Quantum Dots in Perovskites:
Liquid Heteroepitaxy for Optoelectronics

by

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

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University of Toronto

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Abstract

Solution-processed semiconductors have played a key role in advancing next-generation optoelectronics. Among such materials, colloidal quantum dots are particles with nanometer dimensions that have shown excellent properties in light-emitting devices and photodetectors. Metal halide perovskites represent a complementary, recently-advanced, materials set that showcases carrier transport properties that approach those of single-crystal materials.

Each branch has limitations: perovskites to date have not offered short-wavelength infrared absorption and emission; and quantum dots suffer limited transport, something that decreases the efficiency of devices.

Here – by constructing using liquid processing a heteroepitaxial junction – we unite the benefits of quantum dots and perovskites in a new material. First we develop the materials chemistry to produce quantum dots in perovskites (DiP). We investigate the properties of DiP, finding that an epitaxial-quality heterointerface enables efficient transport to, and injection across, the type-I heterojunction between the perovskite matrix and the quantum dots embedded therein.
We then explore three classes of devices that leverage DiP. In the first, we make the most efficient solution-processed infrared light-emitting diode, a device that has both an average external quantum efficiency of 5.2% and a record peak power conversion efficiency of 4.4%. This record PCE represents a fully 2-fold improvement relative to the best prior reports.

We then develop a new class of solution-processed photodetectors--field-emission devices that leverage voltage-driven emission of photoelectrons into the high-mobility perovskite transport phase. The devices exhibit specific detectivities that exceed $10^{12}$ Jones.

Finally, we show how DiP can enable advances in the mechanistic understanding of new optoelectronic materials. We report the application of DiP to characterize the diffusion length of minority carriers in single-crystal perovskites – a metric that has, until this work, been the subject of orders-of-magnitude controversies in prior works. These new insights into diffusive transport enable me to provide quantitative bounds on the ultimate potential of perovskite solar cells.

Overall, this work showcases the promise of dot-in-perovskite materials that unite solution processing, infrared emission, and excellent carrier transport. It concludes with a discussion of paths forward toward further application of these exciting materials in next-generation optoelectronics.
Acknowledgments

I am deeply indebted to Prof. Ted Sargent, my supervisor, a visionary mentor, a great leader, who excels in everything he involves himself in. It is impossible to count all the ways he has helped me in my professional development. I have been extremely lucky to have had the chance to work with Ted - his influence has been life-altering.

I am grateful to all the members from Sargent group for their kind help and active collaboration. In particular, Dr. Oleksandr Voznyy helped connect me with Ted in the first place, and generously provided guidance, wisdom, encouragement, and precious friendship through my studies.

I thank Dr. Zhijun Ning and Dr. Riccardo Comin for helping me learn key lab methods in the group when I first started. They selflessly shared their knowledge and expertise in chemistry and physics, and this put me on the fast track to learning and growing professionally.

I thank Grant Walters, who I had the pleasure to work with through my entire PhD, for being such an awesome colleague with great sincerity and integrity. I also appreciate his help in photoluminescence and language polishing.

I thank Jeannie Ing, Elenita Palmiano, Remigiusz Wolowiec, Damir Kopilovic, and Dr. Larissa Levina. Without their kind help, the work of this thesis would have taken much longer to complete.

I thank Dr. Alex Ip, Dr. Pelayo García de Arquer, Dr. Valerio Adinolfi, Dr. Mingjian Yuan, and Dr. Michael Adachi, for help and advice when I first joined the group.

I thank all the Sargent group members with whom I had the chance to collaborate. Their contributions were of central importance to the completion of each project discussed in this thesis.

Finally, I want to thank my parents, especially my mother Henglan Zhang, who has been the source of support and inspiration throughout my studies.
Statement of Collaborations

In the work reported in this thesis, I benefited from many productive collaborations with colleagues in the lab.

At the beginning of each body chapter of the thesis, I write a brief summary indicating:

- my contributions;
- the contributions of each of my co-first authors (which tend to be similar in amplitude to my role, since we are co-first authors together - but I explain their area of focus and contribution, and also explain my own);
- a little more briefly, that of other coauthors.

Throughout this document, I use “I,” “we,” and I also use passive voice, without any particular significance. To appreciate my contributions and those of others, please refer instead to the discussion of contributions at the start of each chapter.
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Chapter 1
Introduction

Semiconductors—solids whose resistance lies between that of metals and that of insulators—are the essential building blocks of modern electronics and optoelectronics\textsuperscript{1,2}. Computers, smartphones, digital cameras, and the internet are among the resulting technologies.

Conventional semiconductors are inorganic solids with high crystallinity. They can be categorized into four groups based on their chemical composition: IV (e.g. Si, Ge), III-V (e.g. GaAs), II-VI (e.g. CdS), and IV-VI (e.g. PbS) semiconductors\textsuperscript{3,4}. The atomically ordered lattice of single-crystal semiconductors gives rise to extraordinary electronic properties, such as low defect densities, high charge carrier (electron and hole) mobilities, and long minority carrier diffusion lengths. These properties are of essential importance for achieving high performance in devices. Typically, crystallinity is achieved only with the benefits of high temperature and high vacuum syntheses; these add complexity and curtail the ready manufacture of semiconductor devices\textsuperscript{5,6}.

Solution-processed semiconductors have drawn intense research attention in light of their potential for low cost, large-area processing, and physically-flexible and conformal integrations\textsuperscript{7,8}. Organic materials and colloidal quantum dots are contributing to the field of next-generation semiconductor devices, particularly in photovoltaics, light emitters, detectors, and transistors.

1.1 Colloidal Quantum Dots

Colloidal quantum dots (CQDs) are semiconductor particles that have nanometer dimensions and that are synthesized from solution\textsuperscript{9}. Since the early 1980s, research in CQDs has focused on their chemical synthesis and their resulting physical properties. CdSe, PbS, ZnO, and TiO\textsubscript{2} have been explored particularly for use in solar energy harvesting, light emission and sensing\textsuperscript{10}.
1.1.1 Quantum confinement and spectral tunability

Spectral tunability is one of the desirable properties of quantum dots. It stems from the quantum confinement effect: when the size of a semiconductor particle approaches its Bohr exciton radius, typically in the 1-20 nm range, the spatial distribution of the electronic wave function becomes comparable with the geometrical size. Constrained by the particles’ boundaries, electrons experience an increase in their energy levels, and go from possessing continuous energy bands to having discrete levels.\(^\text{11}\) With decreasing size, the quantum dot bandgap increases: for example, bulk lead sulfide (PbS) exhibits a narrow bandgap of 0.41 eV and a large Bohr radius of 18 nm. When the size of PbS particles decreases to 4 nm, the bandgap increases to 1.1 eV\(^\text{12}\).

The size-dependent bandgap (Figure 1.1) means that the absorption spectrum can be readily tuned via control over particle size. A series of CQD layers with different absorption onsets can be stacked together to absorb more fully the broad solar spectrum. The concept of CQD tandem solar cells offers an avenue to fabricate multi-junction solar cells with high power conversion efficiencies (PCE) that overcome the Shockley–Queisser limit\(^\text{13}\).
As a result of quantum confinement, the emission wavelength of CdSe QDs can be tuned from blue to red by increasing QD size, as seen in Figure 1.2.a. The co-localization of the electron and hole wavefunctions in CQDs also contributes to fast radiative recombination and thus to impressive light emission performance.

Photoluminescence quantum yield (PLQY) is a key parameter used to quantify the performance of a light emitter:
Upon photoexcitation, tightly bound pairs of electrons and holes — excitons — are formed in QDs. The exciton binding energies ($E_b$) of QDs are dramatically enhanced compared to bulk counterparts. The high $E_b$ allows the bimolecular recombination to dominate over trap recombination and Auger recombination. As a result, the PLQY of QDs can approach unity$^{14,15,16,17}$.

As shown in Figure 1.2.b, CQDs emit light with much sharper linewidths (< 30 nm) when compared to organic emitters—another type of solution-processed semiconductor. The sharp linewidths arise from the transitions between discrete energy levels caused by the quantum confinement effect. The feature of narrow emission expands the color gamut of CQD LEDs to cover up to 140% of the National Television System Committee (NTSC) standard$^{18}$, while other
technologies generally fail to fulfill this because of their broad emission profile. Thus, CQDs are widely viewed as appealing candidates for next-generation display technologies.

1.2 Perovskites

Perovskites are a class of compounds having a composition of ABX$_3$ and forming with the same type of crystal structure as calcium titanium oxide (CaTiO$_3$). In the case of metal-halide perovskites, A represents an organic (e.g. CH$_3$NH$_3^+$) or small metal (e.g. Cs$^+$) cation; B is a metal cation (e.g. Pb$^{2+}$); and X is a halide anion (e.g. Cl$^-$$^2$). Metal-halide perovskites typically exhibit direct bandgaps and can be synthesized via solution processing.

From 2010 to 2015, researchers engineering metal-halide perovskite based solar cells have made impressive progress. The cells’ power conversion efficiencies have improved from 3% to over 20% in this period$^{19}$. They have rapidly emerged as contenders to rival conventional semiconductors, including monocrystalline silicon, which possesses an indirect bandgap. Their excellent photophysical properties, including large absorption cross sections, low trap densities, high mobilities, and long diffusion lengths, endow perovskite solar cells with their promising performance. The thermal conductivity of perovskites is generally very low (< 1W/mK)$^{20-23}$, which makes them potential candidates in certain thermoelectric applications if the electrical conductivity can be further improved through doping.

Since LEDs and solar cells share a number of common touchpoints – excellent transport and low nonradiative recombination benefit each one$^{24}$ – we sought in this work to leverage major recent advances in perovskite solar cells, and translate these into improved light-emitting diodes. The materials’ high color purities, and emission wavelengths tunable from the near ultraviolet to the near infrared, i.e. from 410 nm to 780 nm, make them of particular interest in the realization of next-generation optical sources.
1.3 Thesis outline

CQDs and perovskites are promising solution-processed semiconductors for next-generation optoelectronics. However, to translate the potential of CQDs and perovskites into impressive and robust devices, there remain challenges in material properties and device structures that have yet to be overcome.

In CQD electronics, challenges include high trap densities, low carrier mobilities, and short diffusion lengths. In view of the excellent properties of perovskites on these fronts, it is interesting to postulate that one might build heterostructures of CQDs and perovskites that could contribute to addressing these limitations in CQD solids.

My doctoral work focused on uniting CQDs and perovskites synergistically. I term the main new material at the heart of this work quantum dots in perovskite (DiP) solids. The architecture of the thesis is depicted in Figure 1.3.

In Chapter 2 I study existing challenges in CQD photovoltaics and photodetectors and in light emission. Chapter 3 proposes a new strategy to address these challenges by building a new material platform—DiP solids. I then investigate the structural and electronic properties of these materials in detail. Chapter 4 and 5 apply DiP in LEDs and photodetectors.

In Chapter 6 I use DiP in a new way: to enable the study of carrier diffusion in perovskites. In the final Chapter, I conclude by summarizing the main findings and paths forward identified in this work.
Figure 1.3 Structure of this thesis.
Chapter 2
Grand Challenges in CQD Optoelectronics

CQD optoelectronic devices achieve conversion of energy between photon and exciton forms. I first review the optical and electronic properties of excitons in the context of generation, recombination, and transport. I then briefly introduce the two major branches of CQD optoelectronics: LEDs and photodetection, and list challenges in exciton manipulation.

2.1 Excitonic process in CQDs: generation, dissociation, recombination, and migration

An exciton is an electrically neutral quasiparticle formed by an electron-hole bound together via the Coulomb interaction. Excitons can be generated in CQDs via the absorption of a photon (Figure 2.1.a) having energy above the bandgap of the semiconductor; or through the association of a pair of free carriers (electron and hole) under electrical injection (Figure 2.1.b) \(^{25}\).


Once formed, an exciton can remain intact, or it can dissociate into a free electron and hole (Figure 2.1.e). The exciton binding energy ($E_b$) is the energy required to break an exciton. Free carriers then migrate until they recombine through defect-assisted, radiative, or Auger recombination.

**Figure 2.1** *Exciton generation, dissociation, recombination, and migration.*

Defect or trap-assisted recombination is a non-radiative process that involves electronic states inside the bandgap\(^{26}\). Trap states originate from a disruption in the periodicity of the crystal lattice. Solution-processed materials can suffer from a high defect density stemming from their low-temperature synthesis and large surface area. On the surface of quantum dots, incomplete passivation can introduce a large density of surface defects including dangling bonds\(^{27}\), surface strain, and vacancies. Trap states associated with these defects then serve as non-radiative recombination centers for both excitons and free carriers\(^{28,29}\).
Radiative recombinaiton occurs when an electron and a hole annihilate, accompanied by the emission of a photon having an energy given by this excitonic transition. The oscillator strength of the transition is proportional to the overlap integral between the electron and hole wavefunctions\(^\text{26,30}\). In the strong-confinement regime exhibited in small quantum dots, the overlap integral increases with decreasing quantum dots size, favoring radiative recombination among decay channels.

