Enhancing quantum-dot luminescence
in visible and infrared light emitting devices

by

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B.A., Trinity College, University of Cambridge (2009)

Submitted to the Department of Materials Science and Engineering
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Abstract

We investigate how the external quantum efficiency (EQE) of colloidal quantum-dot light emitting devices (QD-LEDs) can be enhanced by addressing in situ QD photoluminescence (PL) quenching mechanisms occurring with and without applied bias. QD-LEDs promise efficient, high colour-quality solid-state lighting and displays, and our cost analysis of industrial-scale QD synthesis suggests they can be cost competitive. Efficiency ‘roll-off’ at high biases is among the most enduring challenges facing all LED technologies today. It stands in the way of high efficiencies at high brightness, yet it has not previously been studied in QD-LEDs. Simultaneous measurements of QD electroluminescence (EL) and PL in an operating device allow us to show for the first time that EQE roll-off in QD-LEDs derives from the QD layer itself, and that it is entirely due to a bias-driven reduction in QD PL quantum yield. Using the quantum confined Stark Effect as a signature of local electric fields in our devices, the bias-dependence of EQE is predicted and found to be in excellent agreement with the roll-off observed. We therefore conclude that electric field-induced QD PL quenching fully accounts for roll-off in our QD-LEDs. To investigate zero-bias PL quenching, we fabricate a novel near-infrared (NIR)-emitting device based on core-shell PbS-CdS QDs synthesised via cation exchange. QDs boast high PL quantum yield at wavelengths beyond 1 μm, making them uniquely suited to NIR applications such as optical telecommunications and computing, bio-medical imaging, and on-chip bio(sensing) and spectroscopy. Core-shell PbS-CdS QDs enhance the peak EQE of core-only PbS control devices by 50- to 100-fold, up to 4.3 %. This is more than double the efficiency of previous NIR QD-LEDs, making it the most efficient thin-film NIR light source reported. PL measurements reveal that the efficiency enhancement is due to passivation of the PbS core by the CdS shell against a non-radiative recombination pathway caused by a neighboring conductive layer within the device architecture.

Thesis Supervisor: Vladimir Bulović
Title: Professor of Electrical Engineering and Computer Science
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*If you can fill the unforgiving minute*

*With sixty seconds’ worth of distance run,*

*Yours is the Earth and everything that’s in it,*

*And—which is more—you’ll be a Man, my son!*

From "If—", by Rudyard Kipling.
Dedicated to my family - Mum, Dad, and Jon -
and to a Fossil Free MIT.
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Chapter 1

Introduction

The generational challenges of climate change and global sustainable development compel technological innovations in both renewable energy and energy efficiency. High performance lighting is a key target for energy efficiency improvements and solid state light emitting diodes are already revolutionising this field. In the quest for low cost, large area, high colour-quality lighting, thin-film light emitting devices (LEDs) based on nanostructured materials have emerged, and have already established themselves as multi-billion dollar display markets. This thesis explores the use of visible and infrared colloidal nanocrystal "quantum-dots" (QDs) as bright, wavelength-tunable luminophores in optically- and electrically-driven LEDs.

Near the onset of this work, we conducted two comprehensive literature reviews of the quantum-dot light emitting device (QD-LED) field [1,2]. Our conclusion was that from a device efficiency perspective, the three key challenges facing QD-LEDs today are QD photoluminescence (PL) quenching, poor photon outcoupling, and a limited understanding of the fundamental operating mechanisms contributing to the recombination of electrons and holes, yielding light, in QD-LEDs. We also found that the operational lifetime and cost of QD-LEDs must be addressed if they are to become a commercial reality.

Improving device shelf life and reducing the cost of materials and manufacture are surely the greatest hurdles to the commercialisation of existing QD-LEDs. Enhancing the efficiency with which generated light is outcoupled from QD-LEDs is also a critical
step, yet it is expected that this may largely be a matter of extending to QD-LEDs some of the many structural modifications that have been successfully implemented in organic LEDs (OLEDs) [3, 4] and nitride-based LEDs [5]. Relatively speaking, all three present predominantly manufacturing-based challenges on the R&D chain.

