hörantner, A. Haghighirad, N. Sakai, L. Korte, B. Rech, M. B. Johnston, L. M. Herz, and H. J. Snaith, "A mixed-cation lead mixed-halide perovskite absorber for tandem solar cells," *Science*, vol. 351, pp. 151–155, jan 2016.
155. J.-W. Lee, D.-H. Kim, H.-S. Kim, S.-W. Seo, S. M. Cho, and N.-G. Park, "Formamidinium and Cesium Hybridization for Photo- and Moisture-Stable Perovskite Solar Cell," *Advanced Energy Materials*, vol. 5, p. 1501310, oct 2015.
156. P. Gratia, I. Zimmermann, P. Schouwink, J.-H. Yum, J.-N. Audinot, K. Sivula, T. Wirtz, and M. K. Nazeeruddin, "The Many Faces of Mixed Ion Perovskites: Unraveling and Understanding the Crystallization Process," *ACS Energy Letters*, vol. 2, pp. 2686–2693, dec 2017.
157. M. Saliba, T. Matsui, J.-Y. Seo, K. Domanski, J.-P. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt, and M. Grätzel, "Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency," *Energy & Environmental Science*, vol. 9, no. 6, pp. 1989–1997, 2016.
158. R. J. Sutton, G. E. Eperon, L. Miranda, E. S. Parrott, B. A. Kamino, J. B. Patel, M. T. Hörantner, M. B. Johnston, A. A. Haghighirad, D. T. Moore, and H. J. Snaith, "Bandgap-Tunable Cesium Lead Halide Perovskites with High Thermal Stability for Efficient Solar Cells," *Advanced Energy Materials*, vol. 6, p. 1502458, apr 2016.

-
159. D. Chen, X. Chen, Z. Wan, and G. Fang, "Full-Spectral Fine-Tuning Visible Emissions from Cation Hybrid $\text{Cs}_{1-m}\text{FA}_m\text{PbX}_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{and I}, 0 \leq m \leq 1$) Quantum Dots," *ACS Applied Materials & Interfaces*, vol. 9, pp. 20671–20678, jun 2017.
160. C. Y. Wang, Y. K. Zhang, A. F. Wang, Q. Wang, H. Y. Tang, W. Shen, Z. Li, and Z. T. Deng, "Controlled Synthesis of Composition Tunable Formamidinium Cesium Double Cation Lead Halide Perovskite Nanowires and Nanosheets with Improved Stability," *Chem. Mater.*, vol. 29, p. 2157, mar 2017.
161. E. G. Ripka, C. R. Deschene, J. M. Franck, I.-T. Bae, and M. M. Maye, "Understanding the Surface Properties of Halide Exchanged Cesium Lead Halide Nanoparticles," *Langmuir*, vol. 34, pp. 11139–11146, sep 2018.
162. S. Premkumar, K. Kundu, and S. Umapathy, "Impact of cesium in methylammonium lead bromide perovskites: insights into the microstructures, stability and photophysical properties," *Nanoscale*, vol. 11, no. 21, pp. 10292–10305, 2019.
163. I. Borriello, G. Cantele, and D. Ninno, "Ab initio investigation of hybrid organic-inorganic perovskites based on tin halides," *Physical Review B*, vol. 77, p. 235214, jun 2008.
164. Y. Xue, J. Tian, H. Wang, H. Xie, S. Zhu, B. Zheng, C. Gao, and X. Liu, "Localized incorporation of cesium ions to improve formamidinium lead iodide layers in perovskite solar cells," *RSC Advances*, vol. 8, no. 45, pp. 25645–25652, 2018.
165. Y. Yu, C. Wang, C. R. Grice, N. Shrestha, J. Chen, D. Zhao, W. Liao, A. J. Cimaroli, P. J. Roland, R. J. Ellingson, and Y. Yan, "Improving the Performance of Formamidinium and Cesium Lead Triiodide Perovskite Solar Cells using Lead Thiocyanate Additives," *ChemSusChem*, vol. 9, pp. 3288–3297, dec 2016.
166. A. Friedenberg and Y. Shapira, "Photolysis and conductivity measurements at PbI_2 surfaces," *Surface Science*, vol. 115, pp. 606–622, mar 1982.
-