Auger recombination in semiconductors describes the process whereby an electron recombines with a hole and transfer its energy non-radiatively to a third carrier (electron or hole) and elevates it to a higher energy (hot) state. The Auger process is mediated by Coulomb interactions, the strength of which is greatly enhanced in confined systems. The rate of the Auger process is significantly enhanced in QDs compared to bulk. As a high-order process whose rate is proportional to the cube of the carrier density, Auger recombination accounts for the major source of non-radiative loss under high injection conditions\(^\text{31}\).

2.2 Working principles, challenges, and prior art in CQD optoelectronic devices

Depending on the purpose and the function of quantum dots, the strategy to manage excitons in a device will be different. I first describe considerations in light-emitting devices including LEDs and lasers, and then move on to light-absorbing devices such as solar cells and photodetectors.

2.2.1 CQD LEDs: charge injection and radiative recombination

A good CQD LED should have a high radiative efficiency, a low barrier to charge injection, and low carrier loss during carrier diffusion. Unfortunately, the luminescence efficiencies of CQD films, especially for NIR CQDs\(^\text{32}\), have previously been rather low. This is the result of self-quenching, wherein inter-dot transport facilitates transport-assisted trapping, leading to
recombination even at relatively rare defect sites\textsuperscript{33}. Materials with highly mobile carriers, such as close-packed CQD films, can also exhibit exciton dissociation, and this competes with radiative recombination and further enhances self-quenching\textsuperscript{34}.

Strategies to prevent self-quenching in CQD films typically include the growth of a protective shell\textsuperscript{35}, capping using insulating organic ligands\textsuperscript{32}, and incorporation into a polymer matrix\textsuperscript{36,37,38}. However, these also lead to increased power consumption since a higher voltage is required to inject sufficient current to achieve bright light emission. A trade-off between emission efficiency and charge transport has persisted until now, a fact that accounts for the modest PCEs of CQD-based LEDs. Before the work in this thesis, the highest PCE of a solution-processed NIR QD LED was 2.4\%\textsuperscript{39}.

### 2.2.2 CQD Photodetectors: Exciton dissociation and extraction

In contrast to light-emitting devices, light-absorbing devices including photodetectors and solar cells transform light signals into electric signals. Figure 2.2 illustrates the working principle of photodiodes: excitons are generated within the CQD layer via photoexcitation, dissociate into free

![CQD photodetector diagram](image)

Figure 2.2 CQD photodetectors. Photogenerated carriers are separated and extracted by an applied bias. Copyright 2016 American Association for the Advancement of Science.
carriers, and are extracted separately via the hole transport layer (HTL) and electron transport layer (ETL). The dissociation of excitons and the extraction of free carriers is mediated by drift and diffusion and can be facilitated by an applied electric field ($V_a$).

There are several metrics to evaluate the PD performance that address efficiency, sensitivity, and speed. Responsivity (R) is defined as the photocurrent per incident power. The EQE of a PD is equal to the photocurrent divided by the rate of incident photon arrival.

The sensitivity of a PD is determined by its ability to deliver a high signal-to-noise ratio (SNR) compared to its noise current ($I_{N}$)\textsuperscript{40}. The noise-equivalent power (NEP) is one measure of sensitivity: it is the minimum incident optical power that a device can distinguish from noise\textsuperscript{41}. A more general description of sensitivity is the specific detectivity ($D^*$), corresponding to the SNR at 1 Hz detection bandwidth and with a device area of 1 cm$^2$ and incident power of 1 W. Table 2.1 lists commonly used metrics of PD performance\textsuperscript{41}.

Table 2.1 Metrics of performance in photodetectors. Copyright 2017 Nature Publishing Group.

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<tr>
<th>Metric</th>
<th>Units</th>
<th>Definition</th>
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<tr>
<td>Photocurrent (Iph)</td>
<td>A</td>
<td>Current flowing through a device due to illumination</td>
</tr>
<tr>
<td>Dark-Current (Id)</td>
<td>A</td>
<td>Current flowing in the absence of illumination</td>
</tr>
<tr>
<td>Responsivity (R)</td>
<td>A/W</td>
<td>Ratio of the photocurrent to the incident optical power</td>
</tr>
<tr>
<td>EQE</td>
<td>%</td>
<td>Number of carriers circulating divided by number of incident photons</td>
</tr>
<tr>
<td>Gain (G)</td>
<td>Unitless</td>
<td>Number of carriers divided by the number of photons absorbed</td>
</tr>
<tr>
<td>3dB-bandwidth (BW)</td>
<td>Hz</td>
<td>Modulation frequency at which the responsivity of the device is half of that at steady state conditions.</td>
</tr>
<tr>
<td>Noise current ($I_{N}$)</td>
<td>A/Hz$^{1/2}$</td>
<td>Root mean square of current fluctuation</td>
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<tr>
<th><strong>Noise Equivalent Power (NEP)</strong></th>
<th><strong>W/Hz$^{1/2}$</strong></th>
<th>Optical power that would be required to generate IN. A measure of the sensitivity of the device (NEP=$I_N/R$).</th>
</tr>
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<tbody>
<tr>
<td><em><em>Normalized detectivity (D</em>)</em>*</td>
<td><strong>Jones</strong></td>
<td>NEP normalized to the area of the device ($A_d$) and electrical bandwidth of the noise measurement ($B$). $D^*=A^{1/2}/$NEP</td>
</tr>
<tr>
<td><strong>Spectral selectivity (FWHM)</strong></td>
<td><strong>nm</strong></td>
<td>Full width at half maximum resonance width</td>
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Compared to conventional and organic semiconductors, CQDs possess both low manufacturing cost and the advantage of sensing near infrared (NIR) light. In 2006, a CQD photoconductor reached signal-to-noise performance comparable to that of an InGaAs photodetector, with a $D^*$ of $2\times10^{13}$ Jones.

The best CQD photodiodes should combine low trap density with high carrier mobility in order to achieve a high extraction and collection efficiency. However, the mobility of CQD solids has been reported in the range of $10^{-2}~10^{-3}$. Further, widely-used strategies to passivate surfaces and surface trap densities - such as using long organic ligands and giant shells - further reduce the mobility. The conflict between low trap density and high mobility remained unbroken at the start of my doctoral work.
Chapter 3
Quantum Dots in Perovskites

Chapter 3 contains work from “Quantum-dot-in-perovskite Solids,” published in *Nature*, 523, pages 324–328, (2015) and reprinted with permission from the Nature Publishing Group. I was co-first author on this publication together with Dr. Zhijun Ning and Dr. Riccardo Comin. Zhijun and I lead the experimental design, project implementation, data interpretation and manuscript preparation. Dr. Riccardo Comin carried out the photoluminescence lifetime and excitation measurements and analysis. Zhijun, Riccardo, and I together wrote the manuscript. Density functional theory calculations were performed by O. Voznyy, and A. Buin; PLQY and the carrier transfer efficiency studies were carried out by G. Walters. Transmission electron microscopy (TEM) and the corresponding analysis were carried out by F. Fan and E. Yassitepe.

In the previous chapters, an analysis of the strengths and limitations of CQDs and perovskites led to the idea that heterostructures could usefully be built using these materials. In this chapter, I introduce heteroepitaxy in semiconductors, and then discuss the considerations in selecting a material for liquid epitaxy. DFT simulations indicated that PbS quantum dots and metal-halide perovskites (CH$_3$NH$_3$PbI$_3$) could potentially be united. I then describe the strategy we developed to build heteroepitaxial structures. At the end of the chapter, I present the structural and photophysical properties of DiP.
3.1 Heteroepitaxy in semiconductors

Atomically-aligned growth of a crystalline film atop a substrate—heteroepitaxy—is the foundation of optoelectronics, especially lasers, solar cells, and light-emitting diodes that rely on extremely low interface densities among constituent semiconductor crystalline phases\textsuperscript{42-46}. Crystalline coherence is preserved even when atomic identity is modulated, a fact that is the critical enabler of quantum wells, wires, and dots\textsuperscript{47-50}. The interfacial quality achieved through heteroepitaxial growth allows new combinations of materials with complementary properties, enabling the design and realization of functionalities not available in the single-phase constituents.

For inorganic semiconductors, heteroepitaxy has relied largely on vacuum methods such as molecular-beam epitaxy (MBE), atomic-layer epitaxy (ALE), and metalorganic vapour phase deposition (MOCVD). Through these methods, theoretical predictions have been tested and refined that describe conditions under which crystalline coherence can be preserved even in the presence of a mismatch in the native lattices (strained-layer epitaxy). The result is a considerable body of theory, knowledge, and practice regarding vapor-phase epitaxy. Since interfacial defects can be rendered rare at suitably-designed hetero-interfaces, highly efficient luminescent materials have been created that have enabled efficient electrically-injected lasers and light-emitting diodes for fiber-optic communications and high-efficiency lighting.

CQDs share features with other solution-processed material, including the high chance of defect formation due to the low-temperature synthesis and high specific surface area. As discussed in the previous chapter, low mobility of CQD solid is another challenge to solve in order to achieve electronics with higher performance.
In this vein, and with astonishing rapidity, bulk organohalide semiconductor perovskites exhibiting large and impressively ordered crystalline domains have improved in size, properties, and performance. These remarkable materials have enabled the ascent of the perovskite solar cell\textsuperscript{51–53}.

We postulated that, under the right conditions, heteroepitaxial alignment could be produced between bulk perovskite semiconductors and quantum-tuned nanoparticles. Thin films comprising multi-material, yet internally-epitaxially-aligned, heterocrystals – complex crystals we herein term poly hetero crystalline (PHC) solids – could unite, without undue photocarrier loss, the desired properties of each phase: the excellent charge carrier transport of the bulk perovskites, and the quantum-tuned infrared luminescence/absorption of the quantum dot phase.

### 3.2 Material design for liquid hetero-epitaxy between CQDs and perovskites

To implement the ideas of heteroepitaxy in solution-processed materials, we sought a materials system that would show promise for epitaxial alignment, and would illustrate also its applied potential. From an applied perspective, methylammonium lead iodide perovskite (MAPbI\textsubscript{3}) has led to the most efficient solution-processed solar cells reported. Colloidal quantum dots based on PbS have been widely shown to exhibit highly tunable photophysical properties, including in the near- and short-wavelength infrared which, today, the perovskites fail to access. From a materials science perspective, MAPbI\textsubscript{3} (tetragonal) and PbS (rocksalt) possess related crystal structures, each having a six-coordinated Pb atom, and with Pb-Pb distance (PbS 5.97 Å, MAPbI\textsubscript{3} 6.26 Å) that reside within 4.6% of one another\textsuperscript{54}.
Consequently, we sought to produce a solid solution phase quantum dots in a perovskite matrix (Figure 3.1). Structurally, the PbS CQD lattice can match well with the perovskite structure both two-dimensionally (Figure 3.1.a) and three-dimensionally (Figure 3.1.b).

Pioneering studies have previously elucidated the synthesis and properties of composite organic/inorganic crystalline hybrids\(^4\); here we aimed instead to engineer a heterocrystalline solid-state solution between two different, but structurally affine, materials. Specifically, this work was motivated by the opportunity to combine the strong luminescent efficiency/large absorption cross section of the quantum dots with long-range carrier transport in the perovskite matrix.

Figure 3.1 **Theoretical model of perovskite epitaxial growth on colloidal quantum dots (CQDs).** a, Atomistic model of CQDs in perovskite matrix in three-dimensional (3D) view. b, Cross-sectional (2D view) scheme of single CQD in perovskite. The facets of CQDs can match well with perovskites.
Structural affinity alone is necessary but not sufficient to offer epitaxial bonding between the two phases; energetic considerations must also be taken into account. Density functional theory (DFT) was used to study the interface formation energy between PbS (100 facet) and perovskite (110 facet) (Figure 3.2.a). The interfacial energy is less than 10 meV/Å², suggesting that the growth of perovskite on PbS at room temperature is nearly as feasible as homoepitaxy of PbS-on-PbS or perovskite-on-perovskite. DFT further revealed that the epitaxial 3D embedding of PbS CQDs inside a perovskite matrix can be achieved without the formation of interfacial defects, i.e. the bandgap is predicted to remain open, with no in-gap defects predicted.

Figure 3.2 DFT simulation of DiP. a, b, modelling of PbS and MAPbI₃ crystal structure and their interface, showing that perovskite can match well with PbS from both Z axis [001] and X-Y axis [010]. c, the density of state (DOS) of CQDs that match with perovskite, and the states are mostly localized in CQD, no trap state is introduced.
3.3 Synthesis of DiP

To implement atomic-level coherence between the inorganic PbS and the organometallic MAPbI₃ phase, we required an organic-ligand-free strategy in the capping of the PbS nanoparticles. With this in mind, we leveraged the recent synthesis of colloids stabilized not using traditional aliphatic ligands, but instead using halide ligands introduced from the perovskite precursor methylammonium iodide\textsuperscript{55,56}.

![Image of synthetic route]

Figure 3.3 **Synthetic route toward DiP**, including solution-phase ligand exchange and 2-step deposition to form perovskite thin films.