In contrast, better understanding carrier recombination and QD PL quenching in QD-LEDs compels relatively fundamental research. As our overview of past QD-LED research in Chapter 2 shows, substantial attention has been devoted to improving the efficiency of carrier recombination - bringing electrons and holes together onto QD emitters - through the engineering of four distinct generations of device architectures. In this thesis, we instead focus on the last step of the light generation process, which to date has received less dedicated attention: once an exciton has formed on a QD, what processes dictate its probability of recombining to emit a photon? In particular, we seek to characterise and, where possible, mitigate the influence of zero-bias and bias-driven QD PL quenching on the performance of QD-LEDs. Indeed, the external quantum efficiency (EQE) of QD-LEDs is directly proportional to QD PL quantum yield ($\eta_{PL} =$ number of photons emitted per photon absorbed), and in some devices it is now the limiting factor in efficient light generation [6]. As we shall see, controlling $\eta_{PL}$ presents opportunities for engineering tailored materials solutions, allowing us to make progress towards QD-LEDs with higher efficiency and brightness.

## 1.1 Thesis Organisation

Chapter 1 outlines the need for more energy efficient lighting technologies to help decarbonise the global energy system and describes the challenges faced by white LEDs and OLEDs. Chapter 2 introduces colloidal QDs and the benefits they bring to lighting and display markets, and traces the evolution of QD-LEDs, from invention through to state-of-the-art. It includes a quantitative cost analysis of large-scale QD synthesis, which suggests QDs are cost-competitive with the U.S. Department of Energy (DOE)’s solid state lighting (SSL) cost targets for OLEDs. Chapter 3 presents a rudimentary background on the chemical approaches to QD synthesis relevant to this
thesis and the quantum mechanical origins of QDs’ fundamental optical properties. Experimental methods are summarised at the start of each relevant chapter, and where necessary, further details are presented at their end. We note that, expect where explicitly described, the fabrication and characterisation tools employed in this thesis are standard in the field, and the interested reader is directed to ref. [7–10], which provide a basic contemporary overview of all of these techniques as used in our laboratory.

Chapter 4 begins with an overview of the different processes that may contribute to quenching of QD PL in QD-LEDs. This leads us to broadly categorise PL quenching mechanisms as either ‘zero-bias’ (occurring even without bias) or ‘bias-driven’ (dependent on applied bias). While these quenching pathways have previously been identified for isolated QDs, here, in situ device measurements allow us for the first time to directly observe the detrimental impact of these mechanisms in operating QD-LEDs, and to engineer solutions to mitigate these effects.

In the second part of Chapter 4, we focus on bias-driven PL quenching in QD-LEDs. By simultaneously measuring the PL and EL of operating red-emitting QD-LEDs, we demonstrate for the first time that the so-called ‘roll-off’ in efficiency typically observed at high applied biases in QD-LEDs can be wholly explained by a simultaneous, bias-driven, reversible reduction in QD \( \eta_{PL} \). This understanding is crucial to designing devices with high efficiencies at high brightness.

This leads us in Chapter 5 to explore different possible mechanisms for this bias-dependent QD PL quenching. By measuring the electric field dependence of QD PL, we are able to quantitatively predict the EQE roll-off in our devices and therefore to deduce that it is almost entirely governed by electric field-induced QD PL quenching, and not carrier leakage or QD charging, as is often the conventional wisdom. In situ transient PL measurements of our QD-LEDs suggest that the cause of quenching is either a decrease in radiative exciton recombination rate (for example, due to a decrease in the overlap of electron and hole wavefunctions) [11] or a decrease in the efficiency of thermalized-exciton formation [12,13].

Chapter 6 turns to zero-bias PL quenching in QD-LEDs. Using near-infrared
(NIR)-emitting QD-LEDs as a testbed of relatively unfulfilled technological potential, we show that quenching of QD PL due to the QDs’ local device environment makes $\eta_{PL}$ a limiting factor in EQE. To address this, we fabricate a novel NIR QD-LED architecture based on surface-passivated NIR-emitting QDs synthesised by overcoating core-only QDs with a wide band-gap shell. We show that this shell passivation enhances in situ $\eta_{PL}$ by almost two orders of magnitude by mitigating quenching caused by a neighbouring metal oxide charge transport layer. The correlated increase in EQE, to more than double the previous record value, yields the most efficient thin-film NIR light emitting device ever reported.

