Perovskite Semiconductor Nanostructures for Light Emission

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy

The Edward S. Rogers Sr. Department of Electrical and Computer Engineering

University of Toronto

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2019

Abstract

Perovskite-based semiconductor materials have achieved remarkable progress over the past decade, and are now considered to be promising candidates for low-cost high-performance optoelectronic devices. Wide interest in this material system stems from its versatility, low density of and high tolerance to charge carrier traps, high charge carrier mobilities, and low cost of fabrication. Nanostructures offer a number of additional benefits for light emission applications including a wide range of bandgap tuning, bright photoluminescence, and, in cases, improved long-term stability.

In this thesis, I investigate properties of perovskite nanostructures for light emission applications; my findings shed light on the remarkable performance of these materials, and provide insight into avenues to enhance further their light-emitting behaviour.
First I develop and investigate a dot-in-matrix strategy that enables perovskite quantum dots to exhibit photoluminescence quantum yield of over 90% in the solid-state. Modeling and experimental characterization suggest that lattice matching between the quantum dots and the matrix contributes to improved passivation, while spatial confinement enhances the radiative rate.

Next I investigate perovskite shells on quantum dots as a means to inhibit intradot Auger recombination. I demonstrate experimentally that MAPbI$_3$ perovskite shelling decreases the rate of Auger recombination in PbS quantum dots by over 1 order of magnitude.

I then explore morphological properties of perovskite quantum well thin films. I use in-situ methods during film formation to understand the mechanism by which the two-dimensional perovskites assemble, and I use these observations to explain the energetic and orientational distribution of perovskite quantum wells.

Finally, I study the alignment of perovskite quantum well energy levels. I study their energetic band positioning and find that the work function can be altered by surface interface dipoles across ligands. As a result, perovskite quantum well interfaces can exhibit type-I or type-II alignment depending on the density of ligands on surfaces.
Acknowledgements

I would like to thank my supervisor Ted Sargent for his support and guidance, as well as for giving me the opportunity to join such an extraordinary group of smart and knowledgeable individuals. The graduate student experience in this group is unique and remarkable. I have had the opportunity to work at synchrotron facilities, attend summer schools and participate in conferences across the world, and work with state-of-art equipment I had only read of in textbooks.

Thanks to OCCAM and the Canadian Light Source for supporting my research along the way.

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And of course, thanks to Mireille, my best friend and partner in crime. Thanks for joining me in numerous adventures, both outdoors and in the kitchen. I look forward to many more.
Contributions and Collaborations

Some text and figures presented herein have been adapted from published articles with approval from the authors and permissions granted by the appropriate organisms (see Appendix C: Copyright and Permissions). I only included materials from publications on which I was first or co-first author (unless otherwise explicitly stated). On the first page of each chapter I describe the collaboration and the roles and contributions of other authors.
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<tbody>
<tr>
<td>BTA</td>
<td>n-butylammonium</td>
</tr>
<tr>
<td>CNC</td>
<td>colloidal nanocrystals</td>
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<tr>
<td>CW</td>
<td>continuous-wave</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
</tr>
<tr>
<td>DOS</td>
<td>density of states</td>
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<tr>
<td>EA</td>
<td>electron affinity</td>
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<tr>
<td>EDS</td>
<td>energy dispersive X-Ray spectroscopy</td>
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<tr>
<td>EQE</td>
<td>external quantum efficiency</td>
</tr>
<tr>
<td>FA</td>
<td>formamidinium</td>
</tr>
<tr>
<td>ICP-AES</td>
<td>inductively-coupled plasma atomic emission spectrometry</td>
</tr>
<tr>
<td>IE</td>
<td>ionization energy</td>
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<tr>
<td>LED</td>
<td>light-emitting diode</td>
</tr>
<tr>
<td>NMP</td>
<td>N-Methyl-2-pyrrolidone</td>
</tr>
<tr>
<td>MA</td>
<td>methylammonium</td>
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<tr>
<td>PCE</td>
<td>power conversion efficiency</td>
</tr>
<tr>
<td>PEA</td>
<td>phenethyl ammonium</td>
</tr>
<tr>
<td>PL</td>
<td>photoluminescence</td>
</tr>
<tr>
<td>PLE</td>
<td>photoluminescence excitation</td>
</tr>
<tr>
<td>PLQY</td>
<td>photoluminescence quantum yield</td>
</tr>
<tr>
<td>PQW</td>
<td>perovskite quantum well</td>
</tr>
<tr>
<td>PV</td>
<td>photovoltaic(s)</td>
</tr>
<tr>
<td>QD</td>
<td>quantum dot</td>
</tr>
<tr>
<td>QWi</td>
<td>quantum wire</td>
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<tr>
<td>QW</td>
<td>quantum well</td>
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>SAED</td>
<td>selected area electron diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>TA</td>
<td>transient absorption</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>UPS</td>
<td>ultraviolet photoelectron spectroscopy</td>
</tr>
<tr>
<td>Wf</td>
<td>work function</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<td>XRD</td>
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1 Introduction

1.1 The Lighting and Displays Challenges

Given the ever-growing human population and its continued economic advance, there exists an ever-growing need for renewable sources of energy. The supply of fossil fuels is dwindling and, as we continue to rely on it, our environment suffers. Fossil fuels currently account a startling majority of our global energy supply, with only 14% provided by non-fossil fuels in 2015. Lighting currently accounts for over 15% of the global electricity consumption¹. Improving the efficiency and reducing the cost of light-emitting materials could help reduce our energy demand. Low-cost efficient solid-state lighting could make a transition towards more efficient lighting more attainable.

Solid-state lighting has also directly influenced modern-day society in the form of display technologies. Beyond televisions and computer screens, display technologies have become prevalent amongst all modern technological devices, from watches to kitchen appliances, and most importantly: smartphones. In 2017 1.54 billion smartphones were sold worldwide, which represents a $478.7 billion USD value in that year². This value has increased linearly in the past 10 years, with no hints of subsiding. Smartphones have transformed communities across the world leading to improved healthcare services, better energy and water management, and larger networks to facilitate social justice movements. Furthermore, the display industry has provided sources of revenue and jobs across the world, including developing countries².

State-of-art epitaxial semiconductor materials have enabled highly efficient light-emitting devices (with the notable exception of the green gap in efficiency of such epitaxial materials³-⁵), but remain costly due to expensive fabrication processes. Broad emission linewidths have further dimmed these materials’ prospects as serious contenders in the display technology industry.
Colloidal nanocrystals (CNCs) – solution-processed semiconductor nanoparticles – offer a means to construct low-cost optoelectronic light-emitting devices exhibiting high brightness, a vivid color gamut and high efficiency. CNCs are chemically synthesized in a wet chemical laboratory, making them promising for commercial implementation. Already, CNCs are being adopted in next-generation commercial products\(^6\). In addition to their cost benefits, CNCs exhibit a number of attractive properties for optoelectronic devices, namely bandgap tunability and high photoluminescence quantum yields.

1.2 Colloidal Nanostructures

Semiconductor nanostructures exhibit a number of enhancements and attractive phenomena over their bulk counterparts. Many of these phenomena offer advantages that can be exploited in optoelectronic devices. Most notably, nanostructures exhibit enhanced photoluminescence quantum yield metrics compared to their bulk counterparts, a fact that could benefit light-emitting diodes (LEDs). With increased spatial overlap between electrons and holes, the probability of radiative recombination is enhanced\(^6,7\). If the dimensions of a semiconductor nanostructure are reduced to the size of the exciton Bohr radius or lower, the system may exhibit quantum confinement\(^8\). This phenomenon offers wide tunability in quantum-confined semiconductor nanostructures. In these, the electronic bandgap of the semiconductor can be tuned by varying the size of the nanoparticle, making them useful for customizing optoelectronic devices to a wide range of applications with a given materials system\(^9,10\).

The quantum dot (QD) is a simple example of semiconductor nanostructures: a QD exhibits a crystal lattice that is truncated along all three dimensions such that the nanocrystal has a shape defined by the crystal type and growth facets (i.e. nanocube for perovskite crystal\(^9\), and octahedron/ cuboctahedron for PbS\(^11\)). The QD is denominated as such due to measurable effects imparted by reducing a semiconductor’s dimensions below the exciton Bohr radius. In general the quantum mechanical behavior of an electron is described using the Schrodinger Equation\(^12\):
\[
\left[ -\frac{\hbar^2}{8\pi^2m} \nabla^2 + V(\mathbf{r}) \right] \Psi(\mathbf{r}) = E\Psi(\mathbf{r}),
\]

where \( \Psi, E, \text{ and } V \) are the wavefunction, energy, and potential of the system. In the approximation of the infinite potential well, a spherical QD is described by a system wherein the potential \( V(\mathbf{r}) \) is zero for \( r \) smaller than the radius of the QD \( R_{\text{dot}} \), and infinite for \( r > R_{\text{dot}} \). The allowed energy levels of the spherical QD are found by solving Equation 1.1 for the infinite well potential:

\[
E = \frac{\hbar^2 \chi^2_{nl}}{8\pi^2 \mu R_{\text{dot}}^2},
\]

where \( \chi_{nl} \) and \( \mu \) are the \( n \)-th zero of the spherical Bessel function of order \( l \) and the reduced mass of the electron-hole pair, respectively. One outcome of quantum confinement is an increase in bandgap as the dimensions of the system are reduced. This increase in bandgap can be found by noting the difference in energy between the first quantized level in Equation 2.2, and the unconfined bandedge:

\[
\Delta E = \frac{\hbar^2}{8\mu R_{\text{dot}}^2},
\]

where \( \mu \) is the effective mass of the electron-hole pair. This relation shows that the bandgap energy is increased as the radius of the quantum dot is reduced. The general phenomenon has directly observable implications such that QDs of different sizes can span a wide range of colors without varying crystal structure (Figure 1.1). The treatment above is fairly accurate for intermediate and large QDs but fails to model very small QDs (primarily due to electron-hole Coulomb interactions). Early pioneers in the physics of QDs, L. E. Brus\textsuperscript{13–15} and A. I. Ekimov\textsuperscript{16,17} noted these shortfalls and proposed amendments to the model that offered more accurate predictions. Among these, I highlight a two-band model which assumes that the only two bands of importance are the highest occupied valence band and the lowest unoccupied

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conduction band\textsuperscript{15,18}. The two-band model assumes that both bands are equal in curvature and isotropic, and that the eigenmodes are a product of a plane wave and an envelope function. The resulting bands are hyperbolic, which represent a more accurate approximation than the parabolic bands of the model in Equation 1.1. A number of alternative models have since been proposed in the literature further improving the accuracy of quantum mechanical treatments of QDs\textsuperscript{18–20}.

Another important property of the electronic structure of QDs worth noting is the discrete nature of levels near the bandedge\textsuperscript{21}. Whereas the valence and conduction bands in a semiconductor can indeed be seen as bands, a QD which is built up of approximately 1000 atoms (depending on crystal structure and size), exhibits a much lower density of states within its bands, particularly near band edges\textsuperscript{8}. This has implications on applications such as light-emission and lasing. The low density of states near the band-edge leads to a narrower emission linewidth than that of bulk materials\textsuperscript{9,22}.
In bulk semiconductors, an exciton – a quasiparticle composed of a bound electron and hole – is not easily observed. At low temperatures, it is possible to observe a small feature in the absorption spectrum evidencing the formation of excitons\textsuperscript{23}. At higher temperatures, there is enough energy in the system to preclude their formation and instead lead to electrons and holes as free carriers. In QDs, however, an excitonic feature can be readily identified in the absorption spectrum at room temperature. Spatial confinement in a QD adds an additional barrier preventing the separation of electrons and holes\textsuperscript{21}. This property explains the high photoluminescence quantum yield inherent to QDs\textsuperscript{9}.

It has been proposed that excitonic features in absorption and photoluminescence spectra can also be attributed to a plasma of unbound electrons and holes, particularly at temperatures above 20 K and at high carrier densities. In this scenario, the optically generated plasma can

\textbf{Figure 1.1 Size-tunable bandgap enabled by quantum confinement.} Reprinted with permission from ACS Nano 2011, 5, 3, 2004-2012. Copyright 2011 American Chemical Society.
be reshaped by ultrafast Coulombic carrier scattering to narrow photoluminescence at the excitonic resonance\textsuperscript{24,25}. Under this formalism, excitonic photoluminescence in QDs is enhanced due to the sharper and stronger resonance of the exciton which in turn will reshape the plasma by Coulombic carrier scattering. The mechanism behind excitonic features in absorption and photoluminescence and the relative contribution of excitons and an electron-hole plasma is still a subject of debate\textsuperscript{24}.

It is important to clarify that high photoluminescence can be maintained in nanocrystals beyond dimensions of quantum confinement as it is sufficient to ensure the formation of excitons from electron-hole pairs\textsuperscript{7,26}. Spatial confinement of electrons and holes in a nanocrystal will increase their wavefunction overlap and the probability of radiative recombination without the need of quantum confinement. Spatial confinement is a double-edged sword, however. By the same reasoning, spatial confinement of electrons and holes in QDs also enhances the probability of higher order non-radiative recombination processes like Auger recombination\textsuperscript{27}, which affect high power applications like lasing.

Another challenge that arises with quantum confinement in QDs manifests in the form of increased surface to volume ratio. Because of increased surface in QDs, surface traps typically increase in QD systems, leading to decreased photoluminescence quantum yield (PLQY)\textsuperscript{7}, certain Auger mechanisms\textsuperscript{28}, and reduced conductivity. Surface traps would render most QD-based devices inoperable. Fortunately, inorganic shells can be grown on most QD systems, including InAs\textsuperscript{29}, CdSe\textsuperscript{30,31}, and PbS\textsuperscript{32}, which address most trap-associated issues.

1.3 Why Perovskites?

Metal halide perovskite semiconductors in particular have emerged as promising materials for solution-processed optoelectronic devices\textsuperscript{33–36}. With their ABX\textsubscript{3} crystal structure, where the A\textsuperscript{+} and B\textsuperscript{2+} cations are bound to an X\textsuperscript{−} anion, perovskites offer wide tunability of the bandgap via elemental composition. In addition, this class of material exhibits high charge carrier mobilities\textsuperscript{37}, high tolerance to/ low density of electronic trap states\textsuperscript{38,39}, low energetic barriers to materials formation\textsuperscript{40}, and an anticipated low cost of fabrication.
Perovskites, named after Russian mineralogist Lev von Perovski, were discovered in 1839.
Victor M. Goldschmidt and C.K. Møller were the first to study oxide and halide perovskites in
the early 1900s\textsuperscript{41,42}. Dieter Weber at the University of Stuttgart further advanced
perovskites in 1978 by developing the first organic-inorganic hybrid perovskite\textsuperscript{43}. In the mid-1990s, halide
perovskites were investigated for applications in light-emission\textsuperscript{44}, nonlinear optics\textsuperscript{45}, and later
photovoltaics (PV). In the 21\textsuperscript{st} century, halide perovskite research surged dramatically due to
the rapid increase in power conversion efficiency (PCE) from 3.8\% in 2009\textsuperscript{46} to 23.7\% in
2019\textsuperscript{47} rivaling silicon PVs. Along with the surge in halide perovskite research for PVs,
researchers have investigated a range of fundamental material properties in addition to
studying their applications in light-emitting diodes\textsuperscript{48–51}, lasers\textsuperscript{52,53}, photodetectors\textsuperscript{54},
transistors\textsuperscript{55}, X-ray imaging\textsuperscript{56}, nonlinear optics\textsuperscript{57}, and thermochromic displays\textsuperscript{58}, to name a
few.

Perovskite materials have achieved superior performance in photovoltaics and light-emitting
devices and are also advancing thin-film optoelectronics. Recently, perovskites have also been
explored as a paradigm for high-performance CNCs. In recent literature, perovskite CNC
research has enabled advances in 0D and 2D CNCs, also known as quantum dots (QDs)\textsuperscript{9,59–61}
and quantum wells (QWs)\textsuperscript{62–64}. QDs for instance, have recently enabled advances in
photovoltaics (PV), culminating in the achievement of X\% power conversion efficiency
(PCE)\textsuperscript{61}, and in light-emission, with the achievement of record efficiency red LEDs\textsuperscript{50}.
Quantum wells have led to remarkable improvements in CNC PV and LED device
performance and stability\textsuperscript{62,65}.

1.4 Outline of this Thesis

In this thesis, I focus on perovskite materials as a means to enhance semiconductor nanoparticle
performance for light emission. Along the way, I devote a significant portion of the thesis to
elucidating further the underlying physical and chemical properties of this emerging class of
nanomaterials.
In Chapter 2, I provide a brief overview of the historical context, material properties, and synthesis of halide perovskites. In addition, in this chapter, I introduce the fundamentals behind quantum confinement, the effect of nanostructuring on material properties, and the synthesis of perovskite CNCs. In Chapters 3 and 4, I investigate QD passivation schemes to learn about the physics behind the enhancement of optical and electronic properties. In the former, I present the improvement of photoluminescence quantum yield in perovskite QDs due to solid-state passivation. In the latter, I discuss the inhibition of Auger recombination mediated by low bandgap offsets in core-shells structures, and investigate the effect experimentally in PbS perovskite-shelled QDs. In Chapters 5 and 6, I investigate control of QW morphology and electronic structure and implications in optoelectronic devices. In the former, I studied growth and morphology of perovskite QWs, as well as the effect of various synthesis parameters on the size and orientation of perovskite QWs in films. In the latter, I studied the effect of ligand density on dipole-mediated band shifts in perovskite QWs. In chapter 7 I provide a summary of my findings throughout the thesis and a discussion of future work that could stem from that detailed in this thesis.

Individually each of these projects contributes through the quantitative characterization of nanocrystalline morphology and photophysical properties in perovskite materials. In particular, I focus on photoluminescence quantum yield, Auger recombination, QW size and orientation, and band alignment. Taken as a whole, the thesis offers insights into the benefits offered by perovskite nanocrystals, both QDs and QWs, for light emission applications and for the field of optoelectronics in general; and it articulates the challenges, both fundamental and applied, that remain to be tackled for these materials to have true and widespread impact.
2 Halide perovskites

In this chapter I introduce the perovskite crystal structure and survey the historical context of halide perovskite research and applications. I then detail a few material properties of halide perovskites that make them unique and justify their extensive investigation. Next, I move on to the typical synthesis of perovskite polycrystalline films and single crystals. Finally, I discuss some of the literature on nanostructuring of perovskite materials. In this section, I discuss the synthesis and applications of perovskite nanostructures and specifically discuss the perovskite quantum dots and quantum wells.

2.1 Crystal Structure

Perovskites exhibit the cubic ABX$_3$ crystal structure depicted in Figure 2.1, where the A cation and B cation, are bound to an X anion. Halide perovskites are a subset of this crystal type where the A$^+$ monovalent cation, the B$^{2+}$ divalent cation, and the X$^-$ halide are the components. BX$_6$ octahedra are at the center of the unit cell. A$^+$ cations are located at the corners of the cube, and X$^-$ halides are at the face-centers of the cubic unit cell. Although many perovskites exhibit this idealized cubic structure (Pm3m; or #221), distortions in the perovskite structure are common leading to reduced symmetry. Tetragonal (I4/mcm; or #140) and orthorhombic (Pnma; or #62) space groups are also common among perovskite crystals$^{66,67}$. 
Shown in (a) ball-and-stick and (b) polyhedral models.

Figure 2.1 Perovskite crystal structure unit cell. Shown in (a) ball-and-stick and (b) polyhedral models.

Among Goldschmidt’s many contributions to the field of perovskite crystallography, the introduction of tolerance factors remains most valuable to current perovskite research. Tolerance factors offer a metric that uses only the ionic radii of the A, B, and X components (assuming all ions as solid spheres) to determine the suitability of these components to adopt a perovskite framework\(^68\). At finite temperatures, the cubic perovskite framework can be adopted by components with a tolerance factor between 0.89 and 1\(^69\). Lower symmetry perovskite phases, such as orthorhombic and tetragonal may be supported at lower tolerance factors, typically above 0.8\(^67\). Organic ions such as methylammonium (MA) and formamidinium (FA) can also participate in the perovskite framework. In such cases, it is possible to assign effective radii with the assumption that the molecule is free to rotate about its center of mass. A brief list of typical metal-halide perovskite A, B, and C ions is included in Table 2.1.

\[
    t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)}
\]  

(2.1)

Table 2.1 Ionic radii of typical metal-halide perovskite ions. Data taken from literature\(^70\).

<table>
<thead>
<tr>
<th>A(^+)</th>
<th>R (pm)</th>
<th>B(^{2+})</th>
<th>R (pm)</th>
<th>X(^-)</th>
<th>R (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb</td>
<td>172</td>
<td>Mn</td>
<td>67-83</td>
<td>F</td>
<td>129</td>
</tr>
<tr>
<td>Cs</td>
<td>188</td>
<td>Ge</td>
<td>73</td>
<td>Cl</td>
<td>181</td>
</tr>
</tbody>
</table>
2.2 Historical Context

While CaTiO3 was discovered in 1839, it was only until the 1920s that perovskite crystallography was thoroughly investigated. Goldschmidt studied a range of oxide perovskites, but halide perovskites would not be identified as members of the same crystal group until the 1950s by C.K. Møller in Denmark\textsuperscript{42}. Oxide perovskites were quickly adopted for a range of applications as electromechanical transducers, fuel cells, catalysts, gas sensors, heating elements, and eventually lasers, superconducting devices, and capacitors\textsuperscript{42}.