We therefore proceeded to design the strategy to build a PHC solid as shown in Figure 3.3. We began by exchanging organic ligands on the PbS CQDs, replacing them with short halide (iodide in this case) anionic ligands. We then mixed these inorganically-terminated CQDs with PbI₂ dissolved in butylamine. This solvent strategy was crucial to maintaining CQD surface passivation...
following film growth. Since PbI$_2$ forms a complex with iodide and binds to the CQD surface, PbI$_2$ and CQDs mixed well with one another. By controlling the ratio of PbI$_2$ and CQDs, we were able to tune the nominal CQD concentration – hereafter expressed as the ratio of CQD to total volume – across the range 0.2% to 29%. To fabricate the CQD:MAPbI$_3$ films, we used the previously-established sequential (two-step) method$^{57}$, whereby the PbI$_2$:CQD films are initially deposited via spin-coating onto a glass substrate, and these are then soaked in a CH$_3$NH$_3$I/isopropanol solution. Details of the synthesis will be discussed in the following paragraphs.

**CQD synthesis and solution ligand exchange**

Colloidal quantum dots (CQDs) were synthesized using methods previously reported$^{58}$. For iodide ligand exchange, 3 mL of CQDs dispersed in octane (10 mg/mL) were added into 3 mL of dimethylformamide (DMF) solution containing 350 mg of PbI$_2$ and 150 mg of CH$_3$NH$_3$I. After stirring for 10 minutes, CQDs had transferred from the top octane phase to the bottom DMF. After removing the octane, we washed the CQD solution three more times using octane to remove the organic residue. Subsequently the CQDs were precipitated by the addition of toluene. The nanoparticles were dispersed in butylamine for film fabrication.

**Poly heterocrystalline (PHC) DiP solid fabrication**

A two-step method for perovskite thin film fabrication was employed. It included a first step of fabricating the precursor PbI$_2$ thin film, and a second step of introducing the organic cations via soaking. A given amount of PbI$_2$ (with one quarter weight ratio of CH$_3$NH$_3$I) was added into the CQD butylamine solution for perovskite growth. A spin-coating process was used for film fabrication (spin speed of 6000 rpm, 10 s). Films were then annealed at 70 °C for 10 minutes in an N$_2$ glovebox.
For perovskite growth, methylammonium iodide solution (10 mg/mL in isopropanol) was deposited and left on the film for 30 seconds. After the solution was removed by spin-coating (spin speed 6000 rpm), the film was soaked in pure isopropanol for 10 seconds, and then a spin coating process was carried out to remove the residual solvent. At the end, the film was annealed again at 70 degrees for 10 minutes in an N₂ glovebox.

Table 3.1 shows that by varying the mass ratio between CQDs and perovskite precursors, the ratio of PbS CQDs to perovskite can be systematically controlled. It lists the values for the nominal MAPbI₃ to PbS mass ratio (first column) and volume ratio (second column), PbS to MAPbI₃ volume ratio (third column), and PbS volume percentage over total volume (fourth column).

Table 3.1 Composition of DiP solid.

<table>
<thead>
<tr>
<th>PbI₂: PbS Mass:Mass ratio</th>
<th>MAPbI₃ : PbS Vol:Vol ratio</th>
<th>PbS : MAPbI₃ Vol:Vol ratio</th>
<th>PbS Volume percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>497</td>
<td>0.002</td>
<td>0.2</td>
</tr>
<tr>
<td>100</td>
<td>248</td>
<td>0.004</td>
<td>0.4</td>
</tr>
<tr>
<td>50</td>
<td>124</td>
<td>0.008</td>
<td>0.7</td>
</tr>
<tr>
<td>20</td>
<td>49</td>
<td>0.020</td>
<td>1.9</td>
</tr>
<tr>
<td>10</td>
<td>24</td>
<td>0.040</td>
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<td>12</td>
<td>0.080</td>
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</tr>
<tr>
<td>1</td>
<td>2</td>
<td>0.401</td>
<td>28.6</td>
</tr>
</tbody>
</table>

3.4 Structural and photophysical studies of DiP
As shown above, MAPbI₃ perovskites and pre-formed colloidal quantum dots, combined in the solution phase, can produce epitaxially-aligned dots-in-a-matrix crystals. We will now present
TEM and diffraction studies that revealed that heterocrystals as large as \(~60\) nm and containing at least 20 mutually-aligned dots were formed; and that the dots inherit the crystalline orientation of the perovskite matrix. The heterocrystals exhibited remarkable optoelectronic properties traceable to their atom-scale crystalline coherence: photoelectrons and holes generated in the larger-bandgap perovskites are transferred with 80% efficiency to become excitons in the quantum dot nanocrystals, leveraging perovskites’ excellent photocarrier diffusion to produce bright light emission from infrared-bandgap quantum-tuned materials. By combining the excellent electrical transport of the perovskite matrix and the high radiative efficiency of the quantum dots, we produced a new platform to advance solution-processed infrared optoelectronics.

3.4.1 TEM analysis of heteroepitaxial materials

High-resolution transmission electron microscopy (HRTEM) was used to characterize the crystal structure and orientation of both CQDs and perovskite matrix for a sample with nominal CQD volume percentage of 4%.

Since MAPbI$_3$ is an organic/inorganic hybrid material with lower density than PbS, it shows much lower contrast than inorganic CQDs, thus facilitating differentiation among the perovskite and PbS phases. The higher contrast of CQDs was confirmed using high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), a direct probe of density variations in the material.

HRTEM map of Figure 3.4.a, while Figure 3.4.b shows the corresponding Fast Fourier transform (FFT), with lattice planes indexed as indicated in Figure 3.4.c. The contributions from the perovskite matrix vs. from the quantum dots can be distinguished by analyzing the subregions shown in Figure 3.4.d and Figure 3.4.g for the perovskite and quantum dots, respectively. Well-defined lattice fringes with 2.2 Å separation (Fig. 2d) can be indexed to the (224) plane of the
matrix, as confirmed by the corresponding FFT images (Figure 3.4.e and Figure 3.4.f), which show that the real-space HRTEM image is projected along the [2\overline{2}4] zone axis.

The lattice fringes of the CQDs were also measured. They show the same orientation and can be indexed as the (022) plane of PbS (2.1 Å), (Figure 3.4.g, h, i). This is consistent with simulations that show how the (100) facet of PbS matches well with (110) facet of perovskite. Strikingly, from FFT, the facet angles between (224) and [201] of the perovskite are the same as between the (022) and [111] facets of PbS. Hence, the orientation relationships between MAPbI₃ and CQDs can be identified as below:

\[(022)_{\text{PbS}} \parallel (224)_{\text{MAPbI₃}}; \quad [111]_{\text{PbS}} \parallel [201]_{\text{MAPbI₃}}.\]

From this we concluded that the matrix and CQDs show the same orientation, readily observed both in real-space microscope images and confirmed using FFT. This analysis demonstrates epitaxial orientational alignment between perovskite and CQDs.
Figure 3.4 High resolution transmission electron microscopy (HRTEM) images. CQD:Perovskite hybrid (CQDs volume percentage: 3.9%) a,b,c, MAPbI$_3$ d,e,f, and CQDs g,h,i are shown separately. For the perovskite, the lattice fringes are indexed to the (224) facets. For the CQDs, the lattice fringes are indexed to the (022) facets. In real space, the d-spacing value of the (224) facet of perovskite (2.2 Å) matches well with the (111) facet of PbS (2.1 Å). This is consistent with the modeling, which shows that the (100) facet of PbS matches well with (110) facet of perovskite. The FFT image shows the same intersection angle (60 degree) for both perovskite and CQDs, indicating that they match not only two dimensionally, but also three dimensionally, confirming again that perovskite and CQDs have the same orientation.
3.4.2 Photophysical interaction between CQDs and perovskites

Optical absorption spectra for pure CQD films and for the DiP PHCs are shown in Figure 3.5.a. Absorption signatures corresponding to each constituent, perovskite and CQD, are apparent in the hybrid films (Figure 3.5.a). The photoluminescence (PL) spectra show emission associated with CQDs in film (Figure 3.5.b), indicating that the photophysical properties of CQDs remain substantially intact when the CQDs are incorporated into the perovskite matrix.

As CQD concentration increases, the absorption spectrum red-shifts, consistent with increased inter-dot interaction (potentially partial dot fusion at these high concentrations) which reduces the extent of quantum confinement and thus shrinks the bandgap. This affects absorption and luminescence to the same extent, i.e. it does not, to first order, impact the Stokes shift.

A second effect is increased long-range excitonic and carrier transport from dot to dot, present only at the highest concentrations. Through this process, excitons and carriers are transferred to the smallest-gap dots in an inhomogeneously-broadened population. This effect does not impact absorption, but does red-shift the luminescence, and thus increases Stokes shift\(^{19,20}\).

An additional mechanism produces a blueshift (even relative to dots in solution) at low CQD loading: tensile strain caused by the lattice mismatch between CQDs and the perovskite slightly expands the PbS lattice, leading to an increase in bandgap\(^{21}\) (Figure 3.5.c). This tensile strain acts to the same extent on absorption and emission.
Figure 3.5 **Photophysical response of CQD:perovskite hybrids.** Matrix-tuned absorption a, and photoluminescence b, of CQD:perovskite hybrid. After the growth of perovskite, a representative absorption edge around 770 nm appears, while both absorption and photoluminescence (PL) CQD exciton peaks are preserved, indicating that the properties of CQDs remain unaltered. c, CQDs absorption and PL exciton peak position shift as a function of CQD:MAPbI$_3$ ratio, with different concentration-dependent mechanisms highlighted. d, PL quantum efficiency (PLQE) of CQDs in matrix. For lower CQD concentration the PLQE is increased, indicating that CQDs are well dispersed in the matrix and carrier dissociation between CQDs is blocked. In the MAPbI$_3$ matrix, the PLQE is two orders of magnitude higher than that in a NaI matrix, which reveals that a lattice-mismatched matrix (8.8% mismatch for NaI) cannot grow on PbS. This finding confirms that epitaxial growth of matrix on CQDs is critical for CQD surface passivation. The PLQE of a solution-exchanged CQD film (orange dashed line) is shown for comparison.
We then turned to investigating the CQD PLQY. Initially we employed an excitation wavelength of 815 nm, i.e. below the absorption edge of the perovskite (Figure 3.5.d), to excite the quantum dot phase directly and selectively. The PLQE is highest in low-dot-concentration samples, consistent with minimal quenching associated with the dissociation of excitons into free carriers in the neighboring quantum dots\textsuperscript{22}. The PL quantum yield reaches 9.3%, which is fully two orders of magnitude higher than that in the pure CQD film. As a control to study the importance of lattice matching on photophysical properties, we changed the matrix to sodium iodide (NaI) (rocksalt structure with 8.8% lattice mismatch with PbS): the PLQE of CQDs in a NaI matrix is almost two orders of magnitude lower than in perovskite matrix (Figure 3.5.d).

To elucidate the physical origins of enhanced PL efficiency for dots embedded in a perovskite matrix, we used DFT to investigate whether CQD surfaces can in principle be passivated using the perovskite matrix. Both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are located in the core of PbS CQDs, and the bandgap is trap-free (Figure 3.2.c and Figure A. 1).

### 3.4.3 Energy transfer from perovskite matrix to quantum dots

In addition to providing passivation, the matrix:dot interface will be the critical enabler of any charge carrier injection into the CQDs. To study carrier transfer across this interface, we relied on \(~4\) nm diameter CQDs (bandgap of 1 eV) whose LUMO energy level is predicted to lie below the conduction band of the perovskite and whose HOMO should reside above the valence band edge of the perovskite (Figure 3.6.a).
Figure 3.6 Carrier transfer from perovskite to CQDs. a, Electronic band structure of CQDs and perovskite. The LUMO level of CQD is lower than the conduction band of perovskite and the HOMO level position of CQD is higher than the valence band of perovskite, making the transfer of both carriers from perovskite to CQDs energetically favored. b, CQDs PL excitation spectra. In the perovskite absorption region ($\lambda < 780 \text{ nm}$), for increasing perovskite content, the PL excitation intensity is enhanced, indicating that carriers excited in perovskite are transferred to CQDs. However, considering the partial carrier loss (via recombination) in perovskite, the PLQE of the hybrid is lower than the internal PLQE of CQD when long excitation wavelength is used (inset). c, PL spectra of MAPbI3 for PHC films with different CQDs concentration. d,e,f, Transient PL emission from MAPbI3 (d) and CQDs (e) and corresponding time constants f. As the CQD:MAPbI3 is reduced, the initial PL decay time of both perovskite and CQDs become longer, as a result of longer transit time in the matrix and reduced carriers dissociation across the CQDs, respectively.
By generating excitons in the dots only (via photoexcitation using photon energies lower than the perovskite bandgap), and in separate studies instead photogenerating principally in the perovskite matrix, we investigate carrier transfer to, and across, the CQD-perovskite interface. Photoluminescence excitation spectra (PLE, Figure 3.6.b) reveal enhanced CQD emission when the perovskite is excited ($\lambda_{\text{excitation}} \leq 780 \text{ nm}$)\(^{59}\). Increased perovskite content drives a higher CQD PL intensity when the excitation occurs in the perovskite absorption region. This qualitatively indicates efficient charge diffusion to, and across, the perovskite-CQD interface. Carrier transfer also occurs in other composite nanomaterials\(^{34}\), such as in materials made up of small-bandgap-CQD inclusions in a large-bandgap-CQD matrix; however, we found that the use of a perovskite matrix provided superior passivation of the quantum dot centers as evidenced by the nearly two orders of magnitude higher PLQE compared to an NaI matrix (Figure 3.5.d).