Finally, Chapter 7 presents a summary of this work, as well as an outlook for QD-based light emitting technologies. Note that Chapter 2 draws substantially from our work published in ref. [1,2]. Chapters 4 and 5 appear in ref. [14]. Chapter 6 is based on our work published in ref. [15] (for patent application see ref. [16]).

1.2 Energy efficiency in lighting and displays

A few months before the submission of this thesis, at the end of 2015, the world’s nations adopted the Paris Agreement [17]. As part of the United Nations Framework Convention on Climate Change, this treaty commits countries to "Holding the increase in the global average temperature to well below 2 °C above pre-industrial levels and to pursue efforts to limit the temperature increase to 1.5 °C above pre-industrial levels, recognizing that this would significantly reduce the risks and impacts of climate change". Just a few months earlier, the United Nations General Assembly also adopted the global Sustainable Development Goals, which include "Ensuring access to affordable, reliable, sustainable and clean energy for all" and "Taking urgent action to combat climate change and its impacts" [18]. As it happened, 2015 was also the United Nations’ International Year of Light and Light-Based Technologies, just months after the 2014 Nobel Prize in Physics was awarded "for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources" [19]. The prospect of designing and deploying high efficiency lighting
technologies to improve energy efficiency motivates the - necessarily fundamental - research of novel QD-based light-emitting devices described in these pages.

Climate policy targets intending to limit the global mean temperature increase to 2 °C will likely require that greenhouse gas emissions peak within the next decade, and then fall rapidly to zero (or below) well before the end of this century. While much focus rightly falls on supply-side strategies for reducing the carbon intensity of energy production technologies, the Kaya Identity (which relates greenhouse gas emissions to the complex, self-reinforcing interactions between carbon intensity, energy intensity, population, and affluence) makes clear that demand-side energy efficiency also has a vital role to play [20]. Fig. 1-1 shows how the exponential rise in global greenhouse gas emissions since the Industrial Revolution has been driven by an even faster exponential growth in energy use, only partially offset by a gradual decline in carbon intensity [21]. Indeed, it is an inescapable theme of decarbonization scenarios that three fundamental energy system transformations are required: fuel-switching (electrification); decarbonization of electricity; and energy efficiency and conservation [20,22–27]. As Fig. 1-2 shows, ensuring a reasonable probability of holding global warming below 2 °C requires on the order of a doubling in the rate of energy intensity improvement in tandem with improvements in carbon intensity. Energy efficiency improvements play an even more vital role in lower (1.5 °C) stabilisation scenarios [28]. The Intergovernmental Panel on Climate Change projects that efficiency improvements will be especially important in the near term, prior to roughly 2030, compared to supply-side measures [27]. Buildings, in particular, have the largest low-cost potential for improved energy efficiency [27]. Lighting, which is the second largest user of building energy, and which accounts for roughly 19 % of global electricity consumption (conservatively expected to grow by 80 % by 2030) [29] and 6.5 % of the world’s greenhouse gas emissions [30], has therefore been identified as a key area for early energy intensity reductions [26]. The U.S. DOE, for example, is coordinating a major lighting research effort, and is directed by the Energy Policy Act of 2005 to systematically accelerate SSL development [31]. Pertaining to the U.N.’s Sustainable Development Goals, another key driver for lighting innovation is
the fact that 1.6 billion people today lack access to reliable lighting. Nearly all of them instead rely on kerosene lamps, which account for 1% of global lighting yet 20% of lighting-based CO₂ emissions [32], and which are responsible for 1.5 million deaths per year [33].