Bibliography

167. Y. Shapira and A. Friedenberg, "Dissociation of halide salts by electron beams," *International Journal of Mass Spectrometry and Ion Physics*, vol. 36, pp. 9–17, oct 1980.
168. Z. Morlin and J. Tremmel, "The effect of electron irradiation on some alkali halide single crystals," *Czechoslovak Journal of Physics*, vol. 13, pp. 216–218, mar 1963.
169. A. J. Forty, "The precipitation of lead during decomposition of lead iodide by electron irradiation," *Philosophical Magazine*, vol. 6, pp. 895–905, jul 1961.
170. T. H. Kim and S. G. Kim, "Clinical Outcomes of Occupational Exposure to N,N-Dimethylformamide: Perspectives from Experimental Toxicology," *Safety and Health at Work*, vol. 2, pp. 97–104, jun 2011.
171. J. G. Tait, T. Merckx, W. Li, C. Wong, R. Gehlhaar, D. Cheyns, M. Turbiez, and P. Heremans, "Determination of Solvent Systems for Blade Coating Thin Film Photovoltaics," *Advanced Functional Materials*, vol. 25, pp. 3393–3398, jun 2015.
172. K. L. Gardner, J. G. Tait, T. Merckx, W. Qiu, U. W. Paetzold, L. Kootstra, M. Jaysankar, R. Gehlhaar, D. Cheyns, P. Heremans, and J. Poortmans, "Non-hazardous Solvent Systems for Processing Perovskite Photovoltaics," *Advanced Energy Materials*, vol. 6, p. 1600386, jul 2016.
173. F. Palazon, S. Dogan, S. Marras, F. Locardi, I. Nelli, P. Rastogi, M. Ferretti, M. Prato, R. Krahne, and L. Manna, "From CsPbBr₃ Nano-Inks to Sintered CsPbBr₃–CsPb₂Br₅ Films via Thermal Annealing: Implications on Optoelectronic Properties," *The Journal of Physical Chemistry C*, vol. 121, pp. 11956–11961, jun 2017.
174. P. Liu, W. Chen, W. Wang, B. Xu, D. Wu, J. Hao, W. Cao, F. Fang, Y. Li, Y. Zeng, R. Pan, S. Chen, W. Cao, X. W. Sun, and K. Wang, "Halide-Rich Synthesized Cesium Lead Bromide Perovskite Nanocrystals for Light-Emitting

- Diodes with Improved Performance," *Chemistry of Materials*, vol. 29, pp. 5168–5173, jun 2017.
175. L. Wu, Q. Zhong, D. Yang, M. Chen, H. Hu, Q. Pan, H. Liu, M. Cao, Y. Xu, B. Sun, and Q. Zhang, "Improving the Stability and Size Tunability of Cesium Lead Halide Perovskite Nanocrystals Using Trioctylphosphine Oxide as the Capping Ligand," *Langmuir*, vol. 33, pp. 12689–12696, nov 2017.
176. Y. Tan, Y. Zou, L. Wu, Q. Huang, D. Yang, M. Chen, M. Ban, C. Wu, T. Wu, S. Bai, T. Song, Q. Zhang, and B. Sun, "Highly Luminescent and Stable Perovskite Nanocrystals with Octylphosphonic Acid as a Ligand for Efficient Light-Emitting Diodes," *ACS Applied Materials & Interfaces*, vol. 10, pp. 3784–3792, jan 2018.
177. J. L. Atwood, M. Tsutsui, N. Ely, and A. E. Gebala, "The Crystal and Molecular Structure of Tricyclopentadienylethynyluranium(IV)," *Journal of Coordination Chemistry*, vol. 5, pp. 209–215, sep 1976.
178. M. Zeldin, P. Mehta, and W. D. Vernon, "Phosphorus-31 NMR of triphenylphosphine oxide complexes with compounds of silicon, germanium, and tin," *Inorganic Chemistry*, vol. 18, pp. 463–466, feb 1979.
179. D. Hadži, C. Klofutar, and S. Oblak, "Hydrogen bonding in some adducts of oxygen bases with acids. Part IV. Basicity in hydrogen bonding and in ionisation," *J. Chem. Soc. A*, pp. 905–908, 1968.
180. G. E. Maciel and R. V. James, "Solvent Effects on the Phosphorus-31 Chemical Shift in Triphenylphosphine Oxide," *Inorganic Chemistry*, vol. 3, pp. 1650–1651, nov 1964.
181. C. J. Jameson and J. Mason, "The Chemical Shift," in *Multinuclear NMR* (J. Mason, ed.), pp. 51–88, Boston, MA: Springer US, 1987.