The signatures of carrier transfer from the matrix to the quantum dots are also evident in the PL emission from MAPbI\(_3\) in PHC films as a function of CQDs concentration (Figure 3.6.c). In particular, for concentrations above 0.4%, we observe a complete quenching of the perovskite PL signal, consistent with efficient removal of photogenerated carriers from the matrix and transfer into the dots. At higher CQD concentrations, i.e. in the regime of low densities of injected carriers per dot where radiative recombination is dominant over higher-order (e.g., Auger) processes, we quantitatively estimate the carrier transfer efficiency from perovskite to CQDs based on PL and absorption data. The transfer efficiency attains a remarkable value exceeding 80% at the highest CQD loading (28% CQD volume percentage).

We investigated the carrier dynamics in the PHC using PL decay (Figure 3.6.d, 6e). We used a two-component decay model to analyze transient PL. The fast decay transient in CQDs is assigned to fast exciton dissociation into neighboring CQDs, while the longer dynamics are
ascribed to radiative recombination. Comparison between the PHC and the pure CQD PL transients in Figure 3.6.e shows a dramatic slowdown of exciton dissociation dynamics as soon as the CQDs are embedded in the perovskite matrix (from sub-ns in pure CQD to 20 ns in PHC at high CQD loading). Furthermore, the fast transient component increases from 20 ns up to 70 ns as the CQD concentration is reduced (see Figure 3.6.f) and correspondingly the inter-dot separation is increased, consistent with the expected suppression in the exciton dissociation rate for more isolated dots. Consistent with the CQD excited state lifetime, the perovskite carrier dynamics (Figure 3.6.d) show a rapid quenching of the PL emission, from 25 ns in pure MAPbI$_3$ to ~2 ns in the PHC film at lowest CQD loading. This is attributed to efficient carrier funnelling into the CQDs. The PL lifetime for carriers photoexcited in the perovskite matrix is highest (2 ns) at low CQD concentration (Figure 3.6.f), reflecting the larger interdot separation of ~40 nm at the lowest CQD loading: this delays the capture of carriers out of the perovskite phase and into the quantum dot inclusions. Correspondingly, the reduction in the average dot spacing and consequently in the charge transfer time for higher CQD concentrations causes a larger fraction of carriers to be transferred to the dots and explains the enhanced carrier transfer efficiency.

3.5 Conclusion

This chapter reports the in-situ growth of perovskite and preformed quantum dots together to create a hybrid heteroepitaxial material. The quantum dots are efficiently passivated via the action of the matrix, without the need for conventional organic ligands, when lattice-matching conditions are fulfilled. At the same time, the perovskite matrix provides carrier transport to the CQDs. The new approach paves the way for novel strategies to enhance the performance of CQD-based optoelectronic devices, and to extend towards the infrared the spectral diversity of perovskite-based materials.
Chapter 4
Highly Efficiency Near Infrared Quantum Dot LEDs Enabled by Dots in Perovskite

Chapter 4 contains work from “Highly efficient quantum dot near-infrared light-emitting diodes,” published in *Nature Photonics, volume 10, pages 253–257 (2016)*, and reprinted with permission from the Nature Publishing Group. I was co-first author on this publication together with Dr. Zhenyu Yang. We designed the experiments and wrote the manuscript together. I led the design of the materials, LED device fabrication, photoluminescence studies, optoelectronic simulations, and manuscript preparation. Zhenyu carried out device structure optimization, electroluminescence measurements, and analysis. PLQE measurements were performed by Grant Walters, and Eric Beauregard.

In the previous chapter, I reported a new material – dots in perovskite – that illustrated the fact that only by producing matrix materials exhibiting atom-scale crystalline coherence can photoelectrons and holes generated in larger-bandgap perovskites be efficiently transferred to the quantum dots. By leveraging perovskites’ excellent charge carrier mobilities and diffusion characteristics and the resultant efficient energy funneling, I showcased a material that offers bright light emission from infrared-bandgap quantum-tuned quantum dots.

In this Chapter, I translate this material from a photoluminescent to an electroluminescent application. I begin by explaining present-day challenges in CQD LEDs, and then discuss considerations in designing the next-generation of DiP materials for use in IR LEDs. Next, I demonstrate how the perovskite matrix, with its high mobility and long electron diffusion length, facilitates charge carrier transport, thereby lowering the turn-on voltage in operating LEDs. At the end of this chapter, I report a record power-efficient electroluminescent NIR LED constructed using a DiP active layer.
4.1 CQDs as NIR light emitters

Near-infrared (NIR) light-emitting diodes (LEDs) are used in a wide range of applications including night vision, biomedical imaging, and optical communications and computing. While advanced materials such as organic dyes and semiconductor polymers have shown excellent performance in visible lighting, they have so far failed to produce efficient NIR LEDs because of their large bandgap. In cases, researchers have shown that they can redshift the bandedge; however, this has consistently resulted in a low photoluminescence quantum yield in the NIR regime.

In light of CQDs’ high luminescence efficiency, emission wavelength tunability, and solution processability, researchers have invested considerable efforts exploring NIR emitting devices based on these materials. The reported power conversion efficiencies (PCE) have recently reached 2.4%.

Unfortunately though, as discussed in Chapter 2.2.1, CQD films today suffer a compromise between luminescence efficiency and charge transport, and this leads to unacceptably high power consumption.

Based on my photophysical studies of DiP, we postulated that quantum dots epitaxially embedded in a perovskite matrix could potentially overcome the trade-off between quantum efficiency and voltage efficiency: the perovskite matrix would provide a long diffusion length to enhance charge carriers’ diffusion efficiency, even when CQDs were widely spaced with the goal of avoiding self-quenching and exciton dissociation (Figure 4.1.a). The epitaxial interface between the perovskite matrix and the CQDs would serve to provide excellent passivation, improving both \( \eta_{\text{inj}} \) and \( \eta_{\text{PLQF}} \). The use of a type-I band alignment would enable electrons and holes to be
funneled efficiently from the matrix and be confined inside the CQDs, again preventing exciton dissociation losses.

4.2 Design of 2nd generation DiPs for NIR LEDs

Prior works discussed in Chapter 3 on quantum dot:perovskite solids suffered from a lattice mismatch (~5%) between the iodide-based perovskite and the PbS nanocrystals. We sought to explore the impact of varying the perovskite lattice constant via mixing of iodide and bromide

Figure 4.1 Quantum-dot-in-perovskite LED devices. a, Illustration of enhanced electroluminescence efficiency in PbS quantum dot in MAPbX3 (X=I, Br) perovskite CQD LEDs. b, HRTEM images of a PbS quantum dot in perovskite matrix; LED device architecture used in this study; and corresponding crossed-section SEM image of same device.
(Figure 4.1.a). The PLQY of quantum dot inclusions, as well as carrier transport in the matrix, are greatly increased in the mixed halide perovskite matrix (MAPbI\textsubscript{x}Br\textsubscript{3-x}) compared to the 1\textsuperscript{st} generation quantum-dot-in-perovskites that relied on MAPbI\textsubscript{3}\textsuperscript{64}. The introduction of bromide also enables a pinhole-free morphology and improves the carrier diffusion length in the perovskite matrix, resulting in lower trap-assisted recombination and consequently in more efficient emission from the active layer.

My LED device architecture is described in Figure 4.1.b: indium tin oxide (ITO) / titanium dioxide (TiO\textsubscript{2}, 10 nm) / dots-in-perovskite emission layer (350 nm) (Figure 4.1.c) / poly(9,9'-dioctylfluorene) (F8, 50 nm) / molybdenum trioxide (MoO\textsubscript{3}, 6 nm) / silver (Ag, 100 nm). The energy levels of F8 and TiO\textsubscript{2} layers are suitably aligned with the perovskite matrix to serve as electron and hole blocking layers, respectively, while enabling selective injection of the desired carrier type into the active layer. In addition, a type-I heterojunction between the quantum dot acceptor levels (dashed black line) and perovskite bandedges (blue and red line for the conduction and valence band, respectively) is maintained throughout the emissive QD-in-perovskite layer. Under forward bias, electrons and holes are injected from the cathode (TiO\textsubscript{2}) and anode (F8), respectively, and they are efficiently transferred to the quantum dots where they recombine radiatively.

The EQE curves (Figure 4.2.a) highlight the efficiency increase upon incorporation of small amounts of bromine, with a maximum EQE value of 3.8% for a matrix with 83% iodine molar concentration (the molar ratio between iodine and all halides). The EQE is 2.3 times higher than for the pure MAPbI\textsubscript{3} matrix. However, EQE drops with lower iodine content, with no NIR light emission for iodide molar concentrations below 67%. To investigate the origins of the matrix-
composition-dependent electroluminescence of CQDs, we further investigated the photophysical properties of quantum dots in the MAPbI$_x$Br$_{3-x}$ matrix.
The transport of photogenerated carriers into the quantum dots represents a first important function.
of the perovskite matrix. We found that the diffusion length (Figure 4.2.b), which will determine the efficiency with which electron-hole pairs can be delivered to the CQDs, shows a significant enhancement once bromine is incorporated into the matrix\textsuperscript{65}. The diffusion length and the photoluminescence lifetime (Figure A. 2) both peak at 83% iodine halide content. This perovskite matrix also shows the best stability in moist air (Figure A. 1).

We then studied the quality of the interface between quantum dots and perovskite. Figure 4.2.c shows that the PLQE of CQDs photoexcited below the perovskite bandgap increases with higher bromine concentration and peaks at 50% iodine concentration. As in the preceding discussion, the perovskite matrix grows epitaxially around the quantum dots, providing passivation of the CQD surface, and this leads to higher $\eta_{PLQE}$ and $\eta_{inj}$. We propose that the further-improved lattice matching reported herein through the use of the mixed halide matrix reduces strain at the heteroepitaxial interface, and further lowers the density of defects. We acquired powder x-ray diffraction data for pure quantum dots and also embedded in the MAPb$_{1-x}$Br$_{3-x}$ perovskite matrix to evaluate the lattice mismatch (Figure A. 4). Since the PbS lattice constant (5.91 Å) lies between that of MAPbI$_3$ (6.26 Å) and MAPbBr$_3$ (5.89 Å), the lattice match improves with increasing bromine concentration and peaks at 67% iodine content, where the interface exhibits the lowest strain.

In sum, the addition of bromine reduces the defect density both inside the perovskite matrix and on the CQD surface, improving diffusion efficiency and PLQY. Reduced non-radiative recombination losses should result in higher total luminescence efficiency of the material. Our optoelectronic device modeling shows that trap recombination is the most detrimental mechanism at low driving voltages (low brightness regime) while, at higher injection densities, Auger recombination becomes the dominant loss. Simulations in Figure 4.2.d show that, across the entire
range of achievable LED brightnesses, devices with the lowest trap density give the highest $\eta_{tot}$, highlighting the importance of controlling trap-related losses inside the conductive active layer.

### 4.3 Device performance of DiP LEDs

When CQDs are evenly distributed inside the perovskite matrix at low concentrations, the electroluminescence (EL) properties are dramatically improved compared with pure CQD-based devices. The strongest EL intensity observed in this work was from devices emitting at 1391 nm. The blueshift in the EL signal from CQD-in-perovskite devices compared to CQD-only counterparts is consistent with the shift in PL (Figure 4.3.a and Figure A. 5). We attribute the EL enhancement to the reduced self-quenching and excellent passivation from the perovskite, especially at the low CQD concentration at which dots are well-separated from one other (Figure 4.4.a).

Compared with other matrix materials such as polymers and inorganic crystals, the best perovskites exhibit considerably lower trap densities and higher mobility. This will beneficially affect the driving voltage required to achieve high brightness and thus high power conversion efficiency, a figure of particular relevance to practical device operation. To study how EQE translates into PCE, we investigated the current-voltage ($J$-$V$) characteristics in greater detail (Figure 4.3.c). The higher current density observed in the pure CQD device is due to the smaller bandgap (CQD: 0.89 eV vs. perovskite matrix: 1.73 eV) and a reduced thickness of the active layer. In the quantum-dot-in-perovskite devices, the current density is considerably lower at low applied voltages, producing a higher EQE. We attribute this, once again, to the epitaxially-aligned CQD/perovskite interface which passivates CQD trap states and reduces non-radiative recombination.
We determined a turn-on voltage of 1.0 V for the matrix-based LEDs (Figure 4.3.d), indicating effective carrier injection from the charge transport layer to the CQD inclusions. The brightness at each voltage is dramatically improved. For example, we measured a peak radianc of $2.6 \, W \, sr^{-1} \, m^{-2}$ at 3.5 V applied voltage, which is ~15 times higher than the control pure CQD device (Figure A. 7).
The combination of relatively high radiance and absolute output power, together with high EQE with low driving voltage, allows notable improvements in PCE values relative to prior reports (Figure 4.3.e). A peak PCE of 4.4\% is obtained at 1 V; more than two times higher than previous record values for IR CQD EL (Table 4.1). PCE values exceed 1\% in the full range 1–2 V, beyond which they maintain high radiance (up to 0.92 W sr\(^{-1}\) m\(^{-2}\)).
Table 4.1 Performance summary of PbS-CQD-based NIR LEDs with External Quantum Efficiencies higher than 0.5%.