To this end, almost all OECD (Organisation for Economic Co-operation and Development) governments have implemented policies aimed at phasing out incandescent lighting [35], which converts electrical energy to light with an efficiency of just 5%, and with an efficacy of roughly 15 lm/W [32]. Fluorescent tubes (efficiency ~25%, efficacy ~60-100 lm/W), and increasingly compact fluorescent lamps (efficiency ~20%, efficacy ~35-80 lm/W), have come to provide the bulk of global lighting, but owing to their mercury content and inferior efficacy relative to LEDs (discussed below), they are perceived by many as a stop-gap measure to replace incandescent lamps and their derivatives (halogen and high-intensity discharge lamps) until more efficient, non-toxic white light sources become available and cost effective [29,30].
Figure 1-2: Joint influence of carbon intensity and energy intensity improvements for limiting global warming. The plot, adapted from ref. [34], shows the joint influence of these two factors on limiting warming to below 2 °C during the twenty-first century, in a large illustrative set of scenarios ($n > 100$). Average global rates are for the period 2010 to 2050. The yellow star indicates the historically observed rate between 1971 and 2005, and six-pointed stars indicate the values found in the SRES (Special Report on Emissions Scenarios - see ref. [34]) scenarios. SRES marker scenarios are highlighted in red. The arrow illustrates the direction of increasing climate protection. Other symbols are colour-coded as a function of their probability of limiting warming to below 2 °C, and the shape of the symbols reflects the base level of future energy demand assumed in the scenarios (diamond: high; circle: intermediate; square: low). Note that whereas all scenarios in ref. [34] assume a consistent evolution of climate mitigation over the course of the full century, the SRES scenarios represent baseline scenarios without climate mitigation. The long-term development in the SRES scenarios might thus differ from their short-term trends.
SSL based on inorganic LEDs continues to emerge as the most likely contender. Akin to Moore’s Law for transistors, SSL development has progressed exponentially for more than 40 years according to Haitz’ Law; each decade exhibiting a ten-fold drop in cost-per-lumen and a twenty-fold rise in light generated per LED package (for a given wavelength of emission) [30]. Sales of high-brightness LEDs have had a compound annual growth rate of over 46 % since 1995 [29]. Whereas CFL efficacy has lately remained flat at ∼35-80 lm/W, in just the last part of 2014, the average efficacy of LEDs increased from ∼70 lm/W up to almost 100 lm/W [36]. And unlike incumbent technologies, LEDs are not limited by fundamental physics-based limitations that prevent more than incremental improvements (for example, incandescentes are limited by the laws governing a blackbody radiator) [30]. For SSL to realise decisive energy efficiency benefits, however, even higher performance levels must be achieved. The U.S. DOE’s Multi-Year Program Plan for SSL aims to reduce lighting-based energy use by 40-60 % by 2030 (2,216-3,900 TWh), equivalent to roughly $220-380 billion in energy savings [37]. To do so, a stretch goal of 200 lm/W by 2030 has been set, which envisions LED lighting virtually eliminating the use of high intensity discharge sources (e.g. sodium lamps) and reducing the installed base of linear fluorescent lamps to one-third of its current share. LED lighting sales (in lumen-hours) would need to increase in the U.S., for example, from less than 4 % in 2014 to 88 % in 2030 [31].

Yet in most regions of the world right now, even with government policy support, fewer than 10 % of existing lighting installations (installed base) use SSL products [31]. A major research challenge of reaching the above goals is that white LEDs (WLEDs) based on SSL must achieve such high efficacies while simultaneously delivering exceptional colour quality at low cost. Fig. 1-3b highlights three approaches that are being explored to achieve these aims. The single-chip phosphor-conversion approach based on a blue LED (InGaN, for example) backlight and a yellow or green (and sometimes red, too; Fig. 1-3b, left) down-converting phosphor [38] are presently the commercial technology of choice, but suffer from a tradeoff between efficacy and colour quality (quantified by colour rendering index, CRI, explained in Section 2.1.1)
Chapter 1. Introduction

(Fig. 2-2b). This is due to the absorption and emission losses of the phosphor(s) [39], as well as a 20-25 % energy loss because of the Stokes shift from a blue pump to lower energy phosphor(s) [30]. The optimisation of phosphors, especially narrow-band red-emitting ones with less thermal instability, is a key step to achieving efficacies truly surpassing those of fluorescent lamps while maintaining high CRI [39,40]. Ultimately, however, the Stokes shift may preclude the realisation of very high efficacy (∼200 lm/W) WLEDs [29]. An alternative avenue for achieving higher CRI, illustrated in Fig. 1-3b, right, is the use of multi-chip red, green, blue (and sometimes yellow, too: RYGB) WLEDs. But this approach is simultaneously made complicated and costly by various aspects of assembly, colour mixing, and feedback drive circuitry required to continuously balance the different colour emitters that age at different rates [38,39]. Critically, RYGB WLEDs also face the decade-long challenge of improving the low efficiencies of LEDs in the ‘green-yellow gap’ wavelengths [40,41]. To attain long-term SSL performance targets, high LED internal quantum efficiencies of ≥ 90 % will need to be achieved at particular green and yellow wavelengths [39]. Another LED challenge, relevant to both phosphor conversion and multi-chip approaches, is efficiency ‘droop’, which is the fall in efficiency of (nearly all GaN-based) LEDs of even 70 % or more at desired high operating currents. This phenomenon is discussed in detail in Chapter 4.