Halide perovskites saw their next advance in research in 1978 when Dieter Weber at the University of Stuttgart developed the first organic-inorganic hybrid perovskite\textsuperscript{43}. In the mid-1990s, halide perovskites were investigated for applications in light-emission by David Mitzi at IBM\textsuperscript{44} and S. Saito at Kyushu University\textsuperscript{71}, nonlinear optics by a number of researchers at Boeing\textsuperscript{45}, and later PV. In the 21\textsuperscript{st} century, halide perovskite research surged dramatically due to the rapid increase in PCE from 3.8\% sparked by Tom Miyasaka in 2009\textsuperscript{46} to 23.7\% in 2019\textsuperscript{47} rivaling silicon PV.

In this latest timespan major contributions to the field of perovskite PV were achieved by Michael Grätzel\textsuperscript{72} and Henry Snaith\textsuperscript{73}. Their research groups developed a solid-state thin film framework for perovskite solar cells. Their work paved the way for the achievements in record photovoltaic performance by perovskite thin films. The success of perovskite PV also triggered research into different applications for perovskites.

In 2015, at the outset of my doctoral studies, perovskites were beginning to see some success in research for light emission\textsuperscript{33}. Pulsed amplified spontaneous emission\textsuperscript{74} and lasing\textsuperscript{75,76} had been reported in perovskite nanocrystals and light-emitting diodes had just exceeded 5\%
external quantum efficiency (EQE) in the green\textsuperscript{77}, while other colors still lagged behind. Since 2015, perovskites have seen remarkable success in light emission. Continuous-wave lasing has been observed for perovskite nanowires\textsuperscript{52}. LEDs have exceeded 20\% EQE in the green, red, and infrared\textsuperscript{50,78,79}, with luminance exceeding 1000 cd/m\textsuperscript{2}, increasing their interest in display technologies.

Along with the surge in halide perovskite research for PVs and LEDs\textsuperscript{48–51}, researchers have investigated a range of fundamental material properties and in addition to studying their applications in lasers\textsuperscript{52,53}, photodetectors\textsuperscript{54}, transistors\textsuperscript{55}, X-ray imaging\textsuperscript{56}, nonlinear optics\textsuperscript{57}, and thermochromic displays\textsuperscript{58}, to name a few. Given the focus on halide perovskites in this work, the word \textit{perovskite} will be used to mean \textit{halide perovskites} for conciseness.

2.3 Material Properties

Perovskite materials have achieved superior performance in photovoltaics and light-emitting devices, and are enabling advances in next-generation thin-film optoelectronics. Perovskite semiconductors have attracted interest in recent years due to their versatility\textsuperscript{33,74,80}, low density of carrier traps\textsuperscript{39}, high charge carrier mobilities\textsuperscript{37,81}, and low cost of fabrication.

First and foremost, perovskites are versatile. The perovskite framework offers the possibility to exchange A, B, and X components to vary a range of material properties. Bandgap, for instance can be varied between 2.98 eV (or 416 nm) to 1.73 eV (or 716 nm) which covers most of the visible part of the electromagnetic spectrum, simply by varying the halide in CsPbX\textsubscript{3}\textsuperscript{9} (\textbf{Figure 2.2}). All intermediate bandgaps are made accessible by the use of alloys. Variations in the A\textsuperscript{+} and B\textsuperscript{2+} cations can further tune the perovskite bandgap within a smaller range expanding the range of halide perovskites to 3.17 eV (or 390 nm)\textsuperscript{82} to 1.26 eV (or 984 nm)\textsuperscript{83}.

In constrast with well-established semiconductor materials commonly used in the optoelectronics industry (including PVs and LEDs), such as GaAs, Si, and CdSe, perovskites exhibit a high tolerance to defects. GaAs, Si, and CdSe materials need to be processed at high temperatures in order to ensure a low trap density for efficient semiconductor devices. In halide
perovskites however, defect states manifest within the conduction and valence bands, which are composed of Pb(6p)-I(5p) antibonding and Pb(6s)-I(5p) antibonding states, respectively. This is unlike most semiconductors where the conduction and valence bands are composed of antibonding and bonding states, respectively. In this common scenario, trap states form deep within the band gap, which is detrimental to device performance. As a result, devices made from such defect-intolerant materials must use trap-free crystals that must be grown by costly epitaxial methods.

![Figure 2.2 Bandgap tunability of perovskites.](image)

Figure 2.2 Bandgap tunability of perovskites. Halide perovskite bandgaps span the visible spectrum and part of the NIR simply by substituting the B$^{2+}$ and X$^{-}$ ions in the lattice.

Computational studies of defect tolerance have suggested that this property may arise from a low anion coordination number (2 in perovskites), which reduces dangling bond overlap with an anion vacancy. In addition, it has also been posited that the low valence of perovskite’s cations reduces the effect of charged defects which typically produce deep traps.

Perovskite thin films have been found to exhibit particularly high electron and hole mobilities. Recent theoretical and experimental investigations have found that perovskite thin films’ electron and hole mobilities are fundamentally limited to $\sim$200 cm$^2$/Vs. This value is high,
but slightly lower than GaAs, a well-established semiconductor material used in optoelectronic devices. Charge carrier mobility in ionic semiconductors is typically limited by Fröhlich interactions between charge carriers and the electric fields associated with the LO phonon modes of the ionic lattice. The limits in perovskite mobilities have been linked to the strong ionicity of the metal-halide bond and the low energy of an LO phonon mode associated to the oscillation of heavy lead atoms. Such studies believe that mobilities of perovskite thin films have reached their maximal theoretically achievable limits, which is unprecedented given the age of this relatively young field.

One of the main reasons for the surge in perovskite research in recent years is facile low-temperature synthesis. Halide perovskites are multinary halide salts and as such exhibit primarily ionic bonds. As a result, these materials can be synthesized with rapid kinetics even at room temperatures. It is possible, even, to mix precursors at room temperature under ambient atmosphere and form crystals with high optoelectronic properties. The high performance of such room-temperature synthesis solution-processed thin films can in turn be attributed to the defect tolerance of perovskites, and their high mobilities. It is for these reasons that a trap-ridden solution-processed perovskite thin film has enabled such high performances in optoelectronic devices such as PVs and LEDs.

2.4 Synthesis

Low temperature synthesis has facilitated a worldwide effort to develop, deploy, and understand these materials. In view of the ionic nature of the crystal structure’s bonds, perovskites are synthesized readily at room temperature from AX and BX$_2$ salt precursors. A perovskite thin film can be deposited by a number of different techniques, but spin-casting remains most popular due to the ease with which a homogeneous smooth film can be deposited, reducing parasitic resistances in PV and current leakage in LEDs. Researchers are also exploring scalable deposition methods such as blade-coating, spray-coating, and vapor deposition.
Single crystals, polycrystalline thin films, and colloidal nanocrystals can all be synthesized at low-temperature by facile solution-processed methods.

A typical perovskite thin film synthesis protocol involves the dissolution of AX and BX$_2$ salt precursors in aprotic solvents such as dimethyl sulfoxide (DMSO) or dimethylformamide (DMF). During spin-casting precursors are deposited onto the substrate as a homogeneous thin film, which is subsequently annealed at 70°C for 10 minutes. An additional step may be incurred by depositing an antisolvent of the perovskite precursors, such as chloroform, chlorobenzene, or toluene, halfway during the spin-casting process. This step precipitates the precursors in order to speed up the elimination of solvent and improve film quality. A number of different parameters, and modifications to the standard spin-casting protocol have been explored leading to smoother films with more oriented crystal grains.$^{35,62,91}$ Furthermore, crystal grain size and film thickness can be tuned by changing parameters in the deposition, like annealing temperature, spin-casting speed, and concentration of precursors in the solution.

In addition to polycrystalline thin films, large perovskite single crystals can be synthesized with similar ease. The protocol for single crystal growth will typically involve dissolving AX and BX$_2$ salt precursors in aprotic solvents, like DMSO or DMF, at high concentrations beyond the solubility limit at low temperatures but that can still be solubilized at high temperatures. This way the temperature of the solution can be increased until all precursors are dissolved, and then lowered slowly to enable crystallization and growth of single crystals. Recent work
has shown that some perovskite crystals exhibit an inverse temperature solubility relation such that the crystallization process can be induced at high temperatures\textsuperscript{92}. This method has been found to grow single crystals of mm-dimensions within minutes. Perovskite single crystals have been grown to better understand fundamental properties of their thin film counterparts that have enabled such unprecedented advances. Furthermore, due to lower grain boundaries and thus trap densities, researchers believe that single crystals should surpass thin films in performance\textsuperscript{93,94}. However due to the low quality of single crystal surfaces and the inability to make thin single crystals (as thick-active-layer devices are prone to voltage-losses and parasitic resistance), these have been unable to demonstrate superior performance\textsuperscript{93}.

2.5 Perovskite Nanostructures

As in the case of bulk perovskites, perovskite semiconductor nanostructures are synthesized using solution processing, including at or near room temperature.

In recent literature, perovskite-based CNCs have enabled considerable advances among 0D, 1D, and 2D nanostructure research. These are also known as Quantum dots (QDs)\textsuperscript{6,9,59–97}, Quantum wires (QWi)\textsuperscript{52,98} and Quantum wells (QWs), respectively\textsuperscript{62–64,99}. QD research for instance, has achieved extraordinary progress in PVs and LEDs: PbS QD PVs has achieved 12.6 % PCE with the aid of perovskite-based shells\textsuperscript{47}, whereas perovskite QDs have, in turn, reached 16.6 % PCE\textsuperscript{47}; on the other hand, perovskite QD LEDs have set efficiency records in the red\textsuperscript{50} and blue\textsuperscript{48}. Quantum wires are less common among perovskites, but have been used to achieve continuous-wave lasing in the visible\textsuperscript{52}. Perovskite quantum wells have led to remarkable improvements in CNC PV and LED device stability, and have set brightness and efficiency records in the NIR\textsuperscript{51} and green\textsuperscript{49}.

I have focused my investigations on perovskite 0D and 2D CNCs, and their photophysical and morphological properties. The following sections will detail a brief background of perovskite QDs and QWs, as well as a motivation for my work.
2.5.1 Quantum Dots

Perovskite QDs were developed in 2015\(^9\), when Protesescu \emph{et al.} demonstrated the synthesis of Cl, Br, and I CsPbX\(_3\) perovskite nanoparticles spanning the visible range and having PLQYs of up to 90\% in solution. Their synthesis is similar to that of other semiconductor QDs. Hot injection QD synthesis typically involves heating precursors in high-boiling-point solvents to high temperatures in order to decompose the precursors to monomers or ions that may nucleate and grow nanocrystals\(^8\). Long ligands are typically added in order to stabilize the nanocrystals colloidal. The temperature of the solution, and the duration of growth are the two main parameters available to control QD size\(^8\). As with bulk perovskites, synthesis of perovskite QDs has now been achieved at room temperature and within seconds\(^{100,101}\). This was achieved by supersaturated recrystallization involving the dissolution of perovskite precursors and ligands to stabilize colloidal nanocrystals in an aprotic solvent, like DMF. This solution was in turn deposited into a solvent that exhibits orders of magnitude lower solubility for the perovskite precursors \(\text{e.g., toluene}\).

Core-shell strategies have improved PLQY\(^{102,103}\), long-term stability\(^{104}\), and Auger lifetimes\(^{105,106}\) in other QD systems including II-VI, IV-VI, and III-V materials, however it has not been possible to grown shells on perovskite QDs. However, achieving this heterostructuring in halide perovskite QDs has so far proven difficult due to intermixing of halide anions between the core and the shell, leading to the formation of mixed-halide perovskite QDs instead.\(^{107,108}\) Shells grown in perovskite QDs could lead to increased PLQY of films by preventing agglomeration of QDs and thus increased traps and loss of quantum confinement.\(^{109}\) Developing perovskite QD nanomaterials and shells is an ongoing area of research.\(^{110,111}\) Perovskites have also been studied as a shelling material for QDs of other material systems, including PbS\(^{112,113}\) and PbSe\(^{114}\). These core-shell systems have been found to exhibit higher mobility\(^{115}\), PLQY, and performance in optoelectronic devices\(^{113}\).

2.5.2 Quantum Wells
The same formalism that was used to understand QDs can be used to describe QWs. QWs exhibit a crystal lattice that is instead truncated along one sole dimension. The same infinite potential well can be used to calculate the available modes in the resulting band structure\textsuperscript{116}. This results in discrete confined states for modes with momentum normal to the quantum well layers, but a continuum of states in the planes of the semiconductor. The allowed energies in the system are\textsuperscript{116}:

\[
E = \frac{\hbar^2 n^2}{8\mu L_{\text{well}}^2} + \frac{\hbar^2 |k_{xy}|^2}{8\mu},
\]

where the first term represents the resulting confined states and the second term represents the continuum states along the plane. The first term reveals the same quantum confinement energy observed in QDs. This has the same implications as in QDs: tunability of the band gap. However, QWs exhibit an important difference from QDs. Unlike the discrete states of QDs, due to the continuum of in-plane modes, QWs exhibit sub-bands between the discrete states represented by the first term of Equation 2.2. The density of states for QDs, QWIs, QWs, and bulk are compared in Figure 2.4. Despite the differences, QWs exhibit striking similarities to QDs. Alike QDs, however, excitons in QWs exhibit much higher binding energies than their bulk counterparts\textsuperscript{117–119}. As a result, exciton features in absorption spectra can be observed at room temperature in QWs\textsuperscript{120,121}. In addition, PLQY of QWs tends to be much higher than in bulk materials\textsuperscript{122–124}.\textsuperscript{115}
QDs exhibit discrete states, whereas QWIs and QWs have a region of subbands between these discrete states due to an available continuum of states normal to the direction of confinement.

Perovskite QWs (PQWs) can be synthesized by similar means as perovskite QDs. Colloidal PQWs have been grown by hot-injection by protocols quite similar to those of QDs\textsuperscript{125}. The difference is in the ratio of precursors and the temperature of the reaction. It was found that varying the reaction temperature in hot-injection changes the reaction kinetics and lead to different perovskite nanocrystal morphology. QWs can be achieved at lower temperatures, and QWIs can be synthesized at higher temperatures. Colloidal PQWs can also be grown at room-temperature by supersaturated recrystallization, much like QDs\textsuperscript{123}. In this case only the ratio of precursors differs from the QD synthesis protocol.

PQWs can also be synthesized during the spin-casting process, as in the synthesis of bulk perovskite films. This is achieved with the addition of large ammonium-terminated intercalating cations (such as phenethylammonium\textsuperscript{63,65,126} and n-butylammonium\textsuperscript{62,121}) in the spin-casting process. In these materials, perovskite layers are separated by bilayers of organic cations which are ionically bonded to halide groups in the perovskite (Figure 2.5). It has been found that the halide-rich surfaces at perovskite grain boundaries are better protected from

\textbf{Figure 2.4 Density of states in reduced dimensional semiconductors.} QDs exhibit discrete states, whereas QWIs and QWs have a region of subbands between these discrete states due to an available continuum of states normal to the direction of confinement.
oxidation and degradation in perovskite QWs leading to enhanced long-term stability\textsuperscript{63,127}. Perovskite QWs have also proven exceptional for light-emitting applications, leading to record-performing devices\textsuperscript{64,65}. The crystal system exhibits the R\textsubscript{2}A\textsubscript{n-1}B\textsubscript{n}X\textsubscript{3n+1} structure where R is the intercalating cation, and \( n \) represents the number of perovskite layers in a well. This notation can also be used to represent 3D (\( n \to \infty \)), 2D (\( n = 1 \)), and quasi-2D (\( n > 1 \))\textsuperscript{63,65,126,128,129}.

![Figure 2.5 Perovskite QWs with varying thickness.](image)

**Figure 2.5 Perovskite QWs with varying thickness.** By varying the ratio of precursors, perovskite nanostructures can be grown to span the range between 2D and 3D.
3 Efficient Inorganic Luminescent Perovskite Quantum Dot Solids

As detailed in the previous chapter, perovskite QDs high PLQYs in solution, however transferring this behavior in solid films had not been successful. Growing shells on perovskite QDs has also not been successful as in other QD material systems, such as CdSe, and InAs.

CsPbBr$_3$ quantum dots had reached 90% PLQY in solution; but only a low 18% for films at the time this work was undertaken. Translating this impressive emission efficiency into solid films is an ongoing area of research. The reduction in PLQY of quantum dot films can be attributed to agglomeration of the quantum dots and loss of passivating ligands on the nanocrystal surfaces. These effects open the door to non-radiative recombination mechanisms which outcompete the radiative pathways leading to decreased PLQY.

In this chapter, I present the development of a dot-in-matrix strategy to maintain high PLQY (> 90 %) in solid-state. Additionally, the material composite is robust and air-stable: high PLQY is maintained for > 2 years. Theoretical modeling and experimental characterization suggest that lattice matching between the nanocrystals and the matrix contributes to improved passivation, while spatial confinement enhances the radiative rate of the nanocrystals. In addition, dispersing the nanocrystals in a matrix prevents agglomeration, explaining the high PLQY.

This chapter contains work from “Highly Emissive Green Perovskite Nanocrystals in a Solid State Crystalline Matrix” published in Advanced Materials, 29.21 (2017), 1605945. Text and figures have been adapted with permission from the authors. Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA. First authorship of this work is shared between Dr. Li Na Quan and me. Dr. Quan and I worked together in developing the synthesis of the materials. I led the material characterization, data analysis, and computational investigation. Other authors contributed in ICP-MS and XRD data collection.
3.1 Dot-in-Matrix Endotaxy

Core-shell structures have evolved as a means of addressing low PLQY of quantum dot films. In conventional nanomaterials, such as II-VI, IV-VI, and III-V quantum dots, this strategy has been successful. However, achieving this heterostructure in halide perovskites has proven difficult due to intermixing of halide anions between the core and the shell, leading to the formation of mixed-halide perovskite QDs instead.

I hypothesized that a passivation by endotaxy with the same chemical elements but in a different crystal structure could bypass the halide intermixing between the core and shell. Inspired by the successful fabrication and synthesis of endotaxial systems among two completely different crystal structures, I set out to investigate the potential for endotaxy of perovskite CsPbBr$_3$ quantum dots and a matrix crystal structure made up of the same elements. In order to select a suitable matrix crystal structure, I started by studying the ternary phase diagram of Cs, Pb and Br, shown on Figure 3.1. From the ternary phase diagram, both the cubic-phase CsPbBr$_3$ perovskite compound and the hexagonal-phase Cs$_4$PbBr$_6$ (space group: 167) fall on the same line connecting the PbBr$_2$ and CsBr precursors that are used in
the synthesis of CsPbBr$_3$ perovskite. If endotaxy between CsPbBr$_3$ quantum dots and a Cs$_4$PbBr$_6$ matrix could be satisfied, their solution-processed synthesis would be feasible.

I sought to determine, with the aid of a computational approach initially, whether the Cs$_4$PbBr$_6$ compound could offer an endotaxial match with CsPbBr$_3$ quantum dots. I developed an algorithm that held the perovskite cubic lattice constant, translated and rotated the matrix crystal lattice under test around the quantum dot along the possible permutations, and compiled the results to find the alignment that would lead to the lowest strain. Details of this algorithm are included in Appendix A.1.

I found a permutation along which there was practically no strain: this alignment takes place when the \{100\} planes of the cubic CsPbBr$_3$ quantum dot align with the lattice of Cs$_4$PbBr$_6$ as shown in Figure 3.2. In unit vectors of the matrix, these directions are $h_1=\sqrt{3}(-1,1,1)$, $h_2=\sqrt{6}(-1,-2,1)$ and $h_3=\sqrt{6}(2,1,1)$. The planes at which the optimal alignment takes place are (1$\bar{1}$1), (2$\bar{1}$2) and (211) in a 3-index system and (1$\bar{1}$01), (1$\bar{0}$12) and (101$\bar{1}$) in the more conventionally used 4-index system for hexagonal lattices. The intersecting axis system in Figure 3.2 shows the rotation at which the \{100\} lattice planes a cubic-phase CsPbBr$_3$ dot

![Figure 3.2 Alignment of Cs$_4$PbBr$_6$ and CsPbBr$_3$ that satisfies lattice matching.](image-url)
aligns with the lattice of Cs₄PbBr₆. This match satisfies a CsPbBr₃ QD inside a Cs₄PbBr₆ matrix with enhanced passivation of the surfaces and with practically no strain on the QD. In Figure 3.3, the alignment of the cubic perovskite QD in the matrix is visualized, where the axis system is color coded to match that of Figure 3.2. This alignment between cubic QDs and a geometrically anisotropic hexagonal matrix is of considerable interest. Although the crystalline structure of Cs₄PbBr₆ is intricate, it still composed of PbI₆ octahedra and it is therefore not surprising that endotaxial alignment can be achieved with these materials with minimal strain. The alignment, which is simultaneous along all 3 dimensions, is valid every 5 unit cells of the cubic perovskite quantum dot along all three dimensions.

Figure 3.3 Lattice-matching between matrix and CsPbBr₃ QD inclusions. a) Cut along the (001) plane of system with matrix atoms reduced in size in order to facilitate the observation of the QD inclusion in the matrix. b) & c) Two different cuts along planes of cubic perovskite (direction-guided arrow colors are consistent with those shown in Figure 3.2. The saturation value of the color of the matrix atoms has been reduced to distinguish these atoms from QD atoms. The atoms are presented with the following color-coding: Cs – yellow, Pb – black, and Br – blue.
3.2 Materials Synthesis

In order to synthesize the modelled dot-in-matrix material, a synthesis was hypothesized that was informed by the ternary phase diagram. The ternary phase diagram (often called a Gibbs Triangle) highlights that various mixtures of the CsBr and PbBr$_2$ precursors could produce different proportions of Cs$_4$PbBr$_6$ and CsPbBr$_3$ with no intermediate phases. To overcome the different solubility of PbBr$_2$ and CsBr in polar solvents, aprotic DMSO was used to dissolve PbBr$_2$, and protic H$_2$O for CsBr. The CsBr in H$_2$O solution was slowly injected into the PbBr$_2$ in DMSO solution and stirred at room temperature in air atmosphere for 30 minutes. After bright green precipitates formed in the mixed solution, crystals were centrifuged at 5000 rpm and washed with toluene, followed by drying under vacuum. The synthesis is illustrated in Figure 3.4.