<table>
<thead>
<tr>
<th></th>
<th>EL Wavelength (nm)</th>
<th>Turn-on Voltage (V)</th>
<th>Peak EQE (%)</th>
<th>Peak PCE (%)</th>
<th>Radiance (W sr⁻¹ m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N. Tessler, et al., <em>Science</em>, 2002[5]</td>
<td>1000-1300</td>
<td>2</td>
<td>0.5</td>
<td>0.02³⁹</td>
<td>\</td>
</tr>
<tr>
<td>X. Ma, et al., <em>Org. Electron.</em>, 2012[8]</td>
<td>1050-1600</td>
<td>~2</td>
<td>0.72</td>
<td>0.11³⁹</td>
<td>4.7</td>
</tr>
<tr>
<td>L. Sun, et al., <em>Nat. Nanotech.</em>, 2012[9]</td>
<td>800-1850</td>
<td>0.7-2.1 (depending on the CQD size)</td>
<td>2.0</td>
<td>1.0³⁹</td>
<td>6.4</td>
</tr>
<tr>
<td>This work</td>
<td>1160-1390</td>
<td>&lt;1</td>
<td>5.2</td>
<td>4.4</td>
<td>2.6</td>
</tr>
</tbody>
</table>

In sum, the perovskite-matrix-based devices simultaneously achieve both high radiance and power efficiency (Figure 4.3.f). The device radiance at maximum PCE is ~3.5x higher than in previous record CQD IR EL devices³⁹; similarly, the PCE at maximum radiance is also improved.

We showcased the same architecture and physical principles using a number of different CQD sizes. Consistent with the PLQE results (Figure A. 6), both the peak EQE and PCE average values increase as the CQD size increases (Figure 4.4). Although there is some variance at lower CQD concentrations, the EQE and PCE values are both maximized in devices with low CQDs loadings (3.6% volume ratio). In particular, the EQE values decrease significantly at higher CQD
concentrations (e.g., 16% volume ratio), a behavior we ascribe to the imperfect passivation by the perovskite matrix and the formation of dot-to-dot intercommunication channels. However, regardless of the perovskite/CQD ratio and emission wavelength, all CQD-in-perovskite LEDs exhibited higher EQE and PCE values than those based on pure CQDs as emissive layers, suggesting that the type-I architecture remains beneficial even at high CQD loadings.

4.4 Conclusion

In this chapter, we developed bright NIR-LEDs based on next-generation DiPs. The work built on our findings of Chapter 3 re: quantum-dot-in-perovskite materials, and significantly augmented these findings by creating an efficient-EL-compatible matrix. Thanks to the excellent diffusion length of the iodide/bromide mixed perovskite, as well as its type-I band alignment, charge carriers were transported through the perovskite matrix to recombine efficiently in the CQDs. This yielded devices with a tunable emission wavelength, bandedge-derived turn-on voltages, and record power efficiencies. These results highlight the potential of these emerging materials for use in power-efficient, low-cost, and large-area LEDs and displays.
Chapter 5
Applications of DiPs in Light Detection

Originally, infrared imaging – crucial to gesture recognition, mobile gaming, and iris recognition – was limited by its reliance on epitaxial III-V compound semiconductors. In recent years, infrared photodetectors have advanced in cost-effectiveness and performance with the advent of solution-processed infrared semiconductors such as colloidal quantum dots (CQDs).

In this chapter, we implement the concept of DiP in light-sensing devices. The perovskite phase was shown in Chapters 3 and 4 to provide efficient transport by virtue of its high and balanced mobility, as well as excellent passivassion via crystal lattice matching. Quantum dots sensitize the devices into the NIR spectral region. We then demonstrate the extraction of photocarriers via field-emission, followed by the recirculation of photogenerated carriers, leading to a new photodetector.

Chapter 5 contains work from “Field-emission from quantum-dot-in-perovskite solids,” published in Nature Communications volume 8 14757 (2017), and reprinted with permission from the Nature Publishing Group. I was co-first author on this publication together with Dr. F. P. García de Arquer. We designed and carried out the experiments together. I led the thin film fabrication, photodiode device fabrication, transient absorption studies, and manuscript preparation. Device characterization, analysis and simulations were performed by Dr. F. P. García de Arquer. Dr. Randy Sabatini carried out the transient absorption measurements. Dr. Min Liu conducted SEM measurements.
5.1 Solution-processed materials for photodetectors

Photodetectors have traditionally been made using single-crystalline materials such as silicon and III-V semiconductors. Of interest for many applications such as medical imaging, machine vision, surveillance, and communications is the infrared region of the spectrum. Quantum dot and quantum well architectures, which exploit the confinement of charge at the nanoscale, are particularly attractive to address this region. They benefit from tunable confined volumes that emit carriers into a host phase. For this process to be efficient, well-defined interfaces and high mobilities in the transport phase are required.

The emergence of new nanostructured materials that benefit from low-temperature solution processing holds promise for the scalable manufacturing of large-area devices. The performance of solution-processed photodetectors, and in particular those based on organic semiconductors and colloidal quantum dots (CQDs), has increased rapidly and become competitive with that of silicon and III-V semiconductors\textsuperscript{66–69}.

5.2 Development and challenges in CQD photodetectors

Early CQD photodetectors were based on the sensitization of host transport polymer matrices that served as a channel for carrier collection and transport\textsuperscript{70–72}. These proof-of-concept devices were limited by the morphology of composites and the electronic properties of host materials. The low mobilities of organic materials were particularly limiting, holding performance well below that of heteroepitaxial quantum dot and quantum well photodetectors.

In principle, a well-engineered heterodevice can benefit from suppressed thermal generation – managed through carrier confinement and band engineering – and the separation of sensitization and transport, the latter enabled by the use of crystalline and low-defect materials\textsuperscript{73}. Until recently, implementing lattice-matched heterocomposite devices for infrared photodetection has remained
a challenge in solution-processed soft materials, since several requirements need to be fulfilled simultaneously: an electronically superior host transport material with a low density of defects and high mobility, the presence of a tunable sensitizer, and a materials-processing strategy that enables the compatible incorporation of the sensitizer into the host. Ideally the interface between the host material and sensitizer should be epitaxial to ensure a low density of localized defects and to minimize recombination channels. All this must be achieved with a device architecture that favours the injection of photocarriers into, and collection of photogenerated charges from within, the transport phase. Fulfilling this requirement ensures high quantum efficiency (high primary photocurrent) as well as gain (high secondary photocurrent).

In view of their excellent optoelectronic properties, organometal halide perovskite semiconductors have recently been explored for photodetection applications. Perovskite photodiodes have been reported with high specific detectivity, fast temporal response, high dynamic range, and colour selectivity. This performance has been enabled by a set of compelling electronic properties that include high and balanced carrier mobilities, low trap densities, and high absorption coefficients. However, in spite of these advantageous characteristics, the bandgap of organo-lead perovskites (A)PbI$_3$ (A = MA, FA, Cs$^+$) precludes their application in the important domain of short-wavelength infrared (SWIR) photodetection.

The bandgap of CQDs can, in contrast with those of the best perovskites, be tuned into the short-wavelength infrared. However, the processing steps required for the assembly of CQDs into films are typically associated with the formation of an appreciable density of electronic trap states arising from incompletely-passivated nanoparticle surfaces. A new type of semiconducting material, one that consists of CQDs embedded in an epitaxially grown perovskite matrix, has been recently reported. These quantum-dot-in-perovskite (QDiP) materials combine the advantages of each:
CQD sensitization (therefore bandgap tunability), superior passivation of the CQD surface states in view of their epitaxially matched interface, and the excellent carrier transport properties with low trap density and high mobility of organohalide perovskites. Therefore, in principle, QDiP solids offer an attractive platform for infrared photodetection.

In this Chapter, we first investigate whether one can utilize the benefits of DiP materials to build photodiodes that are sensitive across the visible and into the SWIR. We explore herein whether the combination of CQD sensitization and a dedicated charge transport channel can enhance light detection.

5.3 Concept of field-emission diodes

In the absence of external electric fields, photogenerated excitons are expected to be confined inside CQDs due to the type-I heterojunction formed between the CQD (~1 eV) and the host MAPbI$_{2.5}$Br$_{0.5}$ (~1.6 eV), and to recombine either through radiative or non-radiative channels. We propose that this could change under the presence of a suitably large electric field: excitons photogenerated in the quantum dots will then separate, and the charges may be ejected from the dots, under the action of the field, into the host perovskite matrix. The appropriate bias point needs to ensure efficient photocarrier escape, and circulation that is rapid enough to avoid excessive recapture. Emitted electrons or holes can then be extracted and reinjected at the electrodes, resulting in a multiplicative (i.e. one exhibiting gain) photocurrent.

We focus on field-emission DiP photodetectors having the following structure: a TiO$_2$ electron transport layer (50 nm), deposited using atomic layer deposition, on top of a transparent conductive fluorine-doped tin oxide (FTO) electrode. A 250 nm thick DiP film is formed on top. The host perovskite matrix consists of MAPbI$_{2.5}$Br$_{0.5}$, where the iodide and bromide ratio has been optimized to achieve better lattice matching with the embedded dots and thus both passivation and
excellent transport characteristics. The size of the CQDs was tuned to yield an exciton peak at 1240 nm (~1 eV). This is followed by a 50 nm layer of Spiro-MeOTAD and 200 nm of gold to form the hole-extraction layer.

5.4 Theoretical and experimental assessments of field-emission effect

We sought first to evaluate the conditions under which photoexcited charges in the quantum dots could be ejected into, and collected from within, the MAPbI$_{2.5}$Br$_{0.5}$ matrix. F. P. García de Arquer carried out numerical simulations of photoexcitation, escape, and recapture processes, as well as transport, in the DiP solid (Figure 5.1.a). The energy landscape of a simplified 1D linear stack of perovskite-dot-perovskite clarifies the different injection regimes. For a standard CQD with an exciton peak of 1 eV, band offsets of 0.5 eV and 0.2 eV with the top and bottom of the perovskite valence and conduction bands respectively, ensure that photogenerated electron and hole densities reside within the CQDs (bottom panel). Carriers in the perovskite phase are captured in the quantum dots and undergo recombination.
Figure 5.1 **Exciton harnessing and Fowler-Nordheim emission.** Band alignment of DiP solids as calculated with a SCAPS model at (a) no bias and (b) reverse bias conditions. (c) Carrier capture probability for different thermalization rates as a function of host mobility. (d) electron/hole emission and capture rates as a function of applied field for the DiP system. (e) FN diagram of a DiP device reveals the region where field-emission tunnelling is the dominant injection mechanism. In-situ ultrafast transient absorption maps of DiP devices at (f) 0 MV·cm⁻¹ and (g) 0.2 MV·cm⁻¹ reveals carrier injection within 100 ps. (h) The dynamics of the exciton bleach peak at 1240 nm follow a biexponential behaviour with a fast lifetime accelerated from 164±32 ps to 76±9 ps.
Under reverse bias conditions (Figure 5.1.b), the applied electric field is distributed across the DiP solid, with a higher intensity in the PbS quantum dots in light of their lower dielectric permittivity \( (\varepsilon_{\text{PbS}} \sim 22 \text{ and } \varepsilon_{\text{MAPbI}_2.5\text{Br}_0.5} \sim 70). \) The larger electric field in the quantum dots promotes the separation of the electron and hole wavefunctions (bottom panel) facilitating ejection, via tunneling or emission over the barrier, into the perovskite phase. The simulated photocurrent for this material configuration monotonically increases under increasing electric field, and then begins to saturate above \( 0.2 \cdot \text{MV} \cdot \text{cm}^{-1} \), where the extraction efficiency reaches a maximum.

After carriers escape into the perovskite, they could be potentially re-captured into the dots, as determined by the competition between carrier thermalization and extraction time (Figure 5.1.c). A given cooling rate \( (k_{\text{th}}) \) will result in a mobility \( (\mu_{\text{host}}) \) threshold for a given applied electric field \( (E_N) \). Assuming an external field of \( 1 \text{ MV} \cdot \text{cm}^{-1} \), a typical \( k_{\text{th}} \) in the range of 1-10 ps would require \( \mu_{\text{host}} \) on the order of \( 10 \text{ cm}^2 \cdot (\text{V} \cdot \text{s})^{-1} \) to reduce the capture probability below 0.1. This underpins the necessity of an excellent transport material for this architecture.