Meanwhile, OLEDs have emerged as a potential complimentary white light technology owing to their prospects as flexible, thin, lightweight, large-area, and diffuse light sources. For example, ultrathin, large OLED panels can provide the same light output as a compact GaN-based LED while reducing the brightness per unit area, resulting in a glare-free light source [42]. However, despite research progress, in practice, the development of OLEDs for lighting has lagged behind that of nitride-based LEDs. White OLEDs for lighting are only just nearing commercial availability because it has not been possible so far to simultaneously achieve high brightness at high efficiency with long lifetime [29]. For example, the relatively broad line-width of red OLED emission makes it difficult to achieve excellent colour quality and high efficacy at the same time [31]. Another well-known roadblock to the commercialisation of OLEDs is
Chapter 1. Introduction

Figure 1-3: Evolution, approaches, and challenges of nitride-based LEDs. 

a, Haitz’ Law evolution of LEDs: (filled) Exponential rise in the (highest) flux-per-lumen of commercially available red and cool-white LEDs between 1968 and 2010; (unfilled) exponential fall in the (lowest) original equipment manufacturers (OEM) cost-per-lumen of commercially available red and cool-white LEDs between 1973 and 2010. Adapted from ref. [30]. 

b, Approaches for generating white light from LEDs and their corresponding power spectra: (left) single-chip blue LED pumps red and green phosphors; (right) multi-chip RYGB WLED. Adapted from ref. [39]. 

c, EQEs of various state-of-the-art LEDs based on two material systems, demonstrating the ‘green-yellow’ efficiency gap. InGaN: (1) Thin-Film Flip-Chip LEDs; (2) InGaN vertical thin-film LED; and (3) conventional chip LED. AlGaNp: (4) Truncated-inverted-pyramid LEDs. $V(\lambda)$ is the luminous response curve of the human eye. Reproduced from ref. [39].
the particular challenge of achieving deep blue electrophosphorescence with combined high efficiency, brightness, and long-term operational stability [43]. Deep-blue emission is crucial to realizing a wide color gamut for higher colour quality SSL. In terms of efficiency, while fluorescent organic dyes can certainly achieve deep blue light, they show comparatively much lower efficiencies than their phosphorescent counterparts. Conversely, phosphorescent dyes enable far higher efficiencies, but with only sky-blue or bluish-green emission [44,45]. Likewise, achieving high brightness in deep blue phosphorescent OLEDs leads to a commensurate roll-off in efficiency [43]. And unlike red- and green-emitting OLEDs, achieving industry-standard device lifetimes in blue devices currently requires the use of only inefficient fluorescent emitters [42].

Overall, there has been a gradual market penetration of inorganic LEDs from mobile applications to displays to general lighting [46]. This is because many of the challenges faced by WLED lighting are similar to those in developing display technologies - both requiring high brightness, multi-colour emitters. As Haitz et al. have observed in mapping the evolution of SSL, applications like displays provide critical "stepping stone" markets that help drive the innovation and cost reductions necessary for ultimately penetrating the general illumination sector [30]. OLED displays, too, are already an established multi-billion-dollar market reality [42]. This is in part because of more aggressive, profit-driven research funding in the display market [31], but also because of their low energy consumption, wide viewing angles and high contrast values (in comparison to back-lit liquid crystal displays (LCDs)), and compatibility with high-resolution patterning.