![Figure 3.4 Synthesis of dot-in-matrix perovskite system. CsBr is dissolved in H$_2$O and PbBr$_2$ is dissolved in DMSO. The solutions are mixed and then stirred for 30 minutes.](image-url)
Figure 3.5 Rhombic hexabromide microcrystals with perovskite QD inclusions. SEM reveals the formation of rhombic hexabromide microcrystals. Further characterization corroborates the formation of perovskite QD inclusions within the hexabromide microcrystals.

Scanning electron microscopy (SEM) images of the resulting microcrystals are depicted in Figure 3.5a. The growth of rhombic prisms suggests that the formation of hexagonal Cs₄PbBr₆. However, powder X-ray diffraction (XRD) (Figure 3.6a) confirms the coexistence of the perovskite and the hexabromide compounds in the material system. Wide area compositional SEM imaging (see Appendix B.1) and Energy Dispersive X-Ray Spectroscopy (EDS) mapping (see Appendix B.1) confirm the presence of a single phase, arguing against the possibility that CsPbBr₃ and Cs₄PbBr₆ are present as separate bulk phases. The XRD results indicate more CsPbBr₃ than Cs₄PbBr₆ (i.e. smaller pure-perovskite peaks). An approximate value of the ratio of CsPbBr₃ to Cs₄PbBr₆ is determined by measuring the Cs to Pb atomic ratio using inductively-coupled plasma atomic emission spectrometry (ICP-AES) (Figure 3.6b) from which a ratio of CsPbBr₃ to Cs₄PbBr₆ is deduced.
Powder XRD reveals the coexistence of CsBr$_3$ alongside Cs$_4$PbBr$_6$ in the material system. The perovskite peaks are much weaker suggesting a low ratio of perovskite to hexabromide.

Transmission electron microscopy (TEM), along with Selected Area Electron Diffraction (SAED), offer direct evidence of the material model. TEM cannot be directly measured on the microcrystal due to its large dimensions. After crushing the microcrystal in a mortar, however, it became possible to perform a TEM measurement on thin chips of crystal. One such image is included in Figure 3.7, where it is possible to measure a characteristic Cs$_4$PbBr$_6$ lattice spacing of 3.4 ± 0.1 Å, and a region with a much larger lattice of 13.2 ± 0.1 Å. The latter is a Moiré fringe pattern resulting from the beating of two different overlapping lattice fringes. Given that the Moiré fringe and the Cs$_4$PbBr$_6$ lattice are approximately parallel, the measured matrix lattice (green in Figure 3.7a) and the QD lattice (approximately 2.94 Å) would yield a Moiré interference fringe consistent with experimental observations (blue in Figure 3.7a):

$$d_{Moiré} = \frac{d_{NC}^2}{2(d_{Matrix} - d_{NC})} = 10 ± 3Å$$

The SAED of the crystal system evidences the coexistence of CsPbBr$_3$ and Cs$_4$PbBr$_6$ within the microcrystal. The pattern on Figure 3.7b shows peaks of both phases, after an electron beam has diffracted off a single microcrystal chip. The difference in SAED patterns between
regions with and without QDs is clear evidence of CsPbBr$_3$ QDs in the Cs$_4$PbBr$_6$ microcrystals (see Appendix B.1).

![HRTEM image of crushed microcrystals. Inset: Zoomed-in HRTEM image on Moiré pattern evidencing the overlap of 2 different lattices. Moiré lattice is depicted in blue, and the matrix lattice in green.](image)

![SAED pattern of microcrystal depicting the coexistence of both phases within one microcrystal.](image)

**Figure 3.7 TEM and SAED of microcrystals.** a) HRTEM image of crushed microcrystals. Inset: Zoomed-in HRTEM image on Moiré pattern evidencing the overlap of 2 different lattices. Moiré lattice is depicted in blue, and the matrix lattice in green. b) SAED pattern of microcrystal depicting the coexistence of both phases within one microcrystal.

A detailed material structure emerges from our experimental analysis and theoretical phase matching between perovskite QDs and Cs$_4$PbBr$_6$: rhombic prisms of Cs$_4$PbBr$_6$ that contain small cubic CsPbBr$_3$ QDs (~10 nm dimensions) aligned to the lattice of the matrix. The dimensions of the rhombic prisms range from 4 to 10 μm.

### 3.3 Light-Emitting Properties

The photophysical properties of the microcrystals presented in the previous sections can be further tuned by varying the ratio of precursors in the synthesis. This allows for the optimization of PLQY and some control over the emission wavelength. A precursor ratio (CsBr/PbBr$_2$) equal to 1 leads to the formation of CsPbBr$_3$ microcrystals. As long as the ratio of precursors was kept greater than 1, the synthesis resulted in a highly emissive compound (Figure 3.8). I found a red-shift in the photoluminescence (PL) wavelength of the composite material from 510 nm to 520 nm as the ratio CsBr/PbBr$_2$ was increased, suggesting quantum
confinement of the CsPbBr$_3$ phase (with an onset of 10 nm in CsPbBr$_3$) (Figure 3.9a). The PLQY also varied with precursor concentration (Figure 3.9b): the PLQY reaches a maximum of 92% at a CsBr/PbBr$_2$ ratio of 8.

![Figure 3.8 Photographs of perovskite dot-in-matrix powder. Left and right panels depict powder without and with UV excitation, respectively.](image)

It is possible that micrometric CsPbBr$_3$ impurities are also present in the admixture, but given the high measured PLQY values (which would only decrease with the presence of bulk-like CsPbBr$_3$) and that fact that these are not spotted by SEM imaging (see Appendix B.1), it is unlikely that these would considerably affect the measured optical properties. Furthermore, the material shows stable light emission with very little degradation after years of storage in air.

![Figure 3.9 PL of perovskite dot-in-matrix microcrystals.](image)
a) PL of microcrystals and b) PLQY PLQY of materials resulting from different ratios of CsBr and PbBr₂.

![Figure 3.10 PLE of microcrystals for matrix and QD inclusion emission.](image)

**Figure 3.10 PLE of microcrystals for matrix and QD inclusion emission.** The Cs₄PbBr₆ matrix material has an excitonic-like absorption window at 320 nm which can be observed in the PLE. Within this window, the matrix absorbs all of the excitation inhibiting all QD emission.
A CsBr/PbBr$_2$ precursor ratio of 8 yields microcrystals that exhibit the highest PLQY due to sufficient spatial separation between the cubic perovskite inclusions resulting in the best passivation of the QD surface. At lower CsBr/PbBr$_2$ ratios, the decrease in PLQY can be attributed to the growing size of the NCs, judged by the PL red-shifts. These larger nanocrystals are more bulk-like exhibiting a loss in quantum confinement and thus a decrease in PLQY due to higher exciton dissociation. On the other side of the optimum, at small amounts of PbBr$_2$, the CsPbBr$_3$ growth is impeded leading to smaller, non-uniform QDs high in defects. As the amount of PbBr$_2$ precursor is further reduced (beyond a CsBr/PbBr$_2$ ratio of 20), the microcrystals become smaller, leaving a significant amount of unreacted CsBr. At this point, there is very little CsPbBr$_3$ and also little passivating Cs$_4$PbBr$_6$ matrix.

![Figure 3.11 PL decay of microcrystals at different precursor ratios.](image)

**Figure 3.11 PL decay of microcrystals at different precursor ratios.** The radiative lifetimes of all samples resemble that of perovskite nanocrystals, confirming the source of the photoluminescence. The lifetimes of the different samples can help identify the existence of non-radiative pathways such as surface traps due to insufficient passivation by the matrix.

The wide bandgap matrix allows for a direct photoexcitation of the QD inclusions. The photoluminescence excitation (PLE) spectra for both emission of the NCs, at 515 nm, and the
matrix, with a peak emission at 375nm,\textsuperscript{134} are plotted in Figure 3.10b. Noteworthy is the sharp dip at \( \sim 310 \) nm at which the light is fully absorbed by the matrix, never reaching the NCs. In this region, the \( \text{Cs}_4\text{PbBr}_6 \) matrix exhibits a sharp peak in the absorption spectrum\textsuperscript{135}.

\[ \text{Figure 3.12 PL decay of microcrystals as a function of excitation power.} \]

I carried out PL decay measurements on the dot-in-matrix compound, yielding the traces shown on Figure 3.11. I verified that the PL decay lifetimes do not vary as a function of power (Figure 3.12): this means that they can be compared with the PLQY measurements of Figure 3.9, which were acquired at lower intensities. Multi-exponential functions were found to fit these decay traces, and this analysis produced the values listed in Table 3.1. The radiative lifetime of the QD PL emission was computed under the assumption that all QDs in a microcrystal would exhibit similar radiative rates, but the non-radiative rates may vary from dot to dot, due to surface traps or proximity to neighboring dots or microcrystal edges. It is assumed that the PL decay is given by the function
\[ I(t) = \sum_{i=1}^{n} A_i e^{-t/\tau_{X_i}}, \quad (3.2) \]

where \( A_i \) is the relative fraction of dots with this non-radiative lifetime, and \( \tau_{X_i} \) the single exciton decay lifetime is given by

\[
\frac{1}{\tau_{X_i}} = \frac{1}{\tau_{nrX_i}} + \frac{1}{\tau_{rX}}. \quad (3.3)
\]

The PLQY of each QD is then given by \( q_i = \frac{\tau_{X_i}}{\tau_{rX}} \), and the total PLQY ensemble for a sample of microcrystals with embedded QDs is given by \( Q = \sum_{i=1}^{n} A_i q_i \). The radiative lifetime of the QDs in the samples is then given by:

\[
\tau_{rX} = Q^{-1} \sum_{i=1}^{n} A_i \tau_{X_i}. \quad (3.4)
\]

With similar PL lifetimes to those of colloidal CsPbBr\(_3\) perovskite QDs,\(^9,59,136\) the transient photo-physics further evidences that these QDs are responsible for the high PLQY emission. Furthermore, the radiative lifetimes evidence an increase in radiative lifetime as the size of the QD is increased approaching a maximal value for the bulk-like perovskite microcrystals produced with a CsBr/PbBr\(_2\) ratio of 1 due to an increase in the exciton dissociation as the size of the QD is increased into the bulk-like domain. This finding agrees well with TEM and PL red-shifts which also support the existence of QD inclusions of approximately 10 nm (larger dimensions for smaller CsBr/PbBr\(_2\) ratios and smaller dimensions for larger precursor ratios).

**Table 3.1 Decay and Radiative Lifetimes of microcrystals.** The samples were synthesized with different precursor ratios, and a 1:1 ratio that leads to perovskite microcrystals without a hexabromide matrix.

<table>
<thead>
<tr>
<th>1:8 PbBr:CsBr</th>
<th>1:4 PbBr:CsBr</th>
<th>1:2 PbBr:CsBr</th>
<th>1:1 PbBr:CsBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured ( \tau_1 )</td>
<td>0.1 ns</td>
<td>0.9 ns</td>
<td>0.6 ns</td>
</tr>
<tr>
<td></td>
<td>Measured τ2</td>
<td>2.4 ns</td>
<td>3.9 ns</td>
</tr>
<tr>
<td>----------------</td>
<td>-------------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td></td>
<td>Measured τ3</td>
<td>13 ns</td>
<td>14 ns</td>
</tr>
<tr>
<td></td>
<td>Measured A1</td>
<td>0.17</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>Measured A2</td>
<td>0.54</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>Measured A3</td>
<td>0.29</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>Measured PLQY</td>
<td>92 %</td>
<td>42 %</td>
</tr>
<tr>
<td></td>
<td>Computed τavg</td>
<td>5.2 ns</td>
<td>5.5 ns</td>
</tr>
<tr>
<td></td>
<td>Computed τrad</td>
<td>5.7 ns</td>
<td>13 ns</td>
</tr>
<tr>
<td>Emission λ</td>
<td>516 nm</td>
<td>520 nm</td>
<td>520 nm</td>
</tr>
</tbody>
</table>

### 3.4 Summary

The synthesis of cubic CsPbBr₃ perovskite QDs in robust and air-stable rhombic prism Cs₄PbBr₆ microcrystals enables high emission efficiency in the solid state (over 90% PLQY). I proposed a model informed by experimental characterization and computational evidence of lattice-matching between cubic CsPbBr₃ QDs and a Cs₄PbBr₆ matrix. Powder XRD confirmed the coexistence of the perovskite QDs and the matrix. SEM imaging and PL confirmed the shape and size of the crystallites and inclusions. Compound ratios were estimated from ICP-AES measurements. TEM imaging and SAED patterns provide conclusive evidence in support of the material model. The experimental characterization agrees with the picture of endotaxy of perovskite QDs with a Cs₄PbBr₆ matrix.

Dot-in-matrix and core-shell structures open the door to modulating photophysical QD properties. In the present chapter I used the dot-in-matrix strategy to synthesize bright and air-stable light-emitting QDs in the solid-state. In the chapter that follows, I continue with an examination of dots in a perovskite environment, but focus instead on the crucial question of Auger recombination and its manipulation using the shelling strategy.
4 Perovskite Shells Reduce Auger Recombination in Quantum Dot Solids

Perovskite shells have been shown to grown on lead chalcogenide QDs with effects on improving PLQY and diffusion length. In this chapter, I investigate the promise of core-shell structures in inhibit intradot Auger recombination quantum dots. Continuous-wave (CW) lasing has been demonstrated at visible wavelengths using CQDs, but this has remained elusive in the NIR. IV-VI semiconductor CQDs such as PbS and PbSe are among the most extensively studied for NIR applications. Unfortunately, they have a short gain lifetime ($\tau_{\text{gain}} < 40\,\text{ps}$ at room temperature), a phenomenon that arises from efficient non-radiative Auger recombination in narrow-gap semiconductor CQDs.

I first develop a computational model to NIR PbS CQDs with different shells, and identify shelling strategies that should inhibit Auger recombination. I also experimentally demonstrate, using transient absorption spectroscopy (TA), that MAPbI$_3$ perovskite shelling decreases the rate of Auger recombination by over 1 order of magnitude compared to the unshelled QD. In the TA analysis, I distinguish and quantify the effects of passivation and wavefunction delocalization on the effects on Auger recombination.

This chapter contains work from “Small-Band-Offset Perovskite Shells Increase Auger Lifetime in Quantum Dot Solids” published in ACS Nano 11.12 (2017): 12378-12384. Text and figures have been adapted with permission from the authors. Copyright 2017 American Chemical Society. First authorship of this work is shared between Dr. Randy Sabatini and me. Dr. Sabatini prepared the films used in the study and assisted with optical measurements. I led the effective-mass approximation theoretical work, TA optical measurements, and TA data analysis. Marc Lejay contributed in PLQY data collection.

4.1 Auger Recombination
Auger recombination is a non-radiative recombination mechanism whereby an electron and a hole recombine but then transfer the energy to another bandedge carrier. This bandedge carrier will then be excited further into the continuum of the valence or conduction band, in the case that the carrier is a hole or an electron, respectively (Figure 4.1)\textsuperscript{137}. In most material systems, this hot carrier will then drop to the bandedge in a matter of femtoseconds via thermal relaxation ultimately losing the energy non-radiatively\textsuperscript{138}. It has been found that the rate of Auger recombination increases dramatically as bandgap decreases due to increased coupling between valence and conduction bands.

In a semiconductor under typical operating conditions (i.e. $n \approx p$), the total recombination rate of charge carriers can be described by:

$$R = An + Bn^2 + Cn^3,$$

where A, B, and C are the Shockley–Read–Hall, radiative, and Auger coefficients, respectively. Correspondingly, each term in Equation 4.1 corresponds to the Shockley–Read–Hall, radiative, and Auger recombination rates. As the highest order process, Auger recombination becomes most significant at higher carrier densities. High intensity applications such as lasing and high power LEDs, could therefore exhibit much higher Auger rates which could in turn affect device performance.

![Figure 4.1 Auger recombination.](image)
In QD films, Auger recombination can occur via three possible pathways: (1) intradot biexciton Auger recombination, (2) trap-assisted Auger recombination, and (3) diffusion-assisted Auger recombination (Figure 4.2). Intradot biexciton Auger recombination occurs when two excitons form within a single quantum dot; one exciton then recombines, transferring energy non-radiatively to a remaining charge carrier. The transferred energy will in turn be lost rapidly via thermal relaxation of the hot charge carrier. In trap-assisted Auger recombination, one charge carrier in a biexciton fills a trap, and energy is subsequently transferred to another bandedge charge carrier. Generally, trap-assisted Auger has been found to exhibit faster Auger recombination rates than those exhibited by a typical biexciton, rendering trap-assisted Auger recombination particularly detrimental to PLQY. In diffusion-assisted Auger recombination, the concentration of charge carriers in a quantum dot is increased by means of diffusion. The larger charge carrier concentrations lead to a higher probability of non-radiative Auger recombination. The latter mechanism increases with charge-carrier mobility of a film.

![Figure 4.2 Auger recombination mechanisms in QDs](image)

(a) Radiative recombination (b) Traditional intradot biexciton Auger recombination. (c) Trap-assisted Auger recombination, where a carrier interacts with a trap state. (d) Diffusion-assisted Auger recombination.
A variety of strategies have been investigated to inhibit Auger recombination in QDs. Strategies to reduce these effects have included passivating ligands,\textsuperscript{142} low-trap quantum dot syntheses,\textsuperscript{10,143} and core-shell structures.\textsuperscript{32} Each has improved PLQY by mitigating trap-assisted pathways, and consequently some have had success inhibiting Auger recombination. These strategies have enabled advances in QD photovoltaics\textsuperscript{144} and photodetectors,\textsuperscript{95} although the impact of such strategies on intradot Auger recombination in lead chalcogenide QDs has not been studied.

4.2 Modelling

I sought to quantify the effect of the shell’s properties on the intradot biexciton Auger recombination in a QD core-shell structure. The Auger rate can be calculated using the Fermi Golden Rule\textsuperscript{105}:

\[
\frac{1}{\tau_A} = \frac{4\pi^2}{\hbar} |M_{if}|^2 \frac{1}{\Gamma_f},
\]

where \(M_{if}\) is the electronic matrix transition element of the Coulomb interaction coupling the initial (i) and final (f) excitonic configurations, and \(\Gamma_f\) is the total dephasing rate of the final higher order carrier; the latter accounts for the case when the confinement potential is greater than the energy of the final state and can be understood as a broadening term. In Equation 4.2, the Auger recombination rate is controlled by the transition element \(M_{if}\), which can be determined using one-dimensional wavefunctions by

\[
M_{if} = \langle \Psi_i | V(x_1 - x_2) | \Psi_f \rangle
\]

\[
= \int \varphi_{cbe}^*(x_1) \varphi_{cbe}^*(x_2) V(x_1 - x_2) \varphi_{vbe}(x_1) \varphi_{cbv}(x_2) dx_1 dx_2,
\]
where the potential, $V$, is the Coulomb repulsion between charge carriers: $V(x) = \frac{e^2}{\kappa|x|}$, and $\varphi_{cbe}$, $\varphi_{vbe}$ and $\varphi_{cbc}$ represent the conduction bandedge, valence bandedge and conduction band continuum wavefunctions, respectively. Details of computations are provided in Appendix A.2.

![Graph](image)

**Figure 4.3 Auger recombination rate as a function of shell thickness in QDs.**

I validated the model by calculating the dependence of Auger recombination on shell thickness (Figure 4.3). I found that the rate of Auger recombination is strongly inhibited as the thickness of the shell is increased, agreeing with previous work. As the shell thickness is increased, the contrast is also increased between the localized bandedge carrier and the delocalized Auger-excited continuum mode. This contrast is directly manifested as a reduction in the Coulomb integral determining the matrix element in Equation 4.3. In addition to the general trend, however, the matrix element exhibits an oscillatory behavior as a function of shell thickness, which has been reported previously in theoretical work that employed a Kane model formalism.
I sought to determine whether varying the bandstructure of a shell material in a core-shell structure could modulate Auger recombination in a QD. A core-shell band structure would modulate the wavefunctions involved in Auger recombination, and could thus vary the value of the Coulomb integral determining the matrix element in Equation 4.3 (Figure 4.4). To explore the optimal core-shell band structure for suppressed Auger, we studied the effect of varying core-shell band edge offsets. We identified three distinct regimes of influence of confinement on Auger rates as a function of the amplitude of the conduction/valence bandedge offset (Figure 4.5).

I denoted the first regime – that having a small conduction/valence bandedge offset – the delocalized:delocalized regime: the lowest-lying state extends substantially over the entire extent of the core:shell dot, as does the higher-lying continuum mode. As a result, the matrix element, $M_{df}$, is appreciable reduced relative to the unconfined case. This stems from a delocalization of the single-lobed excitonic mode and a concurrent delocalization of the multi-noded continuum mode reducing the modal overlap. As the offset is increased, we enter the localized:delocalized regime, wherein the lowest-lying state is now localized to the core, whereas the higher-lying state remains unconfined. In this case, the matrix element is reduced
further due to reduced modal overlap. In the third, highest-offset regime, both the initial and final states are strongly localized. This provides a maximum overlap and the highest Auger rate observed herein. The unconfined QD can be seen as an extreme version of this localized:localized regime, and therefore leads to relatively high Auger recombination rates.