Different types of tunneling mechanisms can provide channels for charge injection from the photoexcited dots into the surrounding perovskite matrix. Schottky and thermionic emission are expected to dominate for low and moderate electric fields, and to become outpaced by field-assisted (Fowler-Nordheim) processes at higher biases. Therefore, the rate at which confined carriers can escape from the quantum dots, as well as the capture rate, depend strongly on the applied electric field (Figure 5.1.d). Below \( 0.1 \text{ MV} \cdot \text{cm}^{-1} \), thermionic emission dominates. Above this threshold, Fowler-Nordheim tunneling increases until it becomes the dominant mechanism for electron escape. The capture rate follows a similar trend but requires above \( 1 \text{ MV} \cdot \text{cm}^{-1} \) in view of fast transport throughout the DiP solid. As a result, the majority of the photogenerated carriers will be collected once the field exceeds \( 0.1 \text{ MV} \cdot \text{cm}^{-1} \).
To assess experimentally the dominant tunneling mechanism in the DiP solid, we measured the current density ($J$) through a device as a function of the applied reverse electric field. The Fowler-Nordheim (FN) plot (Figure 5.1.e) provides strong evidence that field-assisted FN tunneling is the dominant mechanism for charge injection at electric fields greater than $3 \times 10^4 \text{ V} \cdot \text{cm}^{-1}$, which corresponds to reverse biases around $\sim 1\text{ V}$. This agrees well with the analytical and simulated predicted values.\textsuperscript{94} We note that this range of voltages is well below the breakdown voltage of the perovskite matrix, above $\sim 7\text{ V}$ (Figure 5.1.e, Appendix A.2).

We then monitored the ultrafast dynamics of the photogenerated carriers using transient absorption spectroscopy (Figure 5.1.f-h). The litmus test of efficient net photocarrier emission is as follows: fast absorption kinetics in the quantum dot phase, accompanied by a slower decay in the perovskite, will indicate net emission from dots into perovskite. Further, a bias-dependence to these trends will signal a role of field. At $0 \text{ V} \cdot \text{cm}^{-1}$ the ground state bleach signal of the quantum dots decays bi-exponentially with a fast lifetime component of $160\text{ ps}$ and a slower component of $1.5\text{ ns}$ (Appendix A.2). With the application of an electric field of $2 \times 10^5 \text{ V} \cdot \text{cm}^{-1}$, the quantum dot bleach shows accelerated decay dynamics ($\tau \sim 80\text{ ps}$) under the same photoexcitation conditions. This significantly accelerated decay stems from the new carrier extraction pathway introduced by the applied field: photogenerated excitons are dissociated into charge carriers, and then emitted into the perovskite matrix, avoiding recapture.

We observe the opposite trend while probing the perovskite phase: the decay rate decelerates upon the application of the electric field, indicating retention of carriers in the perovskite phase (Figure A. 9). In contrast, the photocarrier dynamics of pure perovskite and quantum dot devices show no appreciable dependence on bias.
5.5 Responsivity of the field-emission photodetector

After we identified operation guidelines for this material platform, we sought then to characterize the optoelectronic performance of our DiP photodiodes. The measured specific detectivity ($D^* = R A^{1/2}/i_n$) reaches $5 \cdot 10^{12}$ Jones through the visible and $4 \cdot 10^{12}$ Jones at the CQD exciton peak (1240 nm) (Figure 5.2). The current-voltage characteristics under dark conditions reveal the rectifying behavior of the devices. Further, the DiP devices show lower dark currents than do purely CQD-based diodes (Figure A. 12).

![Detectivity of DiP photodiodes](image)

Figure 5.2 **Detectivity of DiP photodiodes.** Specific detectivity spectrum at the optimum operation conditions. Extended SWIR sensitivity with a detectivity of $4 \cdot 10^{12}$ Jones at the CQD exciton peak is obtained.

We evaluated the bias-dependence of the photoresponse and measured the responsivity ($R$) and estimated gain ($G$) for a wide range of biases under 975 nm illumination, where the QDs are the
only absorbing phase (Figure 5.3). The photoresponse remains constant (~2.2 mA·W⁻¹) up to 0.3 V reverse bias. A 45-fold increase in responsivity is obtained at 0.5 V reverse bias, as photogenerated charges in the QDs start to be emitted into the perovskite matrix. Beyond -2 V, the unity gain threshold is exceeded for this wavelength. We ascribe this photomultiplicative process to the imbalance of electron and hole injection rates (Figure A. 13 Recirculation probability. Predicted recirculation probability of electrons (blue) and holes (red) as a function of applied field. As a result of the recirculation imbalance of different charge types photomultiplicative gain effects appear.). A maximum gain of 10 is achieved at 6 V reverse bias.
This chapter reported the first field-emission solution-processed infrared photodetectors. We achieved this by implementing DiP into a photodiode architecture and programming its operation in the field-emission regime. This exploited both the collection of photogenerated carriers and the

Figure 5.3 **Photodetector responsivity (left axis) as a function of reverse bias under 975 nm (1.31 eV) illumination.** It displays a sharp increase at the field-emission onset, and a photomultiplicative gain (right axis) exceeding unity above 2V reverse bias. An increase of over a two-orders of magnitude is recorded before breakdown occurs.

5.6 Conclusion

This chapter reported the first field-emission solution-processed infrared photodetectors. We achieved this by implementing DiP into a photodiode architecture and programming its operation in the field-emission regime. This exploited both the collection of photogenerated carriers and the
minimization of noise. It led to optoelectronic performance that extended the photoresponse of perovskite photodiodes well into the SWIR.

The reported field-emission solution-processed optoelectronic architecture exploits a set of physical effects previously attained only through more costly vacuum heteroepitaxy. Potential future energy harvesting applications include cascade intermediate-band photovoltaics capable of collecting the IR solar spectrum with high open-circuit voltages\textsuperscript{95}, and photon upconverters for light emission\textsuperscript{96}. 

Chapter 6
Contactless Investigations of the Photocarrier Diffusion Length in Perovskite Single Crystals

In Chapter 4 and Chapter 5, we demonstrated the benefits provided to CQD optoelectronics from their synergy with heteroepitaxial perovskites. In this chapter, we turn instead to the use of CQDs as efficient photocarrier quenchers as a means to probe the diffusion properties of perovskites. We report the mobility, diffusion length, and trap state density of photocarriers in single-crystal perovskites using this new strategy. We conclude by providing an estimate of the potential for perovskite photovoltaics to improve further in solar cell applications, a bound derived from the diffusion length obtained in single crystals.
6.1 Challenges in the accurate characterization of diffusion lengths in perovskite single crystals

Solution-processed photovoltaic materials have facilitated the emergence of third generation solar cell technology with low cost, high efficiency and physical flexibility. Thin film solar cells employing metal-halide perovskites have achieved an exceptional 22% certified power conversion efficiency (PCE)\(^97,98\). In order to reach high PCEs, a long diffusion length (\(L_d\)) — the distance over which photogenerated excitations diffuse before they recombine — is necessary\(^99,100\).

Single crystals are an ideal platform for studying the ultimate potential of a material, for they are not limited by constraints such as the morphology and grain boundaries. The electrical properties of halide perovskite single crystals have been investigated extensively in recent years, with charge carrier mobilities, \(L_d\), and trap densities reported using a variety of methods.

6.1.1 Electrical methods

By probing the photocurrent in solar cell devices, or by combining space charge limited currents with optical measurements, researchers have reported electron diffusion lengths inside perovskite crystals. The range has been between 175 µm and 3 mm\(^101\) using these approaches. In contrast, Shi et al. reported \(L_d\) using mobility measured from electrical methods such as time of flight (TOF) transient photocurrent and Hall effect measurement\(^102\); when they combined the drift mobility with the photocarrier lifetime obtained from transient photoluminescence, the authors estimated the diffusion length of MAPbBr\(_3\) perovskite single crystal to reside in a rather wide range between 3~17 µm.

One of the challenges that may explain these order-of-magnitude discrepancies is that Hall effect, TOF, and SCLC all probe mobilities near the respective Fermi levels during the experiment – and the (nonequilibrium, high-injection-level) Fermi level is widely different in each case. As a result,
different mobility-limiting trap densities and depths are sampled. PL lifetime is acquired under a different set of conditions involving low-level or high-level injection, depending on the excitation pulse intensity. The quasi-Fermi level of the relevant charge carrier in the PL component of these studies may differ from that during the electronic injection based transport studies \(^{103}\).

In light of these past challenges, we pursued the development of a model that would seek to probe diffusion lengths more directly. The technique would measure the decay rate at which the nonequilibrium carrier distribution is diminished by spatial diffusion toward luminescent reporters epitaxially embedded in the perovskite.

6.1.2 Optical methods

Figure 6.1.a illustrates a 1D-diffusion model for an entirely optical method, where a thin film is interfaced with a carrier (electron or hole, electron as an example here) quenching layer. Photocarriers are generated at the active layer/substrate side, diffuse towards the other side, and then are quenched before recombination in the perovskite takes place. By solving the 1D diffusion equation with the sample thickness \((L_0)\) and quench-limited diffusion time \((\tau_0)\), one may acquire the diffusion coefficient D. The diffusion length \(L_d\) therefore can be obtained using \(L_d = D \cdot \tau\) (Eq. 1), where \(\tau\) stands for the carrier lifetime without the quencher. In this case, a successful fit requires one pair of known parameters \((L_0, \tau_0, \tau)\), and also a sample thickness that is below the diffusion length, \((L_0 < L_d)\). This makes the method compatible with the use of, for example, polycrystalline perovskite thin films and quantum dots thin films; but not with macroscopic single crystals.\(^{52,104}\)

Thick single-crystal perovskites do not lend themselves to the 1D method, for they are multiple optical absorption lengths thick. We devised instead a method we term 3D quenching with tunable diffusion distances (Figure 6.1.b). We utilize homogeneously distributed quenching sites with controllable distance \((L)\) inside single crystals, instead of relying on the surface quenching layer
known from the 1D method. In our model, diffusion is investigated in all three dimensions (3D) rather than along a single axis (perpendicular to the quenching layer). $L$ can be modulated to be shorter than, or longer than, $L_d$ by varying the quenching material concentration. With several pairs of [diffusion distance $L_i$, diffusion time $\tau_i$], the diffusion coefficient $D$ can be fit using the diffusion equation $D = \frac{L_0^2}{\tau_i}$. One can then validate the method by checking whether the fit remains excellent – i.e. a single $L_d$ is obtained over each $[L_i, \tau_i]$ combination.

Figure 6.1 **Diffusion-quenching models.** a, 1D diffusion-quenching structure; carrier funneling process occurs at the interface between the active material and carrier extraction layer. b, Configuration of 3D bulk diffusion-quenching model, with quenching sites (brown spheres) dispersed inside the bulk of material. Diffusion processes of electrons (red curve) and holes (blue curve) occur in all three dimensions (over area of semitransparent large sphere).

From a materials design perspective, one key challenge in performing such measurements lies in incorporating the quenching sites into perovskite single crystals in a homogenous manner, and without altering the quality of the single crystals. We pursued a quencher approach that had both type I band alignment with perovskite in order to capture and recombine photocarriers, and a lattice
match with the perovskite so that the crystallinity of the perovskite is retained\textsuperscript{105}. From the discussions from previous chapters, lead sulfide CQDs meet the above requirements when epitaxially grown inside methylammonium lead halide perovskite crystals.

6.2 Ld measurements in perovskite single crystals

6.2.1 Synthesis of quantum dots in perovskite single crystals

We first selected the antisolvent vapor-assisted crystallization method to grow perovskite single crystals\textsuperscript{106}. The method has previously been shown to produce high quality crystals, a fact attributable to the slow diffusion of the antisolvent into the solvent.

Unfortunately, when we added the perovskite capped PbS QDs during the crystallization process, we did not obtain the desired QD-in-single-crystals (QDISCs). Instead, perovskite single crystals in pure phase formed, segregated from the quantum dots.

With the goal of synchronizing the crystallization process with the timescale on which QDs maintain their colloidal stability, we changed our strategy of perovskite crystal synthesis. We sought to shorten the crystallization process to 3 hours using instead the inverse temperature crystallization (ITC) method \textsuperscript{106} (Fig. S1b). Perovskite single crystals (Figure 6.2.a, left) grown via the ITC method have been reported to possess trap densities and transport properties on par with the best reported for MAPbBr\textsubscript{3} crystals to date.

With this new strategy, we found that, once PbS QDs were added during crystallization, the resultant crystals exhibited a similar color to that of a QD solution (Figure 6.2.a, dark crystal on the right). It appeared that the QDs had incorporated successfully.
QDISCs show, at the macroscopic level, the well-defined cubic shape of the (dotless) perovskite single crystals. We observed strong infrared luminescence from QDISCs even under room light excitation (Figure 6.2.b).