Colloidal QDs offer a possible solution to some of the challenges currently facing the design and manufacture of LEDs for lighting and display applications, as we describe in the next chapter. These solution-processed semiconducting nanocrystals boast unique size-dependent optical properties that have motivated increasingly active research aimed at applying them in the next generation of optoelectronic and bio(medical) technologies. Since the first directed QD synthesis three decades ago, use of QD thin-films has been demonstrated in a range of optoelectronic devices including LEDs [47–50], photovoltaics (PVs) [51], photodiodes [52], photoconductors [53],
and field-effect transistors [54], while QD solutions have been used in a myriad of *in vivo* and *in vitro* imaging, sensing, and labelling techniques [55]. In passing, we note that the research of QD-LEDs therefore not only extends the frontiers of lighting and display technologies, but can offer fundamental insights into the photo-physical properties of QDs, which can help inform sister technologies like QD PVs. The infrared-emitting QD-LED architecture described in this thesis, for example, is extremely similar to that used by some of today’s most efficient QD PVs [56].
Chapter 2

Quantum-Dots as Luminophores

2.1 Benefits for solid state lighting and displays

2.1.1 Tunable and pure colours

Colloidal quantum-dots (QDs) are solution-processed nanoscale crystals of semiconducting materials. They comprise a small inorganic semiconductor core (1-10 nm in diameter), often a wider-bandgap inorganic semiconductor shell, and a coating of organic passivating ligands (Fig. 2-1b, insets). They emit bright, pure and tunable colours of light, making them excellent candidates for colour centers in next-generation display and SSL technologies. The greatest asset of QDs for light-emitting applications is their tunable bandgap, governed by the quantum size effect. Confinement of electron-hole pairs (excitons) on the order of the bulk semiconductor’s Bohr exciton radius (5.6 nm for CdSe, a common QD material) leads to quantisation of bulk energy levels, resulting in atomic emission-like spectra. Another result of this confinement is that as its size decreases, the QD’s bandgap increases, leading to a blue shift in emission wavelengths [57]. This is shown in Figure 2-1a, which also illustrates how this spectral tunability can be extended through changes in QD chemical compositions and stoichiometries [58,59]. Such systematic and precise spectral tunability of efficient emission, even in the near-infrared (NIR) region, is a distinguishing and significant technological advantage of QDs over organic dyes, which we exploit
in engineering the NIR QD-LEDs described in this thesis. The quantum mechanical 
origins of this colour tunability are discussed further in Chapter 3. CdSe-based core-
shell QDs are currently the material of choice in visible QD-LEDs [58,60–62] and lead 
chalcogenide QDs dominate NIR devices [63,64]. In the visible, the spectrally-narrow 
emission of QDs (see Figure 2-1b; full width half maximum (FWHM) ∼30 nm for 
CdSe) [65] compared with those of inorganic phosphors (FWHM ∼50-100 nm) [66] 
identify QDs as outstanding luminescent sources of saturated emission colour.

This high colour quality can be quantified using the Commission International 
de l’Eclairage (CIE) chromaticity diagram (Figure 2-2a), which maps colours visible 
to the human eye in terms of hue and saturation. By combining the emission of 
three light sources, such as red, green, and blue (RGB) emissive display pixels, a set 
of apparent colours can be generated corresponding to the colours enclosed by the 
triangle on the CIE diagram defined by the coordinates of the three pixels. Figure 
2-2a shows that, with the highly saturated colours of QD emission, it is possible 
to select RGB QD-LED sources whose subtended colour gamut is larger than that 
required by high-definition television (HDTV) standards (dashed line) [67].

Broad spectral tunability also allows a more controlled combination of colours, 
such that higher quality white light, with a precisely tailored spectrum, can be genera-
ted. The white light’s quality can be measured in terms of correlated colour tempe-
ration (CCT) and colour rendering index (CRI), which compare LED emission with 
that from the Sun (the ‘ideal’ white light source, with a CRI of 100). Conventional 
white LEDs, comprising a blue inorganic LED backlight coated with a yellow phos-
phor optical down-converter (see Fig. 1-3), typically exhibit a cool bluish emission, 
characteristic of high CCTs (>5000 K) and low CRIs (mostly between 80 and 85), as 
shown in Figure 2-2b. For lower CCT lights (for example, 2700 K) it is particularly 
hard to simultaneously maintain high luminous efficacy and high colour quality be-
cause the required red luminophores must have relatively narrow emission spectra so 
as to avoid photon loss as infrared emission. The emission spectra of conventional red 
phosphors is unfortunately too broad (>60 nm FWHM) to avoid this loss. In contrast, 
the narrow spectral emission (∼30 nm FWHM) of QDs in QD Vision Inc.’s Quan-
Chapter 2. Quantum-Dots as Luminophores