![Diagram](image)

**Figure 4.5 Auger recombination rates as a function of core-shell bandedge offsets.** $E_{CS}$, $E_{CC}$ and $E_g$ represent the shell bandedge, core bandedge and core bandgap, respectively. Three regimes are identified: DD (delocalized-delocalized): delocalized bandedge state couples to delocalized high-order mode (left green); LD (localized-delocalized) localized bandedge state couples to delocalized high-order mode (right green); and LL (localized-localized): localized bandedge state couples to localized high-order mode (red).

I found that small-offset shells are best at keeping outside of the localized: localized regime (red in **Figure 4.5**) and minimizing Auger compared to the higher offset cases. This is a general finding for inhibiting Auger in QD core-shell structures.
4.3 Measuring the Auger rate in QDs

In order to determine Auger recombination rates in QD films I used TA spectroscopy. TA data were collected for QD films for 7 ns with time steps exponentially increasing in time delay. QD films typically exhibit a single ground state bleach (Figure 4.6a). As a result of thermal relaxation, this bleach red-shifts over time to the bandedge, and it is at this bandedge wavelength that the transient signal is analyzed.

![Figure 4.6 Auger recombination rate analysis.](image)

(a) Contour plot of CQD-OLA, showing spectral changes as a function of time. (b) Power dependent kinetic traces at the exciton bleach. (c) TA signal at long times, after Auger recombination, as a function of pump fluence. Fitting this curve allows calculation of excitons per dot. (d) Isolated decay curve of biexciton Auger recombination.
TA measurements were collected at various pump fluences in order to ascertain the dependence of the bandedge bleach on the pump power (Figure 4.6b). Measurements at all pump fluences exhibit a slow decay due to radiative recombination in the QDs. The presence of intradot Auger recombination is signaled by the emergence of a second, faster decay rate in addition to the slower radiative recombination transient. It is assumed that photon absorption in a QD follows a Poisson distribution such that the probability that a QD absorbs $k$ photons can be found by\(^\text{147}\):

$$P(k) = \frac{(N)^k e^{-\langle N \rangle}}{k!} ,$$

(4.5)

where the average number of excitons per QD is given by

$$\langle N \rangle = N_p \sigma_c ,$$

(4.6)

where $N_p$ and $\sigma_c$ represent the number of photons incident on the QD and the absorption cross-section per dot, respectively.

After the multiexcitons have recombined via Auger processes, there is a period with a much slower transient due to radiative recombination. The latter process is effectively constant over the course of nanoseconds for lead chalcogenides. At this point in time the total bleach can be seen as an equal contribution of all single exciton and multiexciton processes such that $B_{\text{long-time}} = B_{\text{sample}}(P(1) + P(2) + P(3) + \cdots)$, where $B_{\text{sample}}$ is the bleach for the entire ensemble of QDs in the sample. All multiexciton processes only contribute a single exciton to the total bleach at this point since Auger recombination has reduced all multiexcitons to single excitons. The total bleach after Auger recombination processes can therefore be found by:

$$B_{\text{long-time}} = B_{\text{sample}}(1 - P(0))$$

(4.7)

$$= B_{\text{sample}}(1 - \exp(-N_p \sigma_c)) .$$

(4.8)
I then fit the measured long-time bleach (i.e., ~8 ns) as a function of pump fluence to Equation 4.8 to determine $\sigma_c$ and $B_{\text{sample}}$ (Figure 4.6c). This former is used to determine the average number of excitons per dot produced by a given pump fluence $\langle N \rangle$, according to Equation 4.6 (Figure 4.6b).

At low pump fluences ($\langle N \rangle \ll 1$) multiphoton absorption is negligible, and we observe only single exciton recombination. At intermediate pump fluences ($\langle N \rangle \approx 1$), shorter-lived biexciton intradot Auger recombination can be discerned. At higher pump fluences, Auger recombination dominates. I isolated the various multiphoton Auger processes by employing multiple exponential fittings at each pump fluence, allowing the extraction of the biexciton intradot Auger lifetime (Figure 4.6d).

It is important to identify the effect of diffusion-assisted Auger on the TA traces to avoid misinterpretation and distinguish intradot Auger from the longer-lived diffusion-assisted process. Diffusion-assisted Auger becomes appreciable in highly conductive films, such as perovskite-shelled QD films, which enable charge carrier transfer between dots thus promoting Auger recombination. Diffusion-assisted Auger does not pose an obstacle to achieving gain in these materials, in contrast with intradot Auger, since the gain lifetime is limited by the fastest Auger recombination process, and intradot Auger recombination is faster than diffusion-assisted Auger in each sample studied herein.

To distinguish diffusion-assisted Auger from other transients in TA, it is necessary to investigate ‘flatness’ of the TA signal at long time delays (~7 ns). Samples with appreciable diffusion-assisted Auger recombination do not reach a constant bleach at 7ns but instead continue to decay. For such samples, fitting is used to isolate single exciton radiative recombination, biexciton intradot Auger, any higher order intradot Auger that may be present, and diffusion-assisted Auger. This process is depicted in the schematic of Figure 4.7 (note: this is a schematic, not actual data). Since all intradot Auger processes will take place much faster than radiative recombination and diffusion-assisted Auger, it is assumed that the latter will solely inhibit radiative recombination. Therefore, for the fitting of Equation 4.8 it is assumed that the radiative recombination and diffusion-assisted Auger amplitudes add up to
the total long-time bleach $B_{long-time}$, that would be expected of the sample if diffusion had not reduced the single exciton population.

\[
\delta A(t) = B_{\text{rad}} + B_{\text{diff}} e^{-t/\tau_{\text{diff}}} + B_{\text{AugerXX}} e^{-t/\tau_{\text{AugerXX}}} + f_{\text{AugerXXX}}(t) + \ldots, \quad (4.9)
\]

where $B_{\text{rad}}$, $B_{\text{diff}}$, $B_{\text{AugerXX}}$, and $B_{\text{AugerXXX}}$ represent the bleach amplitudes of radiative, diffusion-assisted Auger, biexciton, and triexciton intradot Auger, respectively. And the long-time bleach is given by $B_{long-time} = B_{\text{rad}} + B_{\text{diff}}$. In poorly conductive films, the long-time bleach is simply $B_{long-time} = B_{\text{rad}}$.

4.4 Perovskite shelling of PbS QDs

Figure 4.7 Schematic depicting the process to account for diffusion-assisted Auger

Samples with appreciable diffusion-assisted Auger recombination do not reach a constant bleach at 7ns but instead continue to decay.
The impact of core-shell structures on intradot Auger recombination in lead chalcogenide QDs has not been studied. The suppression of Auger recombination in core-shell systems has, however, been demonstrated in allied QD systems (CdSe\textsuperscript{30,145} and InAs\textsuperscript{29}). Motivated by my computational findings, I decided to search for a shell system that could inhibit Auger recombination in lead chalcogenide QDs.

Few materials have been found to grow on PbS QDs. CdS shells have been grown on PbS; however, synthetic challenges arise in growing thick shells larger than 1-2 monolayers\textsuperscript{32}. Recently, the development of perovskite shelling has enabled the growth of thicker shells on PbS QDs\textsuperscript{112,113,148}. Interestingly, the PbS-MAPbI\textsubscript{3} perovskite system has a small conduction/valence band offset with respect to PbS\textsuperscript{115}, making it promising to reduce Auger recombination in PbS QDs according to my computational study. I sought to distinguish, and quantify separately, the effects of passivation and wavefunction delocalization associated with bandstructure engineering on Auger recombination in PbS QDs. I isolated these effects by comparing perovskite shelling to a number of different approaches to PbS QD passivation.

![Figure 4.8 Calculated Auger rate in PbS core-shell QDs](image)

**Figure 4.8 Calculated Auger rate in PbS core-shell QDs.** Traces depict normalized Auger rate as a function of core-shell bandgap offset for PbS QDs of 5 and 10 nm.
The Auger rate was first computed for PbS core-shell QD structures according to the methodology presented in an earlier section. Details for these computations are included in Appendix A.2. The calculated Auger rates show reductions in the Auger rate by orders of magnitude with small-band-offsets between the PbS core and the shell (for materials like MAPbl3) (Figure 4.8). For comparison, the x-axis asymptotically approaches the unshelled QD case ($E_{CS} - E_{CC}/E_g \to \infty$). Auger rates decrease for perovskite shelled PbS QDs, but the effect is diminished for larger QDs. The reduced enhancement may be attributed to weaker Coulombic interactions between charge carriers in larger QDs (i.e., large CQDs inherently exhibit slower Auger recombination rates).

I next sought to investigate whether these ideas were borne out experimentally. The Auger recombination lifetime analysis was performed on both 950 nm PbS oleic acid passivated QDs (QD-OA, Figure 4.9a), and also on perovskite shelled QDs (QD-Per, Figure 4.9b). The 950 nm QD-OA film exhibited an Auger lifetime of $17\pm3$ ps, and this agrees well with previously reported values.149,150 After accounting for diffusion-assisted Auger in QD-Per films, the intradot Auger lifetime is found to exhibit an improvement of over one order-of-magnitude when perovskite shelling is employed on 950 nm CQDs. A summary of these decay processes, their lifetime, and their respective contributions to the ultrafast transient is provided in Table 4.1.

Table 4.1 Decay components observed experimentally in 950 nm QD. Data taken from TA decay traces at $<N>\approx 1$ excitation. The single exciton decay is orders of magnitude greater than that of the other decay mechanisms and is therefore seen as a constant (non-transient) component at the ps scale.

<table>
<thead>
<tr>
<th>Decay Type</th>
<th>QD-CdS</th>
<th>QD-Cl</th>
<th>QD-Per</th>
<th>QD-OA</th>
</tr>
</thead>
<tbody>
<tr>
<td>τ (ps) B</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radiative</td>
<td>NA</td>
<td>0.66</td>
<td>NA</td>
<td>0.04</td>
</tr>
<tr>
<td>Auger</td>
<td>40 ± 10</td>
<td>0.25</td>
<td>45 ± 10</td>
<td>0.1</td>
</tr>
<tr>
<td>Diffusion-Assisted</td>
<td>3·10^3 ± 10^3</td>
<td>0.09</td>
<td>4·10^3 ± 10^3</td>
<td>0.15</td>
</tr>
</tbody>
</table>
In order to isolate surface passivation and band structure effects on Auger recombination, two additional samples were tested: Cl-passivated 950 nm PbS CQDs (QD-Cl, Figure 4.9c) and thin CdS shell 950 nm PbS CQDs (QD-CdS, Figure 4.9d). The former had previously been developed as a means of improving passivation in chalcogenide QDs. The latter represents one of a small number of strategies to grow shells on lead chalcogenide CQDs; previous studies have found that thin CdS shells have led to improved PLQY evidencing improved passivation.

Interestingly, QD-Cl and QD-CdS exhibit only moderate improvements compared to QD-OA. The slight improvement can be attributed to the elimination of surface traps and consequently trap-assisted Auger via such passivation schemes. However, passivation does not affect intradot Auger recombination in these systems: intradot Auger recombination can be suppressed only by means of band engineering to manipulate wavefunctions that reduce the matrix element representing the Auger recombination process. The delocalization of wavefunctions caused by the band diagram in QD-Per leads to the much more notable enhancement in Auger lifetime, consistent with the theoretical modeling.
Power dependent kinetic traces at the exciton bleach for (a) QDs-OA, (b) QD-Per, (c) QD-Cl, and (d) QD-CdS. Auger lifetime of QD-Per is much longer than the other samples.

The Auger rate was also investigated in NIR 1300 nm PbS QDs (Figure 4.10b and Table 4.2). In this case, untreated PbS QDs are passivated by oleylamine (QD-OLA). The Auger lifetime has improved for this system as well, albeit to a lesser degree. This result agrees with the theoretical treatment presented earlier. It is evident that smaller QDs exhibit a more drastic enhancement due to an appropriate shell compared to the unshelled Auger rate value \( \frac{E_{CS} - E_{CC}}{E_g \to \infty} \).
(a) Intradot biexciton Auger lifetime for 950 nm QDs. (b) Intradot biexciton Auger lifetime for 1300 nm QDs.

Table 4.2 Decay components observed in 1300 nm QDs.

<table>
<thead>
<tr>
<th>Decay Type</th>
<th>QD-OLA</th>
<th>QD-CdS</th>
<th>QD-Per</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>τ (ps)</td>
<td>B</td>
<td>τ (ps)</td>
</tr>
<tr>
<td>Rad.</td>
<td>NA</td>
<td>0.23</td>
<td>NA</td>
</tr>
<tr>
<td>AugerXX</td>
<td>114±15</td>
<td>0.29</td>
<td>128±11</td>
</tr>
<tr>
<td>Diff.</td>
<td>900 ± 300</td>
<td>0.48</td>
<td>∞ 0.29*</td>
</tr>
</tbody>
</table>

*Both diffusion and single exciton lifetimes were too long to measure accurately for 1300nm QD-CdS. Therefore, the remaining amplitude was split between the two of them; while their sum is accurate, their specific amplitudes are arbitrary. The amplitude of the intradot biexciton Auger is unaffected and should remain accurate.

4.5 Summary

I found that MAPbI$_3$ perovskite shelling decreases the rate of Auger recombination by over one order of magnitude in PbS QD films compared to the unshelled QDs. Ultrafast TA spectroscopy allowed the identification and isolation of 3 different types of Auger recombination: intradot Auger, trap-assisted Auger, and diffusion-assisted Auger. By comparing perovskite shelling to various methods of PbS QD passivation, the effects of
passivation and modal delocalization due to band structure on Auger recombination were separated. Furthermore, calculations corroborate the finding that only modal delocalization, and not passivation, has a large impact on intradot Auger recombination. The enhanced Auger lifetimes enabled by perovskite shelling could make use of the inherently high mobility of perovskite semiconductors to allow the development of solution-processed electrically-injected NIR CW lasing. These results provide the foundation for further work on lead chalcogenides in the pursuit of NIR CW lasing and other high intensity applications.
5 Engineering Quantum Well Morphology

Perovskite QWs (PQWs), unlike perovskite QDs remain unconfined along two-dimensions which suggest anisotropic, albeit improved charge transport among two axes. In addition, PQWs have attracted attention as means of addressing long-term optoelectronic device stability\textsuperscript{127}. PQWs have also proven exceptional for light-emitting applications, leading to record-performing devices\textsuperscript{64,65}. Some characterization has been performed on these materials, yet obtaining a detailed understanding of the nature of films, such as crystal growth, well-thickness distribution, and orientation, remains to be fully developed. These structural properties can have important consequences to device performance due to effects on the energy landscape homogeneity and anisotropic charge transport along different directions of PQWs, respectively. In this chapter, I use in-situ grazing incidence X-ray diffraction and TA spectroscopy to improve understanding of the physical and chemical composition of PQW films. My investigation finds that the deposition technique, intercalating ligand, stoichiometry of precursors, and solvent each can vary the QW orientation and thickness distribution systematically, enabling a level of control for future PQW-based devices.

I focus on methylammonium (MA) lead iodide PQWs with phenethylammonium (PEA) and n-butylammonium (BTA) as the large intercalating cation, but also discuss the generality of the findings. I use the value $n$ to identify the number of perovskite layers in a single well; whereas $\langle n \rangle$ identifies the average number of perovskite layers per well in a film.

This chapter contains work from “Compositional and orientational control in metal-halide perovskites of reduced dimensionality” published in *Nature Materials* 17.10 (2018): 900-907. Text and figures have been adapted with permission from the authors. Copyright 2018 Springer Nature. I led the project, executed TA measurements, TA data analysis, and all theoretical modelling. Aryeh Gold-Parker, Rahim Munir, Zhenyu Yang, and I carried out the various synchrotron X-ray scattering experiments over the course of various months. Aryeh Gold-Parker and I performed the analysis of the X-ray scattering data. I am the sole first author of this work.
5.1 Elucidating the Quantum Well Growth Mechanism

X-ray scattering offers a probe capable of determining the presence of crystalline materials throughout a variety of processes in-situ. I sought to determine the mechanism of PQW formation by investigating the evolution of grazing incidence wide-angle X-ray scattering (GIWAXS) during film deposition. I first present results with DMSO as the solvent and discuss the effect of varying solvents further below.

![Figure 5.1 Formation kinetics of PQWs via in-situ GIWAXS.](image)

(a) X-ray scattering evolution during the film spinning process highlights the formation of an intermediate phase after the antisolvent drip. (b) Measured GIWAXS pattern after spinning and before annealing.

Upon spin-casting the precursor solution, a broad low-angle scattering consistent with a colloidal precursor sol-gel is observed (Figure 5.1a). Chlorobenzene was dropped onto the film about halfway into the spin-casting process in order to precipitate the precursors, speed up the elimination of solvent and improve film quality, as was discussed in Section 2.4. Following the antisolvent drip, the features change abruptly leading to broad diffraction peaks (e.g., \( q=0.65 \ \text{Å}^{-1} \) at 45s) that do not belong to either perovskite or precursor compounds. Similar diffraction patterns have been observed before in 3D perovskites, where such patterns were attributed to intermediate crystalline complexes made up of perovskite precursors and solvent molecules\(^{35,152,153} \). Scattering consistent with this intermediate phase appears after the
antisolvent drip and intensifies during spin-coating, evidencing the formation of the solvent complex phase during spin-coating. Seconds after the drip, some perovskite diffraction begins to appear. At the end of the spin-coating, the film exhibits predominantly solvent complexes coexisting with some PQW diffraction (Figure 5.1b).

A more dramatic transformation is observed as the film is annealed (Figure 5.2a). During this process, GIWAXS clearly depicts the emergence of perovskite peaks with a commensurate subsidence of the intermediate solvent complex peaks over the course of 10 minutes of annealing. More datasets are included in Appendix B.3. Furthermore, the intermediate complex peaks, unlike those of PQWs, exhibit nearly anisotropic ring patterns.

I analyzed the intensity of the perovskite and intermediate solvent complex peaks over time during the annealing process to study the kinetics of PQW formation. Interestingly, the rate of subsidence of solvent-complex peaks mirrors the rate of perovskite peak emergence showing a direct transition from solvent complex to PQW. The same analysis is performed on different \( n \) PQW samples and bulk perovskite showing similar trends, suggesting similar growth mechanisms. The rates of evolution may differ due to increases in enthalpy of formation for PQWs of decreasing thickness\(^6\).

**Figure 5.2 Evolution of X-ray scattering after annealing.** Azimuthally-integrated GIWAXS data for (a) \( \langle n \rangle = 10 \) film and (b) \( \langle n \rangle = 5 \) film during annealing demonstrate the
formation of solvent complexes and their evolution. Evolution of amplitudes of DMSO-complex and PQW peaks over time reveal the mechanism for PQW formation (inset in (a)).

The evolution of the scattered intensity illustrates the formation kinetics of PQWs (Figure 5.3). After the deposition of the precursor solution by spin-casting, the resulting film is made up of largely unoriented intermediate solvent-precursor complexes (ring patterns on Figure 5.1b) amongst dissolved large cation. The latter point is evidenced by the lack of crystalline cation (in this case PEAI) peaks and the fact that the solvent complex diffraction pattern is identical to the complex for bulk perovskite formation, where large cation is not present (see Appendix B.3). Previous reports found that the large solvent complexes slowed down the reaction between perovskite precursors ultimately leading to larger and more uniform bulk perovskite grains. In 2D and quasi-2D perovskites, however, the large solvent complexes provide a framework that may facilitate the construction of PQWs. The results would further suggest that as the film is annealed, solvent molecules begin to weaken the complex as they evaporate out, allowing newly released PbI$_2$ layers, MAI and partially formed complexes to nucleate and grow PQW grains. It was concluded in bulk perovskite studies that the expanded lattice of solvent complexes could allow reagents to enter, which could facilitate the nucleation of organic bilayers in PQW films. During this process, half-formed complexes and PbI$_2$ layers could re-align amid solvent and dissolved cation. This is evidenced by the fact that intermediate crystalline solvent complexes are predominantly unoriented, but as these grow existing grains they align with the rest of the PQW crystallites. By the end of the annealing process, all solvent complexes have been completely replaced by PQW.

**Figure 5.3 Proposed mechanism of PQW crystal nucleation and growth.** In-situ studies indicate the formation of solvent complexes (blue segmented rhomboid) which disintegrate
partially providing a framework for the nucleation (bottom right at each stage) and growth (left/top) of PQWs during the annealing process. Dissolved large cations in the film (PEA in this case) form organic bilayers in the growth process when the local concentration is high enough.

PQW formation characterized in this study agrees with prior work studying two-dimensional nanocrystal formation of different materials. Previous studies have found that unlike formation of layered crystal structures (e.g., MoS$_2$), formation of 2D and quasi-2D nanostructures for non-layered systems (e.g., wurtzite and zinc blende) is mediated by a layered mesophase made up of precursors and solvents$^{155-157}$. These nanosheets provide a template for 2D nanostructure nucleation and growth. These mesophases are in turn facilitated by the use of layered precursors such as CdCl$_2$ and CdI$_2$$^{155,158}$. PQW formation follows a similar pathway. In this case, however, a low activation energy for PQW growth could allow them to form rapidly in-film during the annealing process$^{154}$.

5.2 Quantum Well Size Distribution

![Figure 5.4 Simulated powder XRD of pure PEA$_2$MA$_{n-1}$Pb$_n$I$_{3n+1}$ PQWs.](image)

Diffraction patterns show the clearest distinctive features in the small-angle domain due to (001) PQW reflections.
X-ray diffraction (XRD) was first used to probe the crystallinity of films. Ordered QWs of varying thicknesses can be readily distinguished from the analysis of the small angle domain of XRD patterns. The XRD pattern of QWs of various sizes was simulated in order to facilitate this analysis (Figure 5.4)\textsuperscript{159,160}. The strongest diffraction peak of PQWs corresponds to their (001) diffraction. In PEA-MAPbI\textsubscript{3} for instance, that corresponds to d-spacings of 1.66 to 7.40 nm, for wells of thickness $n=1$ to 10. Grazing-incidence small-angle X-ray scattering (GISAXS) measurements (see Appendix B.3) were performed on films of various $\langle n \rangle$ values to determine the distribution of QW thicknesses. The integrated GISAXS data (Figure 5.5a) can be compared to the theoretical small-angle XRD pattern (Figure 5.5b) to identify the presence of particular crystal grains. Ordered domains of $n = 1, 2$ and 3 can be identified in varying proportions for samples of $\langle n \rangle = 2, 5$, and 10, but no distinct peaks for ordered regions $n > 3$ can be discerned.