The optical absorption spectra of QDISCs in Figure 6.2.c signal the existence of perovskite, with its clear bandedge at ~550 nm, and quantum dots with their excitonic peak at 1000 nm. The steady state photoluminescence spectra of QDISCs show an emission from quantum dots at 1100 nm and, at these dot concentrations, no perovskite emission. The QDs exhibited an absolute photoluminescence efficiency (PLQY) of 24%.

This high PLQE of PbS QDs in the solid state surpasses that observed in previous report$^{107}$. This fact suggests excellent passivation by the perovskite single crystals. We conclude that these QDs possessed a substantially trap-free interface with the perovskite.
6.2.2 Diffusion distance estimation

To elucidate the interaction between the QDs and perovskite single crystal, we used transmission electron microscopy (TEM) to probe the microscopic structure of QDISCs (Figure 6.3.a-d). TEM images were taken from nanosized QDISCs. Figure 6.3 illustrates that quantum dots separate from each other further with decreasing QD concentration (from 1:1 to 1:20 mass ratio). We measured the inter-dot spacing (L) for each concentration, and plotted the distribution of L (Figure 6.3.c-3d). We further developed a 3-dimensional homogeneous distribution model to reveal the dependence of L on QD concentration. Figure 6.3.e shows that the experimental data agrees well with the simulated results (with the quantum dots radius=3 nm). Therefore, the diffusion distance L can be accurately modulated by varying the QD concentration.

6.2.3 Diffusion time measurements

We then proceeded to explore measuring the diffusion length using these new heterocrystals. First, we varied the diffusion distance L_i (limited by inter-dot spacing) from 20 nm to 50 nm by further decreasing the QD concentration (Figure 6.4.a). We used transient absorption spectroscopy (TAS) to study the carrier diffusion time in QDISCs by probing the dynamics of the perovskite bleach. Figure 6.4.b shows that carrier concentration decays faster when we increase the density of QDs (from 1020:1 to 64:1, perovskite: QDs), and the shorter diffusion time is consistent with the shorter diffusion distance. We determined the carrier diffusion lifetime (\(\tau_{\text{diff}}\)) by fitting the TA traces using a monoexponential model. We plot it against the diffusion distance L_i in Figure 6.4.c. The diffusion distance squared (L_i^2) shows a clear linear dependence on the diffusion time (\(\tau_{\text{diff}}\)), consistent with the application of the diffusion model to the QDISCs material system.
6.2.4 3D quenching model fitting

From the slope of the $L_1^2-\tau_{\text{diff}}$ plot, we can extract a diffusion coefficient (D) for the perovskite of 0.07 cm$^2$s$^{-1}$. From the Einstein relation: $D=\mu \cdot k_B \cdot T/q$ (Eq. 2), where $\mu$, $k_B$, $T$, and $q$ stand for mobility, Boltzmann's constant, temperature, and electrical charge, respectively, we calculate a perovskite carrier mobility of 2.7 cm$^2$V$^{-1}$s$^{-1}$. In order to obtain the diffusion length limited by the trap-assisted recombination, we needed to measure the carrier lifetime ($\tau$) of the pristine perovskite single crystals. The photoluminescence lifetime ($\tau_{\text{PL}}$) in MAPbBr$_3$ single crystals is limited by non-radiative recombination (which we know from the low PL of this material even in its pure phase),
so we can estimate the trap-limited carrier lifetime $\tau$ using transient photoluminescence spectroscopy (Figure 6.4.d). When we combine the carrier lifetime and diffusion coefficient, we obtain a diffusion length of 2.6 $\mu$m, corresponding to a defect density ($N_{\text{trap}}$) of $6 \times 10^{10}$ cm$^{-3}$. 
Figure 6.4 **Diffusion-quenching investigations of MAPbBr₃ single crystals.** a, inter-dot spacing tuning via controlling the quantum dot concentration from 64:1 to 1020:1 (mass ratio between perovskite and QDs, QD radius = 2.5 nm). b, transient absorption dynamics at perovskite bleach with different diffusion distance (limited by inter-dot spacing). c, fitting of diffusion coefficient and carrier mobility of MAPbBr₃ single crystals. d, carrier lifetime and diffusion length calculation of MAPbBr₃ single crystals.
6.3 Insights for perovskite photovoltaics

We sought to explore the implications of perovskites’ diffusion lengths reaching the 2 µm frontier, the value achieved in our best samples. We performed optoelectronic simulations of photovoltaic devices ($E_b$=1.6 eV) for a range of carrier diffusion lengths. Figure 6.5.a shows that for $L_D$ smaller than film thickness, increasing $L_D$, improves all of the current density, open circuit voltage and fill factor. Once the $L_D$ exceeds the thickness of the absorbing layer sufficient to substantially absorb all incident above-bandgap light (1 µm), the current density nearly saturates, but nevertheless the PCE keeps improving by up to 3 power points beyond the current state-of-the-art (Figure 6.5.b). This improvement mainly comes from the enhanced product of open circuit voltage and fill factor, thanks to suppressed recombination through traps, otherwise very efficient in view of the high carrier mobility in perovskites.

Figure 6.5 Simulated device performance based on perovskite single crystal diffusion lengths.
a, J-V curve of perovskite single crystal devices with different $L_D$. b, PCE of the devices in Figure 6.5.a.
6.4 Conclusion

This chapter reported the development and application of a contactless method to study 3D carrier mobility, lifetime, and diffusion length. We applied it to the investigation of perovskite single crystals under conditions relevant for PV device operation. Knowing the diffusion length in photovoltaic device active layers allowed us to evaluate further the potential of these materials and devices. Optoelectronic simulations indicated a path to photovoltaic PCEs of 25% for these active layers.
Chapter 7
Conclusions and Perspectives

7.1 Summary of findings

Prior to this work, the fields of metal chalcogenide quantum dots and metal halide perovskites had each advanced, but substantially in parallel. Perovskites had shone particularly in the realization of advanced thin-film solar cells. Quantum dots’ applications were particularly promising in photodetectors and light-emitting devices.

Nevertheless, it was recognized early in this work that each materials system had missing features and limitations that could benefit from innovative resolution. Perovskites generally failed to offer short-wavelength infrared properties; and quantum dots suffered from limited transport, something that increased the overpotentials that were typically required in quantum dot devices.

My contributions began with the realization of a platform material whose use spanned this thesis: quantum dots in perovskite, DiP. A remarkable feature of this material was that it could provide heteroepitaxy, particularly interesting since the quantum dots already had defined lattices and orientations when they were incorporated into the perovskite matrix. This heteroepitaxy proved crucial in providing the excellent passivation of quantum dot surfaces necessary to achieving efficient injection into, and radiative recombination within, the quantum dot light-emitting phase.

We first deployed this heteromaterial to realize near-infrared light-emitting devices. Only by improving further the lattice match, and the passivation, of the quantum dots dispersed in the perovskite were we able to increase further the luminescence efficiency of these materials. As a result, we reported record-EQE and record-power-conversion-efficiencies for solution-processed NIR optical sources.
We then investigated how the quantum dots could be deployed to produce sensitive photodetectors that leveraged a perovskite active layer. We found that field-emission devices were possible, wherein the excellent transport in the matrix, combined with a sufficiently high applied field, could produce photocarrier injection from the dots into the matrix and could substantially avoid recapture of these photocarriers back into the dots while the photocarriers were recycled rapidly across the device.

We concluded with an application of quantum DiP in increasing the scientific understanding of optoelectronic processes within perovskite materials. Specifically, the perovskite community had witnessed a wide range of reported diffusion lengths, a fact we attributed to the use of indirect methods of estimating trap densities and mobilities. We instead developed a means to use quantum dots to sense directly the length over which photocarriers diffused before they recombined. The ~2 um diffusion length we witnessed in perovskite single crystals entails further potential for perovskite solar cells to improve towards a 25% solar power conversion efficiency bound.

7.2 Contributions

During my doctoral work, I was first-author or co-first (†) author of these publications:


7.3 Future Directions

There remain a number of further applications of DiP that we did not fully explore in this work (Figure 7.1). One direction is in CQD lasing, which today suffers from Auger recombination loss partially related to a high surface trap density. Heteroepitaxial perovskites cladding quantum dots can reduce the number of traps, and lower the gain threshold through the carrier funneling effect. This ultimately facilitates achieving population inversion. Eventually, electrically-pumped CQD lasers could potentially be realized, especially considering the extraordinary carrier transport properties of perovskites. It must be pointed out, though, that a number of key advances lie between where we are today, and electrically pumped lasing, not least: the demonstration of pulsed, and then CW, optical gain in DiP; sufficient thermal transport to avoid undue heating in the active layer; and realization of a low-optical-loss structure that is also capable of efficient electron and hole injection at the needed current densities.

Initial results have been reported by other researchers in the use of perovskite shells in photovoltaics. In principle, the trap-passivating qualities of perovskites may offer a useful
advantage. However, perovskites generally form a type-I heterojunction with quantum dots, and this does not favour the charge extraction needed in solar cells. An ultra-thin shell may be one option to help provide both surface passivation and charge extraction. Further development of CQD solar cells with perovskite shells has the potential to build on encouraging initial PCEs of 8.9\%\textsuperscript{108}.

Figure 7.1 Future directions and spin-offs from the concept of DiP (green boxes); summary of the work in this thesis (yellow boxes).
From a materials chemistry point of view, DiPs can exist with a wide range of compositions, which include but are not limited to the combinations of CdX, HgX, and SnX (X=S, Se) as CQDs, and Cs/FAPbY₃ (Y= I, Br, Cl)¹⁰⁹, lead free¹¹⁰, lower dimensional (2D, 2.5D)¹⁰⁸, and double perovskites as matrices¹¹¹,¹¹². This will give rise to the emergence of the 3rd generation DiP that can potentially solve the materials design challenges of removing the heavy metal (Pb), enhancing the material stability.

The electronic band alignment between CQDs and matrix can also be engineered in a variety of interesting configurations. By lifting or lowering the energy level of the CQDs, one can form a type-II band structure at the heterojunction. In this case, one type of the photogenerated charge carrier will be captured by the CQDs, and therefore will benefit from a long lifetime (τₑ). The other can be extracted and flow through the highly conductive matrix under an applied bias (lifetime τₑ). The ability to capture one type of carrier while keep the other one highly mobile can be utilized in photoconductors, and will substantially provide a high gain G (G=τₑ/τₑ) and responsivity¹⁰⁸.

More broadly, the advances presented in this work define a new material platform that unites promising properties from two exciting materials classes. This work has the potential to catalyze the development of new generations of liquid hetero-epitaxy materials, opening a new avenue in solution-processed optoelectronic engineering.
References


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Appendices

Appendix A. Methods

A.1 Density Functional Theory (DFT) simulations

Calculations were performed within the Density Functional Theory (DFT) formalism using the Perdew-Burke-Ernzerhof (PBE) GGA exchange correlation functional. All calculations were performed utilizing the CP2K3 package with mixed Gaussians and plane waves basis set, using the molecularly optimized MOLOPT double $\zeta$-valence polarized (mDZVP) basis set implemented in CP2K code which has very small basis set superposition errors (BSSE) in gas and condensed phases. The charge density cut-off was 300 Ry, which is suitable for the Goedecker-Teter-Hutter pseudopotentials. Spin polarized (LSDA) and spin-unpolarized calculations (LDA) were performed in the case of the odd and even number of electrons, respectively. The structural minimization was performed with the help of the Broyden-Fletcher-Goldfarb-Shanno algorithm (BFGS). Surface slabs were modelled as (110) MAPbI$_3$ of tetragonal structure and (100) cubic PbS with monolayers each. 100 Å of vacuum were added on top of the slab. Dipole correction was used to remove artificial dipole-dipole interaction across periodic images as implemented in the CP2K v2.5. A 3x3 (26.88 Å x 26.88 Å) supercell was used in the xy-plane.

The interfacial energy was computed using the relation:

$$E_{\text{inter}}^{\text{MAPbI}_3/\text{PbS}} = E_s(\text{MAPbI}_3) + E_s(\text{PbS}) - E_{\text{Ad.}}(\text{MAPbI}_3/\text{PbS})$$

where $E_s$ represents the surface energies of the corresponding surfaces (MAPbI$_3$ and PbS, respectively), and $E_{\text{Ad.}}$(MAPbI$_3$/PbS) is the adsorption energy of the MAPbI$_3$ on PbS. It describes the energy required to cut the PbS and MAPbI$_3$ bulk and combine the obtained free surfaces to form the MAPbI$_3$/PbS interface.
A.2 Extraction of transport efficiency from PLQE and PL-decay

We define the total transfer efficiency ($\eta_{tot}$) and diffusion transport efficiency ($\eta_{diff}$) as:

$$\eta_{tot} = \frac{n_{trans}}{n_{all}}$$  \hspace{1cm} (A.1)

$$\eta_{diff} = \frac{n_{diff}}{n_{all}}$$  \hspace{1cm} (A.2)

where $n_{trans}$ stands for the number of charge carriers that are transferred into the quantum dots from the perovskite; $n_{diff}$ is the number of carriers that reach the quantum dots by diffusing across the perovskite matrix; $n_{all}$ is the total amount of photogenerated charge carriers in the perovskite.