Bibliography

182. R. Koole, E. Groeneveld, D. Vanmaekelbergh, A. Meijerink, and C. De Mello Donega, "Size Effects on Semiconductor Nanoparticles," in *Nanoparticles* (C. De Mello Donega, ed.), pp. 13–51, Springer, 2014.
183. M. L. H. Green, "A new approach to the formal classification of covalent compounds of the elements," *Journal of Organometallic Chemistry*, vol. 500, pp. 127–148, sep 1995.
184. A. G. Shard, "Detection limits in XPS for more than 6000 binary systems using Al and Mg K α X-rays," *Surface and Interface Analysis*, vol. 46, pp. 175–185, mar 2014.
185. B. Fritzinger, I. Moreels, P. Lommens, R. Koole, Z. Hens, and J. C. Martins, "In Situ Observation of Rapid Ligand Exchange in Colloidal Nanocrystal Suspensions Using Transfer NOE Nuclear Magnetic Resonance Spectroscopy," *Journal of the American Chemical Society*, vol. 131, pp. 3024–3032, mar 2009.
186. P. K. Nayak, D. T. Moore, B. Wenger, S. Nayak, A. A. Haghighirad, A. Fineberg, N. K. Noel, O. G. Reid, G. Rumbles, P. Kukura, K. A. Vincent, and H. J. Snaith, "Mechanism for rapid growth of organic–inorganic halide perovskite crystals," *Nature Communications*, vol. 7, p. 13303, dec 2016.
187. A. Perumal, S. Shendre, M. Li, Y. K. E. Tay, V. K. Sharma, S. Chen, Z. Wei, Q. Liu, Y. Gao, P. J. S. Buenconsejo, S. T. Tan, C. L. Gan, Q. Xiong, T. C. Sum, and H. V. Demir, "High brightness formamidinium lead bromide perovskite nanocrystal light emitting devices," *Scientific Reports*, vol. 6, p. 36733, dec 2016.
188. Y.-L. Tong, Y.-W. Zhang, K. Ma, R. Cheng, F. Wang, and S. Chen, "One-Step Synthesis of FA-Directing FAPbBr₃ Perovskite Nanocrystals toward High-Performance Display," *ACS Applied Materials & Interfaces*, vol. 10, pp. 31603–31609, sep 2018.

189. G. Almeida, O. J. Ashton, L. Goldoni, D. Maggioni, U. Petralanda, N. Mishra, Q. A. Akkerman, I. Infante, H. J. Snaith, and L. Manna, "The Phosphine Oxide Route toward Lead Halide Perovskite Nanocrystals," *Journal of the American Chemical Society*, vol. 140, pp. 14878–14886, nov 2018.
190. Y. Zhang, M. I. Saidaminov, I. Dursun, H. Yang, B. Murali, E. Alarousu, E. Yengel, B. A. Alshankiti, O. M. Bakr, and O. F. Mohammed, "Zero-Dimensional Cs₄PbBr₆ Perovskite Nanocrystals," *The Journal of Physical Chemistry Letters*, vol. 8, pp. 961–965, mar 2017.
191. Y. Zhang, L. Sinatra, E. Alarousu, J. Yin, A. M. El-Zohry, O. M. Bakr, and O. F. Mohammed, "Ligand-Free Nanocrystals of Highly Emissive Cs₄PbBr₆ Perovskite," *The Journal of Physical Chemistry C*, vol. 122, pp. 6493–6498, mar 2018.
192. H. Zhao, R. Sun, Z. Wang, K. Fu, X. Hu, and Y. Zhang, "Zero-Dimensional Perovskite Nanocrystals for Efficient Luminescent Solar Concentrators," *Advanced Functional Materials*, vol. 29, p. 1902262, jul 2019.
193. A. Weissberger, J. A. Riddick, W. B. Bunger, and T. K. Sakano, *Techniques of chemistry. - 2: Organic solvents. Physical properties and methods of purification. 4.ed.* New York, N.Y.: Wiley, 1986.
194. T. J. Groshens and R. A. Hollins, "New chemical hydrogen storage materials exploiting the self-sustaining thermal decomposition of guanidinium borohydride," *Chemical Communications*, no. 21, p. 3089, 2009.
195. P. Haake, R. D. Cook, and G. H. Hurst, "Evaluation of the basicity of phosphine oxides and phosphine sulfides by measurements of chemical shift in sulfuric acid solutions," *Journal of the American Chemical Society*, vol. 89, pp. 2650–2654, may 1967.
196. M. Shin, J. Kim, Y.-K. Jung, T.-p. Ruoko, A. Priimagi, A. Walsh, and B. Shin, "Low-dimensional formamidinium lead perovskite architectures via controllable

Bibliography

solvent intercalation," *Journal of Materials Chemistry C*, vol. 7, no. 13, pp. 3945–3951, 2019.