![Figure 5.5](image.png)

**Figure 5.5 Small-angle diffraction of PQW films.** (a) Cuts along qz axis of experimental GISAXS measurements on real samples show distinct features that reveal a mixed population of RDP thicknesses (asterisk identifies space between detectors). These peaks can be labelled via (d) theoretical SAXS pattern.
The lack of distinct small-angle XRD peaks for ordered regions with \( n > 3 \) does not preclude the existence of \( n > 3 \) wells; instead, it indicates merely that sufficiently coherent crystallographic regions with \( n > 3 \) are not present. The intensity and width of an XRD peak will depend on the crystallinity or spatial coherence of the given ordered domain. In PQWs, the (001) diffraction peak of a given QW will be determined by its ordered domain’s spatial coherence. For instance, the peak width and intensity of an \( n=4 \) peak will vary depending on whether the ordered region is composed of 4 identical adjacent \( n=4 \) QWs (high intensity and narrow peak) or of a random mix of QWs (low intensity and broad peak) including a few of \( n=4 \). Therefore if a grain is made up of a random assembly of QWs or does not exhibit enough repetitions of the same QW, it will exhibit a weak and broad XRD peak. These effects are enhanced in large-\( n \) quantum wells due to the increased dimensions of a large-\( n \) grain (e.g., 5 repetitions of \( n=10 \) is about 40nm).

**Figure 5.6 TA spectra of single crystal PQWs.** TA spectra of layered single crystals of (a) \( n = 2 \), (b) 3, (c) 4, and (d) a segment exhibiting clear \( n = 3-7 \) phases.
Interestingly, however, in samples $\langle n \rangle = 5$ and 10, scattering below 2 nm$^{-1}$ is observed compared to the baseline in the bulk sample: this suggests incoherent large QWs. In addition, the asymmetry of the $n = 3$ peak in the $\langle n \rangle = 5$ sample suggests the presence of larger QWs, perhaps $n = 4$. To determine the distribution of QWs in the films, I used ultrafast transient absorption (TA) spectroscopy.

Figure 5.7 TA spectra of spin-cast PEA-based films. (a) $\langle n \rangle = 1$, (b) 2, (c) 3, (d) 5, (e) 10, (f) 40, and (g) bulk reveal the broad distribution of QW thicknesses extending well beyond $n=5$. TA on the front (red) and back (blue) side of films indicate a higher concentration of thin wells at the top of films. TA spectra change dramatically after a few ps due to carrier funneling into thicker wells. (l) Predicted TA bleach for QWs of size $n$ enable labelling of PQW thicknesses and fitting of the ultrafast spectra enabling the identification of the distribution of bleach intensities (inset histograms).

Because of quantum confinement in PQWs, the bandgap of the material increases as the thickness of the QW is decreased. With an exciton Bohr radius of 25 Å$^{161}$, a strong dependence of the bandgap energy on QW thickness is expected for QWs with up to 5 perovskite layers, and only small shifts in the bandgap energy thereafter. In order to understand the observed TA spectra of PQWs, we also analyzed single crystals$^{162}$. TA spectra were acquired for these
crystals, allowing us to identify the distinctive bleach peaks for single crystals of \( n = 2, 3, \) and 4 (Figure 5.6a-c). Although these crystals are predominantly pure-phase, it is nonetheless possible to identify regions of crystals with multiple QW thicknesses (Figure 5.6d). TA spectra on PQW films (Figure 5.7), in contrast, illustrate the large distribution in QWs that is not discernable in GISAXS.

In the series of spin-cast and hot-cast PQW films, distinct peaks are seen for QWs of \( n < 6 \), and a separate bulk peak can also be identified. Large \( \langle n \rangle \) quasi-2D samples exhibit distinctive bleach features between those of \( n = 5 \) and bulk, indicating the formation of wells with large \( n \) values. This large-\( n \) TA feature further red-shifts for samples of increasing \( \langle n \rangle \), suggesting an increase in the average QW thickness. To estimate the distribution of QW sizes indicated using TA spectral features, I sought to determine the bandgap dependence on well-thickness. I followed a procedure corroborated by both empirical fitting (validates by data collected in this work and previous literature) and an effective-mass-approximation model (see Appendix B.3). The predicted TA bleach wavelength is obtained by adding a blue-shift (resulting from exciton-exciton interactions and the Moss-Burnstein effect in narrow wells and larger bulk-like wells, respectively) to the calculated bandgap value (Figure 5.7h). The TA spectra are then fit to model the bleach peak of the QWs of varying thicknesses with the predicted bandgaps, and the data are presented through histograms in the insets of Figure 5.7a-g. These allow determination of the QW thicknesses exhibited in an PQW film, but do not directly represent the QW thickness distribution. There are two reasons for this: (1) the oscillator strength for QWs varies as a function of the \( n \) value, and is expected to increase as QW thickness decreases; (2) the positive feature (red-shifted relative to the main bleach peak) identified in pure single crystals inhibits the total bleach observed for the next higher-\( n \) valued QW in films. These effects are expected to lead to a higher measured bleach intensity for low-\( n \) QWs, in particular \( n = 2 \).

The TA bleach fitting demonstrates a QW distribution peaked around \( \langle n \rangle \) with a standard deviation that increases with \( \langle n \rangle \). Among the PEA-based spin-cast films for instance (Figure 5.7), sample \( \langle n \rangle = 2 \) is made up of QWs with \( n = 1, 2, \) and 3; \( \langle n \rangle = 3 \) exhibits \( n = 1 \) through 10; \( \langle n \rangle = 5 \) exhibits \( n = 2 \) through 15; and \( \langle n \rangle = 10 \) is made up of predominantly \( n = 3 \) to 20. Even the \( \langle n \rangle = 40 \) sample exhibits a bleach with a 6 nm blue-shift with respect to the bulk
feature, evidencing some degree of quantum confinement. This sample is made up of very large wells \((n > 20)\), and fitting reveals a small percentage of ultra-large-\(n\) wells \((n > 40)\) that are energetically indistinguishable from bulk. By measuring spectra of both the front and the back of the film, differences in the populations between the top and bottom of the film can be ascertained\textsuperscript{128}. Higher concentrations of low-\(n\) wells are observed at the surface of all films.

Figure 5.8 TA spectra for spin-cast BTA-based PQWs.

Figure 5.9 TA spectra for hot-cast (a) PEA-based and (b) BTA-based PQWs.
Figure 5.10 TA spectra of $\langle n \rangle = 5$ BTA hot-cast films of various thicknesses. TA spectra of hot-cast films of increasing thickness evidence the accentuated grading distribution effect observed for thicker hot-cast films.

The BTA-based spin-cast PQWs exhibit quite similar spectra to that of their PEA-based counterparts. However, low-$n$ features are enhanced in the former (Figure 5.8). Additionally, the large-$n$ feature is concurrently red-shifted in the BTA-based series, as expected due to the depleted organic ligand. Hot-casting dramatically changes the distribution of PQWs (Figure 5.9). Firstly, a stark contrast is observed between the front and back of the film, indicating an inhomogeneous distribution of QWs with a higher concentration of large-$n$ wells near the surface of the film and low-$n$ wells at the bottom. This contrast is further pronounced as the thickness of the film is increased (Figure 5.10). Second, the distribution of QWs is more sharply centered at $\langle n \rangle$ in hot-cast films.

5.3 Modeling Quantum Well Growth

The growth mechanism detailed in Figure 5.11 can be used to estimate a probability distribution of well thicknesses for a given $\langle n \rangle$-valued sample. The ratio of large cations to the intermediate solvent complexes is the defining parameter behind the probability distribution.
for different QW thicknesses. Since ammonium salts are highly soluble in DMSO, I simplify the model by assuming that large cations are homogeneously distributed throughout the as-deposited film. Furthermore, excess DMSO is provided in the synthesis to ensure homogenous precursor distribution and that solvent does not limit kinetics. The model therefore assumes that the probability of forming a well of a given size is constant throughout the film. Statistics of well formation can be computed analytically as permutations with repetition.

Under the assumption of a homogeneous distribution of dissolved intercalating cation that is both temporally and spatially invariant, the probability of forming a PEAI layer or a PbI$_6$ layer for these is set by the ratio of PEAI to all other precursors used in the initial solution, such that the probability of a new PEAI layer at a given site in a sample $\langle n \rangle$ is:

$$\rho \propto \frac{1}{\langle n \rangle}, \quad (5.1)$$

assuming that the precursor ratio and distribution are the only factors determining the probability, the proportionality sign can be replaced for an equality and the probability of getting a well of size $n$ in a sample $\langle n \rangle$ can be found by:

$$P_n = (\rho)(1 - \rho)^{n-1}(\rho)n = \left(\frac{1}{\langle n \rangle}\right)^2 \left(1 - \frac{1}{\langle n \rangle}\right)^{n-1} n. \quad (5.2)$$

To account for inhomogeneities in the local concentration of the large cation during the growth of PQWs, I also developed a Monte Carlo simulation to verify the validity of the assumed homogeneous precursor distribution. As PQWs grow, there is a point in time when there is sufficient dissolved large cation to nucleate an organic bilayer. At this point the availability of the large cation is temporarily depleted around the growing PQW. This would mean that the actual growth of PQWs would lead to a distorted distribution compared to the analytically computed populations. The Monte Carlo Model uses a fixed probability of forming an organic bilayer (the probability of which is set by the ratio of PEAI to all other precursors). Once an organic bilayer is formed the probability of forming an organic layer is temporarily reduced.
and slowly increased as further perovskite monolayers are formed. The rate of variation of large cation ratio will vary in films depending on viscosity, solubility of precursors, and selective reactivity, which would in turn vary the distribution and morphology of PQWs. These variations in film morphology as observed in the model can be enacted by varying precursors (such as the ligand and the perovskite components), solvent, and their ratio.

As soon as an organic bilayer is formed, the PEA around the growing PQW is used up temporarily depleting the distribution. As a result, the probability of forming an organic bilayer is much lower momentarily. As the PQW continues to grow, the local distribution of PEA goes back to normal due to diffusion. The Monte Carlo takes this phenomenon into account thereby correcting the simpler analytical model.

I first computed the probability of forming a single well of size $n$ (in a given film $\langle n \rangle$) and compared it to the probability of forming a highly crystalline domain with well size $n$ that would exhibit a distinct XRD signal (Figure 5.12a). This analysis finds it drastically less probable to form an entire domain of a given well-thickness than it is to form a single well. Furthermore, this probability decreases significantly with well size such that an entire grain of $n > 5$ is highly unlikely. This finding reconciles the results from GISAXS and TA such that despite the abundant presence of large QWs, poor spatial coherence for large QWs leads to broad weak diffraction peaks that merge together as observed in the scattering $< 2$ nm$^{-1}$.

Figure 5.11 Ligand concentration determines probability of forming different n QWs.
As seen in Figure 5.12b, PQWs are predicted to obey a lognormal distribution in well thicknesses, denoting a tighter standard deviation for low-\(n\) wells than large-\(n\) wells. This result agrees well with all other measurements, with one exception. Large bleach peaks for low-\(n\) wells are observed in TA that do not follow the lognormal distribution, which could be attributed to variations in oscillator strength for QWs of different thicknesses. An inhomogeneous distribution of the dissolved large cation throughout the film could also distort the distribution, albeit to a lower degree.

**Figure 5.12 Statistical model of the formation of PQWs.** (a) The theoretical probability of forming a single well or a single grain (defined as 5 consecutive wells) of size \(x\) in sample \(\langle x \rangle\) is computed analytically for the growth model identified assuming a uniform and constant distribution of large organic cation. (b) The population distribution of well thicknesses is computed analytically by the model (continuous) and simulated via Monte Carlo to take into account variations in large organic cation distribution throughout the growth process (squares). Theoretical skew lognormal and symmetric lognormal distributions of well thicknesses centered at \(\langle n \rangle\) are ascertained for the analytical and Monte Carlo models, respectively, agreeing with the measured distributions via TA. The probability distributions in (b) were further normalized by taking into account the total mass difference in different-sized wells.

A Monte Carlo simulation which does not assume constant large cation distribution over time agrees with the analytical expression for distributions at large \(n\) values; however, this more
intricate model leads to a correction in the distribution for thin wells leading to a symmetric lognormal distribution. The adjustment is expected since a depletion in large cation inhibits the formation of very thin wells. For large wells, however, the analytical expression matches the Monte Carlo simulation, i.e., the assumptions in the analytical expression are justifiable in this range.

5.4 QW Orientation

I used GIWAXS to probe the orientation of PQWs in films. These measurements show a strong dependence of orientation of wells on QW thickness (Figure 5.13). QWs with smaller $n$ values are more likely to orient parallel to the substrate, whereas thicker wells ($n > 4$) preferentially orient normal. We observe this behavior to vary gradually as $n$ increases: sample $\langle n \rangle = 1$ yields entirely horizontal-lying wells, whereas $2 \leq \langle n \rangle \leq 4$ exhibit fewer horizontal and increasingly more vertical-standing wells. Hot-cast films exhibit similar trends; but also showed a dramatic reduction in the presence of anisotropic rings, indicating a reduced presence of randomly-oriented wells. Both horizontal and vertical wells are identified in these measurements. Additionally, the thickness of the film is found to have an effect on the orientation of wells: in thin samples of similar precursor ratios horizontal-lying wells far outnumber vertical-standing wells (Figure 5.14).

These observations agree well with nucleation-growth theory and experimental studies in other two-dimensional nanostructures. Previous work has found a substantial energetic barrier in starting a new monolayer in 2D crystals but once nucleated, lateral crystal growth will proceed quite rapidly. In PQWs, precursors are released from their solvent complexes during thermal annealing; these will begin to nucleate monolayers which will grow to certain thicknesses before forming organic bilayers depending on the stoichiometry. The orientation of PQWs could be explained by the varying rates of precursor availability for vertical-standing vis-à-vis horizontal-lying wells due to normal-oriented solvent evaporation. Growth can, however, be cut off depending on the dimensions of the film; a thin film would hinder the growth of vertical-standing wells. This growth model agrees with previous work finding that spin-cast perovskite films undergo homogeneous nucleation. Similar orientation has been
observed in other 2D nanostructures\textsuperscript{167,168}. Multiple examples for each class were studied. The studies in this work were also repeated for different substrates showing the same trends (see Appendix B.3). The morphology of the films was also corroborated by means of topographic atomic force microscopy (see Appendix B.3).

Figure 5.13 Orientational analysis of PQWs. GIWAXS measurements of hot-cast and spin-cast BTA-based (b-k) and PEA-based PQWs (a, d-m) in 4 different size regimes, which along with all other characterizations performed enable a generalized concept of QW morphology in both PEA-based and BTA-based spin-cast films (central diagrams). Pink and yellow circles highlight features that identify parallel-lying and perpendicular-standing PQWs, respectively. All films are 200 nm in thickness, approximately.
The TA and GIWAXS measurements on hot-cast films exhibit some differences compared to spin-cast films. The hot temperature of the substrate in this technique would speed up the transformation from intermediate complexes to PQWs. The rapid transformation could consume the large organic cation in the lower part of the film leaving a lower concentration for the rest of the film, which would explain the gradient in well-thicknesses observed here and in previous literature\textsuperscript{128}, particularly in thicker films. Hot-cast films also exhibit higher degrees of preferential orientation than spin-cast films. This may be due to a change in surface energetics or the fast rate of solvent evaporation. Recent studies on the nucleation of PQWs via hot-casting, find that the hot temperature on one side of the film could alter the nucleation mechanism, leading to heterogeneous nucleation\textsuperscript{169}. As found in previous work, preferential heterogeneous nucleation could lead to such differences in orientation. This could also explain our observations in well thickness distribution.

Among spin-cast films, I identify 4 different types of film formation for PQWs. Films of $\langle n \rangle = 1$ form parallel-aligned pure $n = 1$ wells. Films of $\langle n \rangle = 2$ to 4 are fairly monodisperse, but with more mixing and more random orientation, albeit still a preferential tendency to align

![GIWAXS pattern for thin film $\langle n \rangle = 5$. GIWAXS on a thin-film an $\langle n \rangle = 5$ film reveals a different pattern than that for thick films with the same precursor ratios. Thin films exhibit a higher concentration of flat-lying wells of lower $n$ than thicker films. Thickness is approximately 50 nm.](image)

Among spin-cast films, I identify 4 different types of film formation for PQWs. Films of $\langle n \rangle = 1$ form parallel-aligned pure $n = 1$ wells. Films of $\langle n \rangle = 2$ to 4 are fairly monodisperse, but with more mixing and more random orientation, albeit still a preferential tendency to align
parallel to the substrate. Films of $\langle n \rangle = 5$ to 10 tend to form primarily large wells perpendicular to the substrate, but QWs with small $n$ values parallel to the substrate can still be observed. Finally, films of $\langle n \rangle \geq 10$ still show a preferential orientation of large-$n$ wells to align normal to the surface, but with the addition of anisotropic bulk-like grains present. PEA PQWs no longer exhibit small-$n$ wells in this class, whereas BTA PQWs still do. This could be attributed to the smaller and less bulky nature of BTA which re-distributes more readily than PEA within the solvent enabling a higher probability of forming low-$n$ wells.

An in-depth orientation analysis of GIWAXS patterns was undergone in order to assess orientation of QWs. Here, XRD peaks are identified that distinguish parallel- and perpendicular-oriented wells. The analysis must consider all possible crystallite orientations to ensure that there is not a misinterpretation of the GIWAXS pattern. I used GIXSGUI’s texture mapping features for this analysis\textsuperscript{170}. Figure 5.15 shows the results of texture mapping for $\langle n \rangle=8$ samples assuming that the perovskite unit cell aligns with the (001) surface parallel to the substrate and that the (110) surface is parallel to the substrate. All other alignments were found to lead to GIWAXS patterns that did not match the experimental patterns.

![Texture-mapped GIWAXS of $\langle n \rangle = 8$ sample. Patterns are shown before ‘missing wedge’ correction to facilitate labeling. Plots for linear color scale, texture mapping for alignment of (001) normal to substrate, i.e. horizontal-lying wells (a), and texture mapping for (110) normal to substrate, i.e. vertical-standing wells (b) are shown.](image)

**Figure 5.15** Texture-mapped GIWAXS of $\langle n \rangle = 8$ sample. Patterns are shown before ‘missing wedge’ correction to facilitate labeling. Plots for linear color scale, texture mapping for alignment of (001) normal to substrate, i.e. horizontal-lying wells (a), and texture mapping for (110) normal to substrate, i.e. vertical-standing wells (b) are shown.
The patterns displayed by these two alignments (110 parallel) and (100 parallel) are very similar. It is only with thorough analysis that one can discern the alignment of the crystallites in our quasi-2D films. The clearest peak that can be used to differentiate these two alignments is that at $q=1.6 \ \text{Å}^{-1}$ (due to (211) and (103) in the tetragonal unit cell. This is highlighted in Error! Reference source not found.. (001) alignment should exhibit peaks at both $\sim 20^\circ$ and $\sim 75^\circ$ along the azimuthal angle, but the peak at $\sim 20^\circ$ corresponding to the (103) diffraction has a structure factor that is orders of magnitude weaker than that of the stronger (211) peak at $\sim 75^\circ$. A (110) alignment (with the organic bilayers perpendicular to the substrate) however, exhibits (211) peaks at both $\sim 20^\circ$ and $\sim 75^\circ$, matching the observed experimental patterns for $\langle n \rangle=8$. This alignment can be discerned to some degree in samples with very large wells (e.g. $\langle n \rangle=40$ in Figure 5.13).

![Graph](image)

Azimuthal Angle $\chi$

**Figure 5.16 Intensity as a function of azimuthal angle for $q = 1.6 \ \text{Å}^{-1}$ in $\langle n \rangle = 8$.** The (103) and (211) peaks offer the best distinguishing feature between parallel- and perpendicular-oriented QWs.
The key GIWAXS features used to infer alignment of QWs in PQW films are indicated by pink and yellow circles denoting parallel- and perpendicular-oriented wells in Figure 5.13, respectively. Notably, since thick wells do not exhibit (001) reflections discernible from the bulk, the tetragonal perovskite unit cell within layers is used to determine the orientation of the PQWs.

5.5 Implications for Films and Devices

In the kinetics studies herein, I found that intermediate solvent complexes mediate the formation of wells by slowly providing building blocks to nucleating and growing PQWs as the solvent evaporates out thereby weakening the complexes. The QW polydispersity is thus strongly dependent on the distribution of the large cation throughout the film. Therefore, a homogeneous distribution of large cation should lead to a lognormal distribution of wells centered near the expected \( \langle n \rangle \) set by the precursor ratios. The kinetics of formation of PQWs observed here can be generally applied to most \( R_2A_{n-1}B_nX_{3n+1} \) layered structures in aprotic solvents, although the distribution of well-thicknesses and morphology is dependent on the solvent (e.g., surface wettability) and large organic cation properties (e.g., solubility).