Experimentally, $\eta_{tot}$ can be extracted from photoluminescence quantum efficiency (PLQE) measurement with a modified version of a method previously reported in literature\textsuperscript{41}. We measured the PL from quantum dots in matrix using two excitation wavelength: a short wavelength which can excite both quantum dots and perovskite, and a long wavelength that can only excite quantum dots. The PL of quantum dots in these two scenarios can be written as:

$$PL_{QDs, short} = (A_{QDs, short} + \eta_{tot}A_{P, short}) \cdot PLQE_{QDs} \cdot I_{ex, short}$$  \hspace{1cm} (A.3)

$$PL_{QDs, long} = (A_{QDs, long}) \cdot PLQE_{QDs} \cdot I_{ex, long}$$  \hspace{1cm} (A.4)

$PL_{QDs}$ and $I_{ex}$ represent the photoluminescence yield from the quantum dots (in photons/sec) and the photon intensity of the excitation source (also in photons/sec), respectively. $A_{QDs}$ and $A_P$ are the absorption of quantum dots and perovskite, respectively. $A_{QDs}$ was determined by measuring the change in absorbance at the dots’ excitonic peak and scaling the total material absorbance at the chosen wavelength by this factor. $A_P$ was then determined through the additive property of
absorbances for a mixture. The Beer-Lambert law was used to convert experimental absorption measurements to absorbances for use in these calculations. In particular, due to very low optical density for the absorption of quantum dots in films with low CQD concentration, the values of $A_{QDs}$ have been estimated by linear scaling (according to the CQD concentration) using the measured one for a film with 28% CQD concentration (highest loading). The PLQE is calculated using an integrating sphere and following a method described elsewhere\textsuperscript{113}. The intensity of the excitation source was measured using a power meter (LaserStar). The wavelength-dependent response of the visible and near-infrared photon detectors (for PL and PLQE measurements) were corrected using an Ocean Optics LS-1 calibration lamp with known spectral profile. The short and long in the subscript stands for the corresponding wavelength regime. From Equation A.5 and A.6, we can write:

$$\eta_{tot} = \left[ \left( \frac{PL_{QDs,short}}{PL_{QDs, long}} \frac{I_{ex, long}}{I_{ex, short}} \right) \cdot A_{QDs, long} - A_{QDs, short} \right] \cdot \frac{1}{A_{p,short}}$$  \quad A.7
A.3 Photodiode device simulation

A.3.1 Influence of host mobility in the carrier capture probability

The carrier trap probability of a carrier traversing a CQD embedded in the QDiP solid was calculated as follows:

\[ \eta_{trap} = \frac{\tau_{th}}{\tau_{tra} + \tau_{th}} \] \hspace{1cm} (A.8)

where \( \tau_{tra} \) is the transverse time through the dot conduction/valence band, which we estimated as \( \tau_{tra,\text{dot}} = \frac{d_{\text{dot}}}{v_{\text{tra}}} \), where \( v_{\text{tra}} = \mu E \) is the mobility-field product. \( d_{\text{dot}} \sim 5.5 \text{ nm} \) represents the dot diameter. It is important to note that due to the electronic delocalization that arises as a consequence of the epitaxial incorporation of the quantum dots, the mobility is not that of the CQDs but that of the QDiP solid. The thermalization lifetime \( \tau_{th} \) is varied. An electric field of \( 10^6 \text{ V} \cdot \text{cm}^{-1} \) is assumed for the calculations.

A.3.2 Carrier capture rate as a function of applied electric field

The carrier capture probability (\( \eta_{\text{capture}} \)) of carriers in the QDiP phase is calculated as follows. First, the probability for a carrier to find a quantum dot:

\[ \eta_{CQD} = \sigma_{CQD} \langle v \rangle \cdot N_{\text{host}} \] \hspace{1cm} (A.9)

where \( v = v_{\text{th}} + v_{\text{drift}} \) comprises both thermal and drift components. \( \sigma_{CQD} \) is the cross-Section of the CQDs. \( N_{\text{host}} \) is the carrier concentration of the host medium, in this case the MAPbI\(_{2.5}\)Br\(_{0.5}\) perovskite. The capture probability can be obtained then as:

\[ \eta_{\text{capture}} = \eta_{CQD} \cdot \eta_{\text{trap}} \] \hspace{1cm} (A.10)
A flat, field-independent component appears as a consequence of the thermal motion of the carriers in the QDiP solid. This increases substantially once the drift velocity surpasses the random, thermal motion, and finally saturates once carriers traverse the dot before thermalization occurs.

**A.3.3 Thermionic emission of carriers**

Once carriers are photogenerated or trapped into the CQDs they can escape if thermally emitted over the potential barrier. The rate of emission can be calculated as follows:

\[
GT_j = \sigma_{CQDs} \cdot v_{th} \cdot N_{DOS} \cdot \exp\left(-\frac{E_{bj}}{kT}\right)
\]

where \(j\) represents the type of carrier (\(j=e\) for electrons or \(j=h\) for holes). \(N_{DOS}\) stands for the density of available states in the host material conduction or valence band. \(E_{bj}\) is the activation barrier for the \(j\)-type of carrier.

**A.3.4 Fowler-Nordheim carrier emission**

If the electric field is high enough, carriers will start tunneling through the triangular potential barrier established between the host and the sensitizer. This field-emission process can significantly boost the injection rate by orders of magnitude.\(^{94}\)

\[
GFN_j = \frac{E}{4\sqrt{2qm \cdot E_{bj}}} \cdot \exp\left(-\frac{4\sqrt{2qm \cdot E_{bj}^{3/2}}}{3qhE}\right)
\]

**A.3.5 In operando transient absorption study of DiP photodetector**

(1) Emission of QDs photocharges into the perovskite
We carried out transient absorption spectroscopy measurements to characterize the ultra-fast field emission dynamics of photocharges from the QDs into the perovskite matrix. When we pump both perovskite and QDs phases, we observe that a faster bleaching occurs at the exciton peak when a reverse electric field of $2 \cdot 10^5$ V/cm is applied (Figure 5.1). This has a two-fold implication:

I. That photocharges are being emitted out of the QDs.

II. That, under high enough electric fields, photocharges within the perovskite are not being majoritarily captured into the QDs; or, in case they did, emission from the QDs outcompetes this process.

Appendix B. Supporting Figures

B.1 DFT simulation of DiP

Structural affinity is necessary but not sufficient to produce epitaxial bonding between the two phases; energetic considerations must also be taken into account. DFT further reveals that the epitaxial three-dimensional embedding of PbS CQDs inside a perovskite matrix is achieved without the formation of interfacial defects, that is, the bandgap is predicted to remain open, with no in-gap defects predicted.
Figure A. 1 DFT simulation. Highest Occupied Molecular Orbital (HOMO) (left) and the Lowest Unoccupied Molecular Orbital (LUMO) (right) of quantum dots that are lattice-matched with perovskite matrix.
B.2 Diffusion lengths and stability of MAPbI$_{3}$Br$_{3-x}$ perovskites

The important function of the perovskite matrix is to transport photogenerated carriers into the QDs. We found that the diffusion length, which will determine the efficiency with which electron–hole pairs can be delivered to the CQDs, shows a significant enhancement once bromine is incorporated into the matrix. The diffusion length and the photoluminescence lifetime (Figure A. 2) both peak at 83% iodine halide content. This perovskite matrix also shows the best stability in moist air (Figure A. 3).

![Figure A. 2 Photoluminescence lifetime of MAPbX3 (X=I,Br) perovskite with different amounts of iodine.](image)
Figure A. 3 Stability Test of the quantum-dot-in-perovskite film. Time-dependent UV-Vis absorption spectra of quantum-dot-in-perovskite film in an atmosphere with 50% humidity for one week.
B.3 Structure studies of MAPbI$_x$Br$_{3-x}$ perovskites

We propose that the further improved lattice matching reported herein through the use of the mixed halide matrix reduces strain at the heteroepitaxial interface, and further lowers the density of defects. We measured powder X-ray diffraction of pure QDs and in the MAPbIxBr$_{3-x}$ perovskite matrix to evaluate the lattice mismatch (Figure A. 4). As the PbS lattice constant (5.91 Å) lies between that of MAPbI$_3$ (6.26 Å) and MAPbBr$_3$ (5.89 Å), the lattice matching improves with increasing bromine concentration and peaks at 67% iodine content, where the interface exhibits the lowest strain.

![Figure A. 4](image_url)

Figure A. 4 Structural characterization of bromide doped quantum-dot-in-perovskite solid. a, Powder XRD of pure quantum dots (inset) and MAPbIxBr$_{3-x}$ perovskite matrix, showing that 67% iodine content yields the best lattice matching between quantum dots and perovskite matrix. b, Lattice matching between perovskite and PbS with different amount of iodine. the lowest strain.
B.4 PL spectra of CQD and perovskite from pure CQDS, pure perovskites, and DiP

Figure A. 5 Photoluminescence properties of CQDs in perovskite. Normalized photoluminescence (PL) profiles of CQDs (around 1300 nm) and perovskite (around 750 nm), from pure perovskite, pure CQDs and CQDs in perovskite films; perovskite PL quenching and concomitant CQDs PL enhancement indicates carrier transfer from perovskite to CQDs.
B.5 PL spectra of CQD and perovskite from pure CQDS, pure perovskites, and DiP

Figure A. 6 Size dependent PLQE of CQDs-in-perovskite. The PLQE values were normalized to that of 1500 nm CQDs in perovskite. PLQE increases with increasing size of CQDs. Consistent with EQE and PCE results.
B.6 Comparison of CQD LED output power between pure CQD devices and DiP devices

Figure A. 7 Comparison of absolute output power from of the device emitting at 1391 nm using CQD-in-perovskite (3.6% volume ratio) and CQD-only films as emissive layers.
B.7 *In operando* transient absorption analysis: charge extraction under applied bias in DiP photodetectors.

![Graph 1](image1.png)

**Figure A. 8** Emission of QD photocharges and associated dynamics.

<table>
<thead>
<tr>
<th>Model</th>
<th>ExpDecay2</th>
<th>( y = y_0 + A_1 \exp(-x-x_0) + A_2 \exp(-x-x_0) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduced Chi-Sqr</td>
<td>0.00848</td>
<td></td>
</tr>
<tr>
<td>Adj. R-Square</td>
<td>0.8164</td>
<td>0.82288</td>
</tr>
</tbody>
</table>

For 0 V/cm:
- \( y_0 = 0.31337 \)
- \( x_0 = -25.69258 \)
- \( A_1 = 0.27471 \)
- \( A_2 = 0.27266 \)
- \( t_1 = 1565.69866 \)
- \( t_2 = 163.83168 \)

For 2 \( \times 10^4 \) V/cm:
- \( y_0 = 0.10568 \)
- \( x_0 = -6.64553 \)
- \( A_1 = 0.40149 \)
- \( A_2 = 0.25215 \)
- \( t_1 = 75.92568 \)
- \( t_2 = 1172.95222 \)
We then monitored the visible absorption spectrum of the DiP photodiode. We observed that the bleach corresponding to the perovskite phase is slowed down (i.e., it is receiving carriers) under the application of a reverse electric field of $2 \cdot 10^5$ V/cm (Figure A. 9).

Figure A. 9 Collection of QD photocharges emitted into the perovskite phase. a, Transient absorption spectra at 0 V·cm$^{-1}$ and b, $2 \times 10^5$ V·cm$^{-1}$. c, Time evolution slices at 750 nm. The data was fitted with a single exponential decay. A 1000 nm pump at a fluence of 225 $\mu$W·cm$^{-2}$ was used in the experiment to excite the quantum dots.
As a control reference we monitored the transient absorption of CQD only devices, and we observe no significant difference in the bleaching kinetics of this sample (Figure A. 10).

Figure A. 10 Transient absorption at the QD exciton peak under different electric fields. (a-c). Absorption maps at open circuit, 0 V/cm and $2 \cdot 10^5$ V/cm (d) No significant different in the decay is observed at the different scenarios. Pump: 450 nm at a fluence of 11 µJ/cm$^2$. 
As a control reference we monitored the transient absorption of perovskite only devices, and we observe no significant difference in the bleaching kinetics of this sample under the condition with or without bias (Figure A. 11).

Figure A. 11 Transient absorption of perovskite diodes under different electric fields. No significant different in the decay is observed at the different scenarios. Pump: 450 nm at a fluence of 11 µJ/cm².
B.8 Comparison of dark current characteristic between pure CQD, DiP and pure perovskite photodetectors.

Figure A. 12 Dark current-voltage characteristics: Reverse current-voltage characteristics for DiP (red) and perovskite photodiodes (black). Above $3.5 \times 10^5 \text{ V/cm}$ the perovskite sample breaks down with irreversible damage. The J-V curve for QDs only device using the same architecture is shown for comparison.
B.9 Predicted recirculation probability of electrons (blue) and holes (red) as a function of applied field.

Figure A. 13 Recirculation probability. Predicted recirculation probability of electrons (blue) and holes (red) as a function of applied field. As a result of the recirculation imbalance of different charge types photomultiplicative gain effects appear.