To study the effect of solvent on growth and distribution, in-situ GIWAXS was collected for various solvents. DMSO solutions exhibit the intermediate complexes analyzed earlier which allowed the kinetic analysis. DMF, another commonly used aprotic solvent has been found to form solvent complexes in bulk perovskite as well, but due to lower melting and boiling points has been found to anneal at room temperature in certain conditions. As one might expect, no intermediate complexes were observed, likely due to the volatility of DMF. This likely leads to faster growth kinetics that would hinder crystallinity and film quality. On the other hand, N-Methyl-2-pyrrolidone (NMP) solutions were found to yield a broad peak under 1 Å⁻¹ which disappeared during the annealing process. The weak and broad nature of the intermediate peak would suggest disordered solvent-precursor complexes, which would explain the anisotropic orientation of the resulting films. The selection and ratio of solvents were also found to modify the distribution of QWs (Figure 5.17-19). Increasing the concentration of DMSO and NMP
was found to lead to a red-shift in the QW distribution, whereas the concentration of DMF was found to lead to a blue-shift. This arises from differences in the solubility of the large cation (BTA or PEA) in the different aprotic solvents. In sum, the solvent holds the key to controlling the rate of PQW formation which can ultimately enable tunability of the QW distribution and crystallinity. Furthermore, the formation of precursor complexes in a given solvent also lead to variations in the QW orientation. Different solvents and combinations could enable further fine-tuning of PQW properties.

I also found that the choice of large cation and film deposition method led to variations in the QW distribution. Using BTA instead of PEA in PQWs leads to a higher concentration of low-n PQWs and a concurrent red-shift of the large-n wells. This could be attributed to differences in viscosity due to the variations in solvent which would affect the diffusivity of precursors across the solution. In addition, the selective reactivity between the various ions in the precursor solution, and its modulation by varying the large organic cation, could also affect the

Figure 5.17 TA of PEA-MAPbI₃ spin-casted samples with variations in the solvent ratio. The solvent in these cases is composed of GBL and DMSO. The ratio was calculated with respect to the sum of all perovskite precursor ingredients. For instance, DMSO 1:3 means 1 part DMSO for every 3 parts of perovskite precursor. Samples are PEA-MAPbI₃ deposited by spin-casting of <n>=5 (on left) and <n>=10 (on right).
kinetic rates in PQW formation. Hot-casting leads to well-defined PQW orientation, and QW thickness inhomogeneity: low-n wells tend to form at the bottom whereas large-n wells congregate near the surface of films.

Figure 5.18 TA of normal spin-casted samples with different solvents. The solvent in these cases is composed of GBL and X (where X is either DMSO, DMF or NMP). The ratio was calculated with respect to the sum of all perovskite precursor ingredients. All samples are PEA-MAPbI$_3$ of $<n>$=5 deposited by spin-casting.

Figure 5.19 Diffusion lengths of PEA-based PQWs.
These measurements illustrate the effect of morphology on device performance.

To understand the effect of morphological properties on key device parameters, I measured diffusion lengths PQW films (Figure 5.19)\textsuperscript{171}. I found that films with more vertical-aligned wells ($\langle n \rangle > 4$) exhibit much longer diffusion lengths, comparable to that of bulk perovskite. This is likely due to a decreased occurrence of horizontal wells, and randomly oriented crystal grains.

5.6 Summary

I sought in this chapter to explore how solvents, cations, and film processing impacted the distribution, composition, and orientation of PQWs, a material at the center of investigations of optoelectronic devices with improved stability and performance. In particular, by using in-situ GIWAXS during PQW film deposition, I discovered that intermediate solvent-precursor complexes form and mediate the nucleation and growth of PQWs. By modelling the growth mechanism, I found that variations in the distribution of ligand and rates of depletion can vary the distribution of QWs in a film, which would also lead to morphological variations. TA spectroscopy and GIWAXS characterization of PQW films reveal the distribution and orientation of PQWs, respectively. I found that PQW films are made up of a wide range of QW thicknesses and orientations, but these can be controlled to some degree by varying solvent, ligand, and their ratio.

In addition, I established a remarkable dependence of PQW morphology on the temperature of the substrate during crystal growth. Increasing this temperature modulates the mechanism from homogeneous to heterogeneous nucleation at the interface. This in turn makes orientation more defined. However, an energetic gradient becomes starker as the thickness of films is increased at higher temperatures.

This has implications on devices: the study allowed me to posit new strategies that provide control over the morphology and distribution of the crystallites within PQW films. The two-dimensional nature of PQWs, with their long insulating organic ligands, means that PQWs
exhibit particularly anisotropic charge transport properties, making orientational understanding and control an important ongoing priority for the field.
6 Quantum Well Band Alignment towards Device Enhancement

As detailed in the previous chapter, PQWs have enabled advances in device performance and stability for a number of optoelectronic applications. However, much like the morphological structure of PQWs, their energetic band alignment remains poorly understood. Whereas some studies have found that PQWs exhibit an unconventional type-II band alignment as the number of layers $n$ is increased, others report a typical type-I band alignment between these materials. These conflicting reports have direct implications on charge carrier transport and charge balance in optoelectronic devices.

In this chapter, I propose a material model that rationalizes these seemingly conflicting results. I propose a model wherein film inhomogeneity and surface interface dipoles across ligands shift PQW band alignment. With the aid of density functional theory (DFT) and ultraviolet photoelectron spectroscopy (UPS), I report that the apparent work function of a given quantum well can be varied by the density of ligands at the interface. By surface treating 2D perovskite films, I find that the apparent work function can be shifted down by up to 0.9 eV. I then corroborate the model by a series of pump-probe transient absorption experiments observing selective transfer resulting from these band misalignments in a normal (untreated film). This work has direct consequences on our understanding of 2D, quasi-2D, and mixed 2D/3D devices, since these misalignments form unintentionally in solution-processed PQW films. As a result of these studies, 2D/3D mixed devices can now be understood as type-II interfaces which may block charge transport for electrons but retain efficient hole transport, whereas well- and homogeneously-passivated mixed 2D/quasi-2D devices can act as type-I interfaces without selective charge transfer.

This chapter contains work from a manuscript in preparation. I conceived the idea, led the project, performed UPS and XPS measurements and analysis. Andrew Proppe and I conducted film preparation, TA measurements and analysis. Petar Todorovic measured XRD. Arup Mahata and Filippo de Angelis performed DFT calculations related to this work.
6.1 Band Alignment of 2D Single Crystals

The energy of valence and conduction bandedge levels in semiconductors is central to optoelectronic device design. The ionization energy (IE: energy between the vacuum level and the valence bandedge), electron affinity (EA: energy between the vacuum level and the conduction bandedge), and work function (Wf: energy between the vacuum level and the fermi level), inform the selection of transport layers and contacts to minimize turn-on voltage and ensure charge balance in LEDs, and maximize \( V_{oc} \) and minimize parasitic resistances in PV.

Confinement modelled by an infinite potential well in quantum mechanics finds that the lowest energy mode increases by \( \Delta E = \frac{\hbar^2}{8\mu R_{dot}} \) \((Equation 1.2)\)\(^{116}\). This increase in energy depends on the width of the confinement as well as the effective mass of the charge carrier in question, \textit{i.e.}, electron or hole. Therefore, under this framework a type-I band alignment is expected to result as quantum confinement increases the bandgap of PQWs. Numerous reports in the literature, however, report that PQW films form type-II alignments as the number of layers \( n \), is increased\(^{63,65,121}\). In support of this alignment, ultrafast TA studies have shown that charge carriers indeed transfer from low-\( n \) to high-\( n \) PQWs in a film\(^{128,172}\).

On the other hand, PQWs have been found to exhibit high PLQYs for the lowest bandgap QWs in a film despite a broad distribution of QW thicknesses, evidencing funneling of both electrons and holes towards the largest \( n \) PQWs\(^{65,173}\). Funneling has also been observed by TA\(^{65,174}\). This finding would instead support type-I alignment between PQWs of increasing \( n \). Silver \textit{et al.} recently investigated the IE of BTA \( n=1 \) films by a mix of experimental and computational studies, with the conclusion that BTA \( n=1 \) exhibits type-I alignment with bulk perovskite\(^{175}\).

These conflicting reports of type-I and type-II band alignments among PQWs, have propagated in citing literature leading to contradictory explanations for optoelectronic device performance across the perovskite research community, some attributing their performance to type-I alignments\(^{65,176,177}\), some to type-II alignments\(^{178,179}\), and some speculate that their devices are phase pure such that PQW interfaces are irrelevant\(^{62}\). One source of inconsistency in PQW
band alignment studies could be attributed to film inhomogeneity. As I reported in the previous chapter, PQW films exhibit a wide distribution of well thicknesses\textsuperscript{174}. This makes the interpretation of ionization energy measurements of PQW films misleading. Furthermore, the bandgap distribution in PQW films can even vary across the film thickness, such that the surface \(<n>\) distribution might not reflect the average across the entire film.

A common technique for determining the valence bandedge in semiconductors involves a linear extrapolation to zero to determine the photoemission onset in UPS. Previous studies have noted that this analysis although successful in epitaxial semiconductors, can be difficult to perform and easily misinterpreted in solution-processed materials due to the low density of states (DOS) near the bandedge in such materials\textsuperscript{180,181}. Another source of disagreement among results in the literature could be attributed to issues arising from linear fitting of PQW UPS data\textsuperscript{63,121}. In order to mitigate such factors, the photoemission onset in UPS data is determined in a logarithmic scale.

![Figure 6.1 Band alignment of BTA and PEA perovskite single crystals.](image)

Valence bandedges and valence band spectra obtained by UPS measurements on perovskite single crystals. The conduction bandedges were determined by adding the bandgap reported previously\textsuperscript{174} to the here-measured valence bandedge.
Therefore, in an effort to reduce sources of misinterpretation, I here report the valence and conduction bandedge values with respect to the vacuum level, as measured by UPS on BTA and PEA perovskite single crystals of $n = 1, 2, \text{ and } 3$ in Figure 6.1. These measurements are performed on crystals aligned with the (001) axis normal to the substrate (i.e., PQWs parallel to substrate), to reduce surface-dependent variations in photoemission onset$^{182,183}$. This series of measurements find that both PEA- and BTA-based PQWs exhibit type-I alignment. This is in agreement with Silver et al.’s studies on $n=1$ BTA films, which are the only value of $n$ for PQW films that will yield a pure phase due to the lack of an $A^+$ cation in the synthesis. The results do, however, disagree with the literature supporting a type-II alignment amongst PQWs. This is addressed in the following section. The valence spectra for all PQW samples also exhibit clear features that can be attributed to I 5p orbitals, and ligand orbitals, as shown in previous computational work$^{175,184}$.

6.2 Electrostatic Dipole-Mediated Band Shifting

![Figure 6.2 Schematic energy levels of neighbor PQWs with different surface interfaces.](image)

Alkyl- and phenyl alkylammonium halide ligands exhibit electrostatic dipoles that can shift the alignment of neighboring PQWs as a result of the strongly oriented dipole moments of the ligands with respect to the PQW surfaces. Variations in the concentration of ligands at the surfaces of a PQW interface can cause such band misalignments.
Oriented electrostatic dipoles at material interfaces have been known to shift the apparent work function of semiconductors. The phenomenon has been observed in a variety of systems and interfaces, including semiconductor-semiconductor and semiconductor-metal\textsuperscript{185–188}. In PQWs, electrostatic dipole moments across ligands could enact such apparent work function shifts that could in turn, misalign energy levels with respect to neighboring PQWs. This mechanism is illustrated in Figure 6.2. Under this framework, a fully passivated PQW would exhibit a lower work function than an unpassivated one, and increasing the concentration of ligands on one surface would effectively raise its bands with respect to its neighboring PQW. This becomes particularly interesting at the interface of two PQWs of different $n$ with contrasting ligand concentrations at the interface (Figure 6.3). With enough contrast of ligand concentrations at the interface surfaces, the work function shifts illustrated in Figure 6.2 could lead to a type-II interface.

6.3 Manipulating Band Alignment in 2D Perovskites

I next sought to quantify the magnitude of work function shifts effected by oriented dipoles in PQW surfaces. To do so, I explored different surface treatment techniques that would add a layer of PEAI or PbI$_2$ on PQWs without degrading or modifying the material in any way. IPA-based treatment solutions were found to be suitable at treating surfaces without degrading the underlying film. $n=1$ films were investigated for this study due to their purity in phase and versatility over single crystals for spin-casting. X-ray photoelectron spectra (XPS) were acquired on control and treated films to ascertain the state of the exposed surface following the various treatments (Figure 6.4a). The atomic ratios determined from integrating Pb, I, N, and C XPS spectra confirm that soaking the $n = 1$ films with PEAI treatment solutions of increasing concentration results in a greater concentration of PEAI on the film’s surface, evidenced by higher counts for C and N relative to the Pb counts. PbI$_2$ treatments lead to reduced N and C content relative to Pb content.

UPS measurements on control, PEAI-treated and PbI$_2$-treated $n=1$ films reveal that only PEAI treatments are able to modify significantly the Wf of PQWs, and that they do so by as much as 1 eV (Figure 6.4b). The magnitude of the band upshift can be controlled by varying the
concentration of PEAI in the treatment solution. The band upshift is observed in the photoemission onset as well as in the shifts in the valence spectral peaks. Beyond 6 mg/mL, however, both the photoemission onset and valence spectral peaks blur and become difficult to discern. PbI₂-treatment, on the other hand, leads to a negligible effect on the band alignment. The absence of upshifts may be attributed to the absence of a strong dipole given the low incidence of PEAI surfaces; and to the limited interaction of PbI₂ with undercoordinated surface sites.

Figure 6.3 Dipole-mediated band shifting in PQWs can lead to type-II alignment. Graphical depiction of a scenario when otherwise type-I aligning PQWs exhibit a type-II interface as a result of ligand-rich and ligand-depleted surfaces in neighboring PQWs.
Figure 6.4 Treatment of films modifies the exposed surface to increase PbI₂ or PEAI

(a) Atomic ratios as determined by XPS on control and treated \( n = 1 \) films normalized to Pb content corroborate the effect of PbI₂ and PEAI film surface treatments. *C atomic ratios are reduced to 25% of their actual magnitude, and all atomic ratios for 6 and 8 mg/mL treatments are reduced to 10% of their actual magnitude in the plot for improved visual comparison. (b) The photoemission onset in UPS varies for increasing PEAI concentration in treatments of \( n = 1 \) films. This reflects the upshifting of energy levels, and consequently a reduction in Wf or IE. (c) XRD on control and treated films indicates that the film is still pure-phase post-treatments. (d) DFT confirms energy level upshifts as a result of increased coverage PEAI on both (001) and (100) PQW surfaces.
Previous work has found that increasing I$_2$ concentration in PEA$_2$PbI$_4$ can lead to new crystalline phases. I therefore measured XRD on post-treatment films to ensure that the phase purity of the $n=1$ film has not been altered (Figure 6.4c).

The effect of ligand concentration at PQW surfaces to upshift its bands and thus reduce Wf and IE was also investigated using DFT calculations (Figure 6.4d). The change in IE was calculated by modifying the concentration of PEAI at both (001) and (100) surfaces of an $n = 1$ structure. The IE and Wf indeed decrease with increased PEAI at the surface, a finding that is in agreement with photoemission studies on PEAI-treated RDP films. Interestingly, the magnitude of the upshift varies depending on the surface on which the ligand is adsorbed.

Table 6.1 Surface energies of $n=1$ phases with various surface terminations. Surface energies computed by DFT. The labels in brackets refer to the atomic simulation schematic on Figure 6.4d.

<table>
<thead>
<tr>
<th>Surface</th>
<th>No PEAI</th>
<th>With PEAI vacancy</th>
<th>Full PEAI-terminated</th>
</tr>
</thead>
<tbody>
<tr>
<td>001 Surface</td>
<td>1.18 eV/nm$^2$ (i)</td>
<td>2.03 eV/nm$^2$ (ii)</td>
<td>1.02 eV/nm$^2$ (iii)</td>
</tr>
<tr>
<td>100 Surface</td>
<td>0.94 eV/nm$^2$ (iv)</td>
<td>0.99 eV/nm$^2$ (v)</td>
<td>1.30 eV/nm$^2$ (vi)</td>
</tr>
</tbody>
</table>

Figure 6.5 UPS data for $\langle n \rangle = 20$ and bulk films. The bands are shifted up in the PQW film due to the prevalence of PEAI surfaces relative to the bulk perovskite film.
These observations agree with the hypothesis that the dipole moment in ammonium halide terminated ligands can misalign PQW energy levels. The XPS ratios suggest that all corner-shared sites of the control \( n=1 \) film are passivated (i.e. there are > 2 N atoms for every Pb atom), and that there are no I-vacancies (i.e., there are > 4 I atoms for every Pb atom). It is therefore most likely that the PEAI treatments passivate interstitial I-sites on the 2D plane, as well as passivating edge I-sites. However, as discussed in the previous chapter, PQW films can be inhomogeneous, such that there could be a number of unpassivated I-sites on the 2D plane. Thus, it is possible for the unpassivated structures depicted in Figure 6.4d to form, despite their higher enthalpies of formation (Table 6.1), in light of their kinetically- (as opposed to thermodynamically-) driven growth\(^{174}\). In this scenario, PEAI treatments will first passivate these I-sites before covering interstitial and edge I-sites.

Interestingly, beyond a surface saturation point, increasing the ligand concentration will lead to broadening and blurring of features in the valence spectra. This is assigned to the fact that increasing ligand concentration beyond the saturation point leads to unoriented PEAI ligands on the surface. The disordered nature of dipole moments in this scenario will broaden and blur valence spectral features and even counteract the dipole-mediated upshifts.

These findings suggest an explanation for the discrepancy among UPS studies in the prior literature. Different film deposition techniques and ligand concentrations used in synthesis might alter the surface of PQW films by increasing ligand-rich surfaces relative to PbI\(_2\)-rich surfaces, dramatically altering the photoemission onset for films that could otherwise exhibit fairly similar properties. Furthermore, these film treatments have direct implications on perovskite semiconductor device design. Alkyl- and phenyl alkylammonium halide ligands offer interfacial layers to modify the interface between perovskite and transport layers and contacts in order to improve charge transport and balance, and reduce parasitic resistances.

Another implication of these studies is that PQW-PQW interfaces will exhibit dipole-mediated misalignments only if the PQW surfaces exhibit different ligand concentrations. However, 2D/3D interfaces will inherently exhibit dipole-mediated misalignments due to the nature the
surfaces incurred in the interface, *i.e.*, the bulk surface is depleted of ligand contrary to the PQW surface. It is for this reason that a 2D/3D interface has a higher likelihood of exhibiting a type-II interface. This rationale was confirmed by contrasting UPS on bulk and an \( \langle n \rangle = 20 \) sample (*Figure 6.5*). The valence bandedge of the PQW sample is higher than that of the bulk sample which can be attributed to the presence of PEAI-passivated surfaces in the former.

### 6.4 Direct Observation of Dipole-Mediated Band Misalignments

I posited that dipole-mediated band upshifts could manifest unintentionally within PQW films as a result of a varying ligand distribution throughout the film\(^{174}\). For example, the alignment between \( n = 2 \) and \( n = 3 \) PQWs in a given thin film should be type-I and lead to exciton and charge transfer solely from \( n = 2 \) to \( n = 3 \). But if some of the \( n = 2 \) wells have upshifted bands due to increased ligand coverage, this could potentially result in type-II alignment relative with \( n = 3 \), facilitating hole transfer from \( n = 3 \) to \( n = 2 \). Such a photophysical picture would explain how films based on mixed-dimensional PQWs use type-I alignment to form a natural energy gradient that increases recombination and improves quantum yield in LEDs in well-passivated PQW films\(^{65}\), but the same materials used in solar cells are prone to trapping of holes in highly confined (low-\( n \)) PQWs due to occasional type-II alignment\(^{121,172,178,179}\).

I also considered that a type-II alignment between an upshifted \( n = x \) PQW and unshifted \( n = x+1 \) would not necessarily mean a type-II alignment between the same upshifted \( n = x \) well and an unshifted \( n \geq x + 2 \), as the energy of the valence band states in the \( n \geq x + 2 \) wells could still be higher than the upshifted energies of \( n = x \) well (exemplified schematically in the bottom panels of *Figure 6.6*). If this were to be the case, then one could anticipate that direct photoexcitation of the PQW \( n = x \) in a transient absorption experiment should result in dynamic photobleaching of \( n = x-1 \) wells due to favorable hole transfer; but hole transfer to \( n \leq x-2 \) wells may not be thermodynamically favorable. In the case that type-I alignment persisted between all PQWs in a thin film, no dynamic photobleaching at energies above the photoexcitation pulse would be observed, since hole transfer from high-to-low \( n \) would be globally disfavored. Conversely, if type-II alignment persisted between all PQWs, then hole transfer would categorically take place from high-to-low \( n \) (i.e. regardless of photoexcitation energy) instead.
Transient absorption experiments were performed by selectively photoexciting $n = 2, 3, 4, 5$ and 6+ PQWs (Figure 6.6). In all cases but one, dynamic bleaching is observed for the $n = x - 1$ excitonic resonances over 10s of picoseconds due to hole transfer resulting from type-II band alignment, whereas dynamic bleaching of the $n = x - 2$ peaks is often absent, and never occurs for $n \leq x - 3$. Photoexciting $n = 5$ (Figure 6.6d) for instance, results in transient bleaching the $n = 3$ and 4 peaks, but does not affect $n = 2$. Similarly, lower energy photoexcitation at $n = 6+$ (Figure 6.6e) causes transient bleaching of $n = 4$ and 5, but not $n = 2$ and 3. The single exception is that of the $n = 1$ peak which is never bleached by any sub-bandgap photoexcitation, strongly suggesting that type-II alignment between $n = 1$ and all other PQWs does not occur. In all cases, it is noted that the population of upshifted PQWs that can act as hole acceptors is small relative to the total population of unshifted wells, assessed from the peak amplitude in absorption spectra.

These results do not agree with total and unconditional type-I nor type-II PQW alignments. These observations are instead consistent with my hypothesis that a minority population of each of the PQWs can have their energy bands upshifted to the extent that they switch from a type-I to type-II alignment relative to PQWs with smaller bandgaps. The exceptions for $n = 1$ can be explained by its wider bandgap compared to $n = 2$ such that a greater band upshift is required to form type-II alignment.

These results shed new light on how both type-I and type-II alignment can form in PQW thin films: in well-passivated films with a high degree of mixed-dimensionality used for light-emission, type-I alignment can dominate the photophysical dynamics due to ligand homogeneity. In films with more homogeneous-dimensionality used for solar cells, e.g. $<n> = 10$ or 20, the occasional presence of an upshifted low-$n$ PQW leads to type-II alignment that can render it into a trap for holes\textsuperscript{128}.

My proposed mechanism of dipole-mediated band misalignments occurring spontaneously in thin films of mixed PQWs is able to reconcile the otherwise incompatible observations of both type-I and type-II alignment between the various QWs throughout the literature.
Figure 6.6 TA on PQWs with varying photoexcitation energy reveals dipole-mediated TA spectra of \( \langle n \rangle = 2 \) (a) and \( \langle n \rangle = 3 \) (b-e) samples where photoexcitation energy matches the bandgap of \( n = 2 \) (a), \( n = 3 \) (b), \( n = 4 \) (c), \( n = 5 \) (d), and \( n = 6 \) (e). The series reveals that although exciton transfer should take place primarily towards higher \( n \) phases (which is indeed observed in these experiments) dipole mediated upshifts can allow a small subset of hole transfer towards lower \( n \) phases (as observed by increasing bleach intensity over time). The asterisk denotes the region of the spectrum hidden by the excitation scatter. The band schematics below depict the allowed and observed transfer for each case.

6.5 Summary

In this chapter, I report an investigation on the band alignment of PQWs. In doing so, I attempt to mitigate common sources of error and misinterpretation: I do so by analyzing single crystals, determining the onset of photoemission with a logarithmic y-axis, and measuring crystals with PQWs aligned parallel to substrate to avoid surface-dependent photoemission onset variations. I then propose a model that explains the variations that have been measured in energy level alignments of PQWs in the literature consisting of electrostatic dipole-mediated work function shifts enacted by charge across the ligands. This model is verified experimentally by treating \( n=1 \) films by increasing the relative incidence of PEA1 and PbI\(_2\) surfaces by solution-processed spin-cast treatments, leading to shifts in the valence bandedge of up to 0.9 eV. Finally, these work function shifts are observed experimentally in common (untreated) PQW films by TA measurements validating my initial hypothesis that these misalignments can occur inadvertently in solution-processed PQW films due to ligand inhomogeneity across the film.
This work has consequences for our understanding of 2D, quasi-2D, and mixed 2D/3D devices: these ligand-mediated band shifts can occur inadvertently in solution-processed films, leading to reductions in PLQY in films, or sources of hysteresis and trap-like states in devices. These studies depict 2D/3D mixed devices as type-II interfaces which may block charge transport for electrons but retain efficient hole transport, whereas well and homogeneously passivated mixed 2D/quasi-2D devices can act as type-I interfaces without selective charge transfer. These different interfaces can be systematically engineered to maximize transport in optoelectronic devices in general, minimize turn-on voltage and ensure charge balance in LEDs, and maximize \( V_{oc} \) and minimize parasitic resistances in PV.
7 Conclusions and Outlook

Here I summarize the main findings contained in the body of this thesis. I then discuss the potential research impact of this work and future directions that could build upon these findings. Finally, I list my publications during my time as a doctoral student.

7.1 Summary of Findings

Perovskites have shown remarkable progress and are now attractive candidates for low-cost high-performance optoelectronic devices. Perovskite semiconductors have attracted interest in recent years due to their versatility\textsuperscript{33,74,80}, low density of carrier traps\textsuperscript{39}, high charge carrier mobilities\textsuperscript{37,81}, and low cost of fabrication. Nanostructures offer a number of additional benefits, in particular for light emission applications. Among such benefits, I highlight a wider range of bandgap tunability due to quantum confinement, higher PLQY than bulk materials due to increased spatial overlap between electrons and holes, and as is the case of PQWs, improved long-term stability. In this thesis, I study some properties of perovskite nanostructures for light emission applications shedding some light on the remarkable performance of these materials and offering some hints at further optimizing them.

I first investigated photophysical properties in 0-dimensional perovskite nanostructure systems. Chapter 3 details a dot-in-matrix strategy to improve radiative recombination over non-radiative pathways in perovskite QDs. The synthesis of cubic CsPbBr\textsubscript{3} perovskite QDs in robust and air-stable rhombic prism Cs\textsubscript{4}PbBr\textsubscript{6} microcrystals enables over 90\% PLQY in the solid state. Experimental characterization supports a material model consisting endotaxial lattice-matching between cubic CsPbBr\textsubscript{3} QDs inside a Cs\textsubscript{4}PbBr\textsubscript{6} matrix.

In Chapter 4 I investigated the potential of perovskite shells in core-shell QD systems to reduce the rate of non-radiative recombination pathways. First, I conducted theoretical calculations to determine that only modal delocalization can have a large enough impact on intradot Auger recombination to inhibit lifetimes by over an order of magnitude, and that this effect is
maximized with small bandedge core-shell offsets. With TA, I identified and isolated 3 different types of Auger recombination: intradot Auger, trap-assisted Auger, and diffusion-assisted Auger. By comparing perovskite shelling to various methods of PbS QD passivation, I separated the effects of passivation and modal delocalization due to band structure on Auger recombination. Finally, this chapter finds that MA5 PbI3 perovskite shelling decreases the rate of Auger recombination by over 1 order of magnitude in PbS QD films.

In the ensuing two chapters, I investigated similar properties in two-dimensional perovskite nanostructures. In Chapter 5, I studied the formation of PQWs and the potential of controlling synthesis parameters to modulate the distribution, composition, and orientation PQW films. In-situ GIWAXS reveals that during PQW film deposition intermediate solvent-precursor complexes form and mediate the nucleation and growth of PQWs. I found that variations in the distribution of ligand and rates of depletion can vary the distribution of QWs in a film by analyzing a theoretical model supported by in-situ GIWAXS. This in turn, also explains morphological variations. TA spectroscopy and GIWAXS characterization of PQW films were used to depict the distribution and orientation of PQWs, respectively. I found that PQW films are made up of a wide range of QW thicknesses and orientations, but these can be controlled to some degree by varying solvent, ligand, and their ratio. I also found a remarkable dependence of PQW morphology on the temperature of the substrate during crystal growth. Increasing this temperature modulates the mechanism from homogeneous to heterogeneous nucleation at the interface, making orientation less random. However, increased temperature during film formation also leads to a PQW bandgap gradient for thicker films.

In Chapter 7, I reported a study on the band alignment of PQWs. First, I analyzed the conduction and valence bandedges in PQW single crystals showing that these exhibit type-I alignment. I then proposed that PQW ligands could produce work function shifts due to electrostatic dipole moments. I corroborated this hypothesis experimentally by treating $n=1$ films by increasing the relative incidence of PEAI and PbI$_2$, leading to shifts in the valence bandedge of up to 0.9 eV. Finally, I observed these work function shifts experimentally in common (untreated) PQW films by TA measurements validating our initial hypothesis that
these misalignments can occur inadvertently in solution-processed PQW films due to ligand inhomogeneity across the film.

7.2 Outlook

The work presented in this thesis studies the effect on nanocrystalline morphology in perovskite materials on various optical and electronic properties. These findings offer means of controlling fundamental material properties by nanostructuring, potentially enhancing the performance and long-term stability of optoelectronic devices.

My work on dot-in-matrix CsPbBr₃ QDs in Cs₄PbBr₆ microcrystals presented a strategy to synthesize bright and air-stable light-emitting QDs in the solid-state which could see applications in all sorts of displays and lighting applications. Smooth films of the microcrystals can be fabricated by incorporating the microcrystals in an organic material, like PMMA. However, the large dimensions and insulating nature of the microcrystals I report preclude their use in thin-film devices like light-emitting diodes. Since my work was published, a number of studies have built upon our work to expand the applicability of the material. The same material system has been studied for optical gain, leading to the discovery of temperature-independent emission wavelength in this material. Studies have reported the synthesis of smaller nanometric matrices and larger centimeter-sized matrices. Xu et al. investigated the synthesis of smaller Cs₄PbBr₆ matrix crystals with embedded CsPbBr₃ QDs, which led to decreased PLQY but enabled the fabrication of LEDs. The crystal type has also been grown with Cl and I halides, enabling the synthesis of such crystals with blue and red emission, respectively. Furthermore, fundamental theoretical and experimental studies have sought to explore the reason behind the intimate coupling between the CsPbBr₃ and Cs₄PbBr₆ crystal structures. These studies have found that the crystal lattices can easily transform from one to the other with minimal energetic barriers, explaining the nucleation of CsPbBr₃ QDs within the matrix.

Unfortunately, Cs₄PbBr₆ is a very good insulator and hinders charge carrier transport in devices, limiting LED EQEs to below 1%. Future studies could explore a similar dot-in-
matrix approach with a non-insulating matrix. Furthermore, the blue Cl- and red I-based crystals are much less developed than the green Br crystals presented in this work. It would be worth further investigating optimizing PLQY in the blue and red-emitting crystals by improving passivation and trap-management in order to have bright air-stable phosphors in the three main RGB colors with this material system.

My work on inhibiting non-radiative Auger recombination in lead chalcogenide QDs reported over an order of magnitude longer Auger recombination lifetimes effected by MAPbI$_3$ shelling. CW QD lasing has been achieved in the visible part of the spectrum with CdSe QDs. Near infrared counterparts, of interest in communications, computing, and biology, remain less advanced along the path to CW lasing. Lead chalcogenide QDs have been demonstrated to exhibit optical gain, ASE, and lasing when excited using picosecond pulses; however, CW lasing has so far been elusive. One major limitation, their short gain lifetime arises from efficient non-radiative Auger recombination in narrow-gap semiconductor QDs. The enhanced Auger lifetimes enabled by perovskite shelling could make use of the inherently high mobility of perovskite semiconductors to allow the development of solution-processed electrically-injected NIR CW lasing. These results provide the foundation for further work on lead chalcogenides in the pursuit of NIR CW lasing and other high intensity applications. Furthermore, QDs require at least four excitons to achieve population inversion, a regime in which Auger recombination is strongly enhanced. Therefore for the purposes of achieving lasing, future work should explore perovskite shelling in NIR QDs of materials with a lower bandedge degeneracy where gain can be more easily achieved, such as InAs, or HgTe.

My work on understanding the formation of PQWs, has clear implications on devices. This study defines new strategies that provide control over the morphology and distribution of the crystallites within PQW films. The study shows that the selection of, and stoichiometry between, the large cation and the solvent, as well as temperature of the substrate during film deposition, each has the power to manipulate the distribution of nanoplatelet thicknesses and orientation - both their median values and their variances. These findings pave the way towards engineering higher quality materials for more efficient and stable optoelectronic devices.
In PV devices, for instance I identify three main film properties that would affect PV performance based on this work: orientational disorder, energetic disorder, and inefficient light absorption. (1) QW orientational disorder and the prevalence of horizontal wells, particularly among low-\(\langle n \rangle\) films can be identified as a source of resistive losses in the device, limiting fill factor. (2) The bandgap distribution in PQWs leads to voltage losses in PV devices. Bandgap is increased in low-\(\langle n \rangle\) films, and as such \(V_{oc}\) is expected to increase. However, \(V_{oc}\) is identical for most PQW samples. This voltage loss (particularly among mid-range \(\langle n \rangle\) devices, e.g., \(\langle n \rangle = 5\)) is mainly attributable to the QW polydispersity. In addition, the presence of low-\(n\) wells can act as traps for charge carriers due to the type-II band alignment of thin wells\(^{121}\), an effect that leads to \(J_{sc}\) losses. (3) As \(\langle n \rangle\) is decreased, so is the probability of generating photocarriers due to the decreased absorbance of films (see Appendix B.3); this is likely caused by the reduced density of perovskite in PQW films as the proportion of organic ligands is increased. The last issue could be addressed by increasing film thickness and decreasing organic ligand length. Hysteresis in photovoltaic devices is also increased by the introduction of PQWs in PVs. Thin wells could act as shallow traps for holes, as discussed in the previous chapter\(^{121}\).

The methods used in this study to understand PQWs have more recently been used to better understand growth in bulk perovskites and new PQW morphologies\(^{204,205}\). In-situ GIWAXS of perovskite films during deposition and annealing offer a novel method for understanding the formation and growth of these interesting materials. Concerning future work, in-situ GIWAXS and TA spectroscopy could be used to understand the nucleation and growth of perovskites (bulk or reduced dimensional) with a number of additives that have been found to improve device performance\(^{206}\).

Finally, my work on dipole-mediated work function shifts in PQW ligands has direct implications in quasi-2D, and mixed bulk-2D optoelectronic devices. My work proposes a material model where contrasting ligand concentration on neighboring perovskite surfaces misalign their energy levels. As I show in Chapter 6, these ligand-mediated band shifts can occur inadvertently in normal (untreated) solution-processed PQW films. These misalignments can in turn lead to reductions in PLQY in films, or sources of hysteresis and trap-like states in...
devices. On the other hand, the mixed 2D/3D perovskite system is being increasingly investigated for efficient, robust, and stable PV devices. My work sheds light on this system by showing that although PQWs exhibit type-I alignments, a bulk-PQW interface will typically exhibit a type-II interface due to the ligand-depleted nature of a bulk perovskite surface compared to the PQW surface. This type-II interface may block charge transport for electrons but retain efficient hole transport. Future work could quantitatively explore the band shifts at the bulk-PQW interface by TA and UPS to determine whether the interface could be further improved to optimize PV performance.

7.3 Contributions

The work contained in this thesis was reported in the following articles.


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9 Appendices

A. Methods
A.1 Chapter 3

*Synthesis of bulk Perovskite NCs in Cs$_4$PbBr$_6$:*
1M to 0.001M (depending on the ratio of precursors) of PbBr$_2$ (99.9%, Alfa Aesar) was dissolved in 1ml DMSO (99.9%, Aldrich). At the same time, 1M of CsBr (99.999%, Aldrich) was dissolved in 300 µl H$_2$O (Deionized water). CsBr/H$_2$O solution was then slowly injected into the PbBr$_2$/DMSO solution and stirred at room temperature in air atmosphere for 30 min to 2 hr (depending on the concentration of PbBr$_2$). After bright green precipitates formed in the mixed solution, crystals were centrifugated at 5000 rpm and washed with toluene, followed by drying under the vacuum.

*Fabrication of film Perovskite NCs in Cs$_4$PbBr$_6$:*
Perovskite NCs in Cs$_4$PbBr$_6$ precursor solution were prepared via the same method described above, but the concentration of PbBr$_2$ was fixed to 0.1 M. The series of precursor solution were then spin-coated on the glass substrate and followed by annealing for AFM and TA measurements.

Photoluminescence measurements (decay, emission spectroscopy and PLQY): All photoluminescence (PL) measurements were done with a Horiba Fluorolog time correlated single photon counting (TCSPC) system with a single grating spectrometer and photomultiplier tube detector. Steady state PL and PL excitation (PLE) measurements were done using monochromatized light from a xenon lamp as the excitation source. Transient measurements used a laser diode (lambda = 375 nm) as the excitation source. The time resolution according to the instrument response function is delta t ~0.13 ns. The standard published method for measuring quantum yields was used with a Quanta-Phi integrating sphere. Excitation and emission intensity were measured in empty-sphere, direct illumination, and indirect illumination configurations. Light was coupled between the Fluorolog system and...
the sphere with optical fiber bundles. The detector and integrating sphere were corrected for spectral variance using a calibrated white light source.

*Photoluminescence measurements:*
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*XRD:*
The XRD measurements were collected at the MAX Diffraction Facility at McMaster University, using a Bruker Smart6000 CCD area detector with a Bruker 3-circle D8 goniometer, a Rigaku RU200 Cu Kα rotating anode and a Göbel cross-coupled parallel focusing mirrors. Bisecting angle scans were performed with a 300s frame exposure, a detector distance of 16.740cm and an X-Ray beam at 90mA and 50kV.

*Inductively Coupled Plasma Atomic Emission Spectrometry:*
The atomic composition of samples was determined using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), with the Perkin Elmer Optima 7300DV. We used 1 ppm, 10 ppm, 100 ppm, 1000 ppm Pb and Cs as standards for the calibration. The perovskite in hexabromide samples were dissolved in 10% HCl before ICP-AES characterization.

*Computational Algorithm to Determine Lattice-matching:*
This problem was simplified by the fact that the CsPbBr₃ perovskite QD is cubic with a unit size of dimensions \( d = 5.87 \, \text{Å} \). Firstly, a file is compiled with a list of the atomic positions of
all Pb-sites in a Cs$_4$PbBr$_6$ large crystal (of 10 repeating unit cells) with Vesta Software. Then the file is analyzed by the following algorithm:

1. A for-loop scans through each individual Pb-atom and determines the distance between it and all neighboring Pb atoms. All pairs of Pb-atoms that are a multiple of $d$ away from each other (within a 3% error) are logged. Within each iteration in this for-loop it is also determined whether the vector from a given Pb-atom to the origin Pb-atom (in each iteration) is in the same direction as a previously logged Pb-atom pair. If so, to simplify the complexity of the next steps only the outermost Pb-atom pairs are kept in these scenarios.

2. For each pair of Pb-atoms logged in the previous step, a line in 3D space is represented analytically. This line will be referred to as the diagonal.

3. A for-loop scans through all logged diagonals and for each diagonal scans through all other Pb-atoms (not within the diagonal). For each Pb-atom, the following values are computed by linear algebra:
   a. The distance from the given Pb-atom to the diagonal (upon drawing a line perpendicular to the diagonal, which will be referred to as the intersect). This value is labelled $i$.
   b. The point on the diagonal where the intersect meets the diagonal. This value is labelled $x$.
   c. The azimuthal angle of the intersect. The line intersecting the first Pb-atom in the for-loop is defined as 0 degrees. All other lines are reference to this one. This value is labelled $\theta$.

4. The algorithm then scans through the list of Pb-atoms and their computed parameters and groups Pb-atoms that share similar $x$ and $\theta$ values, i.e., they lie on the same line.

5. Only Pb-atoms that are multiple of $d$ away from each other (within a 3% error) are logged.

6. The algorithm then searches for two separate groups that have been logged and are 90 degrees from each other. These cases are marked as likely to exhibit lattice matching, given the periodicity matching that of the cubic perovskite along all three axes simultaneously. These are then visually inspected to ensure lattice matching is met.
A.2 Chapter 4

*Synthesis of Oleic Acid-capped Lead Sulfide (all ~950 nm dots, ~1300 nm CQD-CdS dot cores)*: Quantum dots were synthesized according to literature.\(^{208}\) The lead oleate precursor was made by heating PbO in the mix of Oleic Acid and 1-Octadecene at concentrations 0.05±0.2 M under Ar at 100 \(^{\circ}\)C for 16 h. The sulfur precursor was prepared in the glovebox by mixing 420 µL of hexamethyldisilathiane (TMS) with 10 mL of pre-pumped ODE.

*Synthesis of Oleylamine-capped Lead Sulfide (~1300 nm CQDs and CQD-PVK cores)*: Quantum dots were synthesized according to literature.\(^{143}\) However, final PbS dots capped with oleylamine were not stable and over time resulted in aggregation and PbCl\(_2\) precipitation. To overcome this issue, we slightly modified the synthesis. A mix of octylamine and hexylamine was introduced before quenching with hexane. Based on our observations, short carbon chain amines serve as extra capping ligands and prevents dot aggregation.

*Chloride Passivation*:  
Chloride treatment was performed in synthesis during the cooling stage. Tetrabutylammonium chloride (TBAC) was prepared by heating at 200 °C in Oleylamine followed by one hour pumping at 100 °C. TBAC (0.6mM) was injected into crude solution at 100 °C during the cooling stage. The reaction mixture was cooled down to 35 °C and the dots were isolated *via* precipitation with acetone and redispersion in toluene.

*CdS Passivation*:  
PbS cores were passivated according previously reported protocols.\(^{32}\)

*Perovskite shell growth*:  
The perovskite shell was grown on 950 nm CQDs according to literature.\(^{113}\) The perovskite shell was grown on 1300 nm CQDs with some modifications to the literature. 1300 nm CQD cores with oleylamine capped ligands were found to undergo ligand exchange much more readily than 1300 nm CQDs cores with oleic acid capped ligands. In the redispersion step, pure
butylamine did not redisperse the CQD-PVK. We mixed some of the initial perovskite precursor solution (in DMF) with butylamine (~1:20) to solubilize the CQD-PVK. We also found that redispersing the CQD-PVK with hexylamine and butanone\textsuperscript{209} worked as well.

*Steady-state Characterization:*
Films were measured for linear absorption with a PerkinElmer Lambda 950 UV/Vis/NIR spectrophotometer. Photoluminescence quantum yield measurements were collected with an integrating sphere using a Horiba Fluorolog TCSPC system with an iHR monochromator and either a H10330-45 or H10330-75 photomultiplier tube.

*Transient Absorption Spectroscopy:*
A Yb:KGW regenerative amplifier (Pharos, Light Conversion) was used to generate the 1030 nm fundamental (5 kHz). A portion of the beam was sent through an optical parametric amplifier (Orpheus, Light Conversion) to generate the pump pulse. For ~950 nm and ~1300 nm dots, we chose 800 nm and 1030 nm pumps, respectively; this was done to keep excitations a fixed energy above the bandgaps. The pump and residual fundamental were then sent into an optical bench (Helios, Ultrafast). The fundamental was passed through an optical delay stage to control the time delay between pulses. The fundamental was then focused through a NIR crystal (Ultrafast) to generate a NIR white light continuum probe. The frequency of the pump was halved with an optical chopper. Both the pump and probe were then focused onto the sample, which was translated 1 mm/s. The probe was then directed toward a fiber, which was coupled into a NIR detector (Ultrafast).

*Theoretical Modelling:*
The 1D wavefunctions are computed as an extension on the simple particle-in-a-box model. The core-shell QD potential used to represent that of the bandedge (conduction bandedge or valence bandedge depending on whether electron or hole Auger is analyzed) is shown on figure 1, where a, b, and $V_0$, represent the QD radius, entire core-shell QD radius, and difference between the shell and core bandedge, respectively. For clarity, b-a represents the shell thickness.
The wavefunctions are computed via Schroedinger’s Equation which takes the form:

\[- \frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} = (E + V_0) \psi ,\]

for when \(|x|<a\), and

\[- \frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} = E \psi ,\]

when \(a<|x|<b\).

The form of the solutions is different for modes with \(E<0\) and \(E>0\). Furthermore, we can simplify the math by focusing on even solutions. In the case where \(E>0\), the solutions take the form:

\[\psi(x) = A \sin(kx)kx + B \cos(kx) ,\]

in the shell region, and

\[\psi(x) = C \cos(rx) ,\]

in the core region. Here, we define

\[k = \sqrt{\frac{2mE}{\hbar^2}} ,\]
and

\[ r = \sqrt{\frac{2m(E + V_0)}{\hbar^2}}. \]

Next, we impose continuity of \( \Psi \) and \( \Psi' \) at \( a \) and at \( b \), which leads to the transcendental equation:

\[
\sqrt{\frac{\omega_0^2}{\omega^2} + 1} = \frac{1 + \tan \omega \tan \omega \frac{b}{a}}{\tan \sqrt{\omega_0^2 + \omega^2} \left( \tan \omega \frac{b}{a} - \tan \omega \right)},
\]

where,

\[ ra = \sqrt{\omega_0^2 + \omega^2}, \]

and

\[ \omega = ka, \]
\[ \omega_0 = \frac{\sqrt{2mV_0}}{\hbar} a, \] and
\[ r^2 - k^2 = \frac{2mV_0}{\hbar^2}. \]

The transcendental equation can then be solved numerically in order to find the energy, \( E \), of a given eigenmode. With \( E \), we can now compute \( k \) and \( r \), and all the constants involved (one of which will need to be set first).

In the case where \( E < 0 \), the wavefunctions take the form:

\[ \Psi(x) = A \exp(kx) kx + B \exp(-kx), \]

in the shell region, and

\[ \Psi(x) = C \cos(rx), \]

in the core region. The same process is undergone in this case leading to the transcendental equation:
\[
\exp(-ka) - \frac{\exp(-kb) \exp(ka)}{\cos(la)} l\sin(la) \frac{\exp(-ka)}{k} + \frac{\exp(-kb) \exp(ka)}{\exp(kb)} = \exp(-ka) + \frac{\exp(-kb) \exp(ka)}{\exp(kb)},
\]

where we define

\[
k = \sqrt{-\frac{2mE}{\hbar^2}},
\]

and

\[
l = \sqrt{\frac{2m(E + V_o)}{\hbar^2}}.
\]

The absolute magnitude of the wavefunction is determined by the normalization equation:

\[
\int_{-b}^{b} |\Psi(x)|^2 dx = 1.
\]

The wavefunctions are in turn used to compute the Auger recombination rate as described in the manuscript.

Likewise, in 3D, the Schrödinger equation for the QD potential of figure A1 can be solved. In this case however, the potential depicted is a function of the radius, r. The Schrödinger equation is given by:

\[
-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[ \frac{\hbar^2}{2m} \frac{l(l + 1)}{r^2} - V_o \right] = Eu,
\]

for when \(|x|<a\), and

\[
-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[ \frac{\hbar^2}{2m} \frac{l(l + 1)}{r^2} - V_o \right] = Eu,
\]

when \(a<|x|<b\), where \(u=R(r)r\).

In this case, the transcendental equations take the form:
\[
\begin{align*}
\left[ \frac{l}{\tau a} k_l(\tau a) + k_{l+1}(\tau a) \right] - \frac{k_l(\tau b)}{i_l(\tau b)} \left[ \frac{l}{\tau a} i_l(\tau a) + i_{l+1}(\tau a) \right] \\
= \left[ \frac{k_l(\tau a)}{j_l(pa)} - \frac{k_l(\tau b) i_l(\tau a)}{j_l(pa) i_l(\tau b)} \right] \left[ \frac{l}{pa} j_l(pa) - j_{l+1}(pa) \right]
\end{align*}
\]

when \( E < 0 \), and

\[
\begin{align*}
\left[ \frac{l}{va} n_l(va) + n_{l+1}(va) \right] - \frac{n_l(vb)}{j_l(vb)} \left[ \frac{l}{va} j_l(va) - j_{l+1}(va) \right] \\
= \left[ \frac{n_l(va)}{j_l(pa)} - \frac{j_l(va) n_l(vb)}{j_l(pa) j_l(vb)} \right] \left[ \frac{l}{pa} j_l(pa) - j_{l+1}(pa) \right]
\end{align*}
\]

where

\[
\tau = \sqrt{\frac{2 m (V_0 + E)}{\hbar^2}},
\]

\[
p = \sqrt{\frac{-2 m E}{\hbar^2}},
\]

and

\[
v = \sqrt{\frac{2 m E}{\hbar^2}}.
\]

Here, \( j_l(r) \), \( n(r) \), \( i_l(r) \) and \( k_l(r) \) represent the Bessel Spherical Harmonics of the first and second kind, and modified Bessel Spherical Harmonics of the first and second kind, respectively. And \( l \) represents the angular momentum, an additional degree of freedom that appears upon the addition of dimensions. The solutions, then take the form:

\[
R(r) = A j_l(\tau r),
\]
in the core region, and

\[
R(r) = C j_l(vr) + D n_l(vr),
\]
in the shell region for \( E > 0 \), and

\[
R(r) = E i_l(pr) + F k_l(pr),
\]
In theory, it is possible to perform the same theoretical analysis discussed in the manuscript in 3D. However, an issue arises in the computation of the Coulomb integral (Equation 2). This integral is now a function of 6 independent variables, and as such this 6-dimensional integral requires much greater computational resources in order to be computed with any reasonable accuracy. As the 1-dimensional model reasonably estimates the form of the wavefunctions in the QD potential, this treatment is sufficient.

All modelling results with the exception of the specific PbS simulations (Figure 4.8) presented in the manuscript were simulated using the normalized units listed below:

\[
m=1; \\
hb=1; \\
a=1; \\
b=1; \\
Egap=8;
\]

PbS simulations (Figure 4.8) study the effect of varying core-shell bandedge offsets of both the valence and conduction bands concurrently. In order to verify the applicability of the results for PbS QDs, the simulations were repeated for PbS QDs of different sizes with the real units listed below:

\[
eC=1.6e-19; \quad \text{in C} \\
m=0.08*9.1e-31; \quad \text{in kg} \\
hb=1.05e-34; \quad \text{in Js/rad} \\
as=5e-9; \quad \text{core radius in m (these are 10nm dots)} \\
bs=1e-9; \quad \text{in m} \\
Egap=0.4*eC; \quad \text{in J}
\]

A.3 Chapter 5

Material Synthesis:
Reduced-dimensional \((\text{PEA})_2(MA)_{n-1}\text{Pb}_n\text{I}_{3n+1}\) perovskite solutions were prepared by dissolving the appropriate stoichiometric quantities of \(\text{PbI}_2\), MAI, and PEAI in \(\gamma\)-butyrolactone/DMSO (1:1, volume ratio), or DMF (for hot-cast films) at 70 °C for 1 h with vigorous stirring. The resulting solution was filtered with a PTFE syringe filter (0.2 μm) before deposition. The next step depends on whether spin-casting or hot-casting is used:

- **Spin-casting:** The solution was then deposited onto the substrate via a consecutive two-step spin-coating process at 1000 and 5000 rpm for 10 and 80 s, respectively. Halfway into the second spin step, 200 μL of chlorobenzene was deposited onto the substrate. The resulting films were annealed at 70 °C immediately thereafter for 20 minutes.

- **Hot-casting:** The substrates are heated to 150 °C. The substrate is quickly placed on the spinner, the solution is dropped on to the substrate followed by a one-step spin-coating process at 5000 rpm for 20 s.

Unless otherwise specified, the molarity was chosen so that the films would exhibit commensurate thickness. In this case, 200 nm is identified as a suitable thickness. The molarity required to achieve a 200 nm thickness was found to depend on the target \(\langle n \rangle\) (verified by atomic force microscopy, AFM). The amount of precursor to add is determined by the following equation:

\[
M = \frac{XV}{\left(M_{\text{PbI}_2} + 2 \frac{M_{\text{PbI}_2}}{\langle n \rangle} + \frac{M_{\text{MAI}}(\langle n \rangle - 1)}{\langle n \rangle}\right)} \cdot A
\]

where

\[
A = M_{\text{PbI}_2} \quad \text{or} \quad 2 \frac{M_{\text{PbI}_2}}{\langle n \rangle} \quad \text{or} \quad \frac{M_{\text{MAI}}(\langle n \rangle - 1)}{\langle n \rangle}
\]

and \(V\) is the volume of the solvent, and \(X\) is a molarity factor. Using this equation is found to lead to samples of commensurate thickness. \(X\) is 1.1, 0.9, 0.5, and 0.3, for spin-cast BTA films, spin-cast PEA films, hot-cast BTA films, and hot-cast PEA films, respectively, for films of 200 nm.
Layered perovskite single crystals of n = 2, 3 and 4 were synthesized according to previous literature\cite{162}. These are significantly purer than the PQW films, however, regions can be found with some mixed n phases. Figure 2d, for instance, was measured on a single crystal grown with the n = 3 synthesis.

**Transient Absorption Spectroscopy:**
Femtosecond laser pulses of 1030nm generated by a Yb:KGW laser at a 5 kHz repetition rate (Light Conversion, Pharos), passed through an optical parametric amplifier (Light Conversion, Orpheus) selected for 480 nm light. The latter served as the pump pulse, whereas the probe pulse was generated by focusing the initial 1030 nm pulse into a sapphire crystal resulting in white-light continuum (Ultrafast, Helios). With a temporal resolution of the system of $\sim$350 fs, each time step meant delaying the probe pulse with respect to the pump, with time steps increasing exponentially. Every other pump pulse was blocked with a chopper in order to determine the $\Delta$OD. After going through a grating spectrograph, the pulses were measured by means of a Charge-Coupled Device (Ultrafast, Helios). Multiple scans were taken for each sample at each power, and the average of these scans was used.

**Grazing-Incidence X-Ray Scattering:**
Grazing-Incidence Wide-Angle X-Ray Scattering (GIWAXS) data (\textit{ex-situ} and \textit{in-situ} during annealing) was collected at the Stanford Synchrotron Radiation Lightsource. Two-dimensional scattering was collected at a 2° incidence, with monochromatic 12.7 keV X-Rays and recorded on a Rayonix Mx-225 detector measuring 225x225 mm$^2$. Samples were measured in a chamber filled with helium. Images were calibrated using LaB6 and integrated to 1D patterns using the Nika software package\cite{210} and the GIXSGUI MATLAB plugin\cite{170}. In the kinetics analysis, scans were recorded every 20 seconds. To calculate the intensity of a peak, the region of Q +/- 0.05 Å$^{-1}$ around the peak was fit to a linear background and a Voigt profile. The integrated intensity of the Voigt profile is plotted and normalized to the highest intensity of that peak in the measurement.

Additional ex-situ GIWAXS measurements were conducted at the Hard X-ray MicroAnalysis (HXMA) beamline of the Canadian Light Source (CLS). An energy of 17.998 keV ($\lambda = 0.6888$ Å) was selected using a Si(111) monochromator. Patterns were collected on a SX165 CCD
camera (Rayonix) placed at a distance of 175 mm from the sample. A lead beamstop was used to block the direct beam. Images were calibrated using LaB6 and processed via the Nika software package and the GIXSGUI MATLAB plugin.

Grazing-Incidence Small-Angle X-ray Scattering (GISAXS) data and time-resolved in-situ GIWAXS measurements performed during spin coating were collected at the D1 beamline of the Cornell High Energy Synchrotron Source (CHESS). A Pilatus 200K detector was employed to record the scattering from the sample. Sample to detector distance was set to 815.24 mm and 165.83 mm for GISAXS and GIWAXS measurements, respectively. Incident angle was kept at 0.5° with respect to the sample plane. Wavelength of x-rays was 0.117 nm. Spin coating experiments were conducted using a custom-built spin coating stage which was computer-controlled remotely from outside the hutch, as explained previously \textsuperscript{152,154}. The splashing of the solution during spin-coating, was collected using a x-ray-transparent Kapton splash-guard. There was a delay of around 20 – 30 seconds between the solution dropping and the start of spin-coating and measurement. All these experiments were performed with the exposure time of 0.2 s and in an ambient environment where relative humidity was around 20 – 30%.

Additional ex-situ Grazing-Incidence Side-Angle X-Ray Scattering (GISAXS) data was collected at the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. Two-dimensional scattering was collected at a 0.2° incidence, with monochromatic 15 keV X-Rays and recorded on a Pilatus detector. Samples were measured in air.

*Atomic Force Microscopy:*  
Atomic Force Microscopy measurements were performed with an Asylum Research Cypher system. The AFM was operated in AC mode in air to obtain topographical and phase images. Silicon ASYELEC-02 probes with titanium iridium coatings from Asylum Research were used for all imaging. Probes typically have a spring constant of 42 N/m.

*Computing XRD Patterns:*  
XRD patterns, Structure Factors were computed from Crystallographic Information Files (details in Supporting Information) by means of 3D atomistic visualization, manipulation and computation software Mercury\textsuperscript{211} and VESTA\textsuperscript{212}.  

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**Bandgap predicting and EMA modelling:**

In order to predict the size-dependent bandgap of quantum wells, the TA bleach wavelength was determined for each distinguishable QW feature (all wells \( n \leq 5 \) can be distinctly discerned), and the bulk perovskite bleach. These energy values were plotted and compared to the bandgap of these materials reported in previous literature\(^{119,128,164}\) to ensure that the results agree with each other (shown below). Using a method similar to that of Moreels *et al.*, I used our data points to fit a predicted bandgap dependence on nanostructure size\(^{163}\). In this case, I fitted to a function of the form: 

\[
E_g = E_g + \frac{1}{0.25d^2 + 0.25d + 1.038},
\]

where the last term in the denominator is added in order to reduce the slope of the function for small thickness values. In order to validate the empirical fitting, I corroborated the predictions by means of an effective-mass-approximation (EMA) model\(^{18}\) (Figure S8a). The EMA model finds, as expected, an agreement with the empirical fitting near the exciton Bohr radius\(^{161}\), but deviates at very small quantum well thickness values (due to the size-dependent Coulomb interaction among other features that become prominent in very strong confinement)\(^{18}\).

I then computed the predicted bandgap alongside the bulk bandgap of MAPbI\(_3\) perovskite. The ultrafast TAS bleach is expected to exhibit blue-shifted features in both quantum confined and bulk-like perovskite materials due to strong exciton-exciton interactions\(^{119}\) and Moss-Burnstein phenomena\(^{165}\), respectively. This blue-shift is determined experimentally by means of TA and used to compute the predicted ultrafast TA bleach. This analysis is by no means expected to provide an infallible bandgap value for each PQW quantum well size, but instead meant to provide a good estimate for identifying PQWs in TA features.
A.4 Chapter 6

Film Preparation:
All perovskite solutions were prepared by following protocols in the literature. The appropriate stoichiometric quantities of PbI₂, MAI, and PEAI were dissolved in 1:1 volume ratio γ-butyrolactone/DMSO (for films of \(\langle n\rangle \geq 10\)), or DMF (for \(\langle n\rangle < 10\)) at 70 °C for 1 h with vigorous stirring. The resulting solution was filtered with a PTFE syringe filter (0.2 μm) before deposition. The next step depends on whether DMF or DMSO is used:

- **DMF**: The solution was then deposited onto the substrate and spin-coated at 5000 rpm for 20 s. The resulting films were annealed at 70 °C immediately thereafter for 10 minutes.

- **DMSO**: The solution was then deposited onto the substrate via a consecutive two-step spin-coating process at 1000 and 5000 rpm for 10 and 60 s, respectively. Halfway into the second spin step, 200 μL of chlorobenzene was deposited onto the substrate. The resulting films were annealed at 70 °C immediately thereafter for 10 minutes.
Film Treatment:
Treatment solutions were prepared by dissolving PEAI or PbI₂ in IPA. The treatment solution was then subsequently dropped onto the substrate and held for 5 s, after which the film was spin-casted at 5000 rpm for 20 s.

Photoelectron Spectroscopy:
Both X-ray and ultraviolet photoelectron spectroscopy were measured in an Escalab Xi+ Microprobe system. The XPS measurements were carried with an Al Kα source with energy steps of 0.05 eV. The ultraviolet photoelectron spectroscopy measurements were carried out with a He Iα source with energy steps of 0.02 eV. Film samples were spun on ITO substrates, and a corner of the film was scratched of where electrically-conductive carbon tape was adhered to avoid charging. All UPS measurements were conducted with a 5 V bias. Single crystal samples where fixated onto the holder by carbon tape. The ultraviolet photoelectron spectroscopy measurements were carried out first followed by the XPS measurements so as to avoid sample damage by the latter on the former more surface-sensitive measurement.

Transient Absorption Spectroscopy:
A regeneratively amplified Yb:KGW laser (PHAROS, Light Conversion) was used to generated femtosecond laser pulses at a wavelength of 1030 nm as the fundamental beam with a repetition rate of 5 kHz. The fundamental beam is passed through a beam splitter, where the majority of the beam is used to pump an optical parametric amplifier (ORPHEUS, Light Conversion) to serve as a narrowband pump (pulse duration ~200 fs, bandwidth ~10 nm FWHM) which ranged between 400 and 750 nm in order to selectively excite each of the various PQWs. The remaining part of the beam was focused into a translating sapphire crystal in order to generate a white light probe ranging between 450 – 950 nm. The pump and probe pulses were directed into a commercial transient absorption spectrometer (Helios, Ultrafast). The probe pulse was sent to a retroreflector mounted on a delay stage, where multiple reflections off the retroreflector allows for a delay relative to the pump pulse of up to 8 ns. Measurements were performed with pump powers of 100 μW for each photoexcitation wavelength (570, 610, 645, 666, 700 nm corresponding to n = 2, 3, 4, 5 and 6+, respectively) with a spot size of 0.30 μm² (assuming a Gaussian beam profile).
B. Additional Figures

B.1 Chapter 3

**Figure B1.** Low magnification SEM image of CsPbBr$_3$ in Cs$_4$PbBr$_6$ microcrystals. No phase segregation is discernable.

**Figure B2.** Low magnification SEM image of CsPbBr$_3$ in Cs$_4$PbBr$_6$ microcrystals with High Angle – back-scattered electrons. No phase segregation is discernable.
**Figure B3.** Various TEM images of CsPbBr$_3$ in Cs$_4$PbBr$_6$ microcrystals.

**Figure B4.** SAED of regions with CsPbBr$_3$ NCs (a) and without NCs (b).
Figure B5. Elemental Mapping from EDS imaging. Atomic ratios normalized to Pb: Cs 4.3, Pb 1, Br 6.1.

Figure B6. Elemental Mapping from EDS imaging. Atomic ratios normalized to Pb: Cs 4.8, Pb 1, Br 6.2.
B.2 Chapter 4

Figure B7. Linear absorption spectra of 950nm CQDs.

Figure B8. Linear absorption spectra of 1300nm CQDs.
Figure B9. Linear absorption spectra of 1300nm CQDs.

B.3 Chapter 5

Figure B10. GIWAXS of PEA-MAPbI\textsubscript{3} samples $\langle n \rangle = 1$ (a), 2 (b), 3 (c), 4 (d), 5 (e), 8(f), 10 (g), 40 (h) and bulk (i) on glass substrates.
Figure B11. GISAXS of samples of \( \langle n \rangle = 1, 2, 3, 4, 5, 10, 40, \) and bulk. All are displayed with a log scale for the color axis.
**Figure B12.** AFM of PEA-based spin-casting samples $\langle n \rangle = 2$ (a), 5 (b), 40 (c) and bulk (d). Inset in (a) shows zoom-in scan of $\langle n \rangle = 2$ (scale bar: 200 nm). Films of low $\langle n \rangle$ form plate-like grains parallel to the substrate, whereas bulk perovskite films produce grains of various shapes, sizes and orientations. Films of $\langle n \rangle = 5$ and larger however, produce corrugated structures resembling that of perpendicularly aligned configurations.

**Figure B13.** Pre-annealed GIWAXS cuts (along $q_z$ axis) of $\langle n \rangle = 5$ film and bulk film reveal the same patterns indicating that PEAI does not participate in the pre-annealed intermediate complexes.
Figure B14. Absorptivity of PQWs of different $<n>$ values

Figure B15. GIWAXS of samples on a Si substrate of $<n>$ = 2(a), 5(b), 8(c), 10(d).
Figure B16. UPS data for increasing PEAI concentration in treatments. As treatment concentration is increased beyond 6 mg/mL it becomes hard to determine the photoemission onset due to blurring/merging of features. In addition, the appearance of multiple peaks makes it hard to discern peaks within the valence spectra.
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Title: Compositional and orientational control in metal halide perovskites of reduced dimensionality

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