Figure 2-1: Tunable and pure colour light emission from colloidal quantum dots. a, Solutions of colloidal QDs of varying size and composition, exhibiting PL under optical (ultraviolet) excitation [58]. b, PL spectra of CdSe-ZnS and PbS-CdS core-shell colloidal QDs [67,68]. The upper inset shows a schematic of a typical core-shell colloidal QD. The lower inset is a high-resolution transmission electron microscope image of a CdSe QD (scale bar, 1.5 nm). a demonstrates the size- and composition-dependent tunability of QD emission colour, whereas b shows the extension of this narrowband emission into the near-infrared. QD-LED electroluminescence typically closely matches corresponding PL spectra.
Chapter 2. Quantum-Dots as Luminophores

Tum Light™ optic offer supplementary and more selective optical down-conversion of some of the backlight’s bluer emission (generated by Nexxus Lighting, Inc. LED lighbulbs) into redder light, leading to a CRI >90 % and a superior CCT of 2700 K, while maintaining a very high 65 lm/W efficacy [67] (see Figure 2-2b for a comparison with other LED light sources). QDs thus enable higher colour quality and, accordingly, lower power consumption in SSL sources. Through analogous approaches, QDs can be utilised as backlights in high-colour-quality liquid crystal displays (LCDs). In fact, Sony’s 2013 line of Triluminos LCD televisions use edge-mounted red and green QDs from QD Vision, Inc. to optically downconvert some of the television’s blue LED backlight (absorbing some of the blue light and re-emitting it as red and green light), optimising its colour balance so that it fulfills >100 % of the NTSC colour television standard gamut, compared with ~70 % for conventional LCD screens [69,70]. The result is a television picture with colour quality comparable to that of organic LED (OLED) screens, but achieved at the cost of an LCD display [2].

2.1.2 Bright emission

Overcoating QDs with wider bandgap inorganic semiconductor shell(s) (Figure 2-1b, inset) has been shown to dramatically enhance their PL quantum yield (\(\eta_{PL}\)) and photostabilities. Overcoating passivates surface non-radiative recombination sites more effectively than organic ligands alone, and, simultaneously, shifts the electron wavefunction, confining excitons to the QD core, away from surface trap states [71–73]. For example, solutions of CdSe-ZnS core-shell QDs can be routinely synthesised with \(\eta_{PL}\) of between 30 % and 95-plus %, almost one order of magnitude greater than those of native CdSe cores [74]. As noted above, the extendibility of QD emission into the NIR is of significant technological interest. Whereas organic molecules have negligible optical activity beyond wavelengths of \(\lambda=1\ \mu m\) (\(\eta_{PL}\) is <5 % at these wavelengths) and exhibit poor chemical and photostability, QDs are relatively stable and retain \(\eta_{PL}\) >50 % throughout the NIR [74–78]. As with visible-emitting QDs, this high NIR brightness is owing in large part to improvements in \(\eta_{PL}\) with overcoating [75].
Figure 2-2: Optical advantages of colloidal QDs for display and solid-state lighting applications. a, CIE chromaticity diagram showing that the spectral purity of QDs enables a colour gamut (dotted line) larger than the high-definition television standard (dashed line). b, Plot showing the luminous efficacy and colour rendering index (CRI) of various lighting solutions. The first commercial QD-based solid-state light source, developed by QD Vision and Nexxus Lighting, consists of sheets of red QDs backlit by a blue LED with a yellow phosphor coating, resulting in a high CRI without compromising high luminescence efficacy. Recently, Philips’ A-Style LED, which employs remote phosphors, has demonstrated even more energy-efficient lighting. There is evidently an emerging market for high-quality optical downconverters, such as QDs.
Since QD-LEDs often comprise neat films of QDs, it is their $\eta_{PL}$ in this close-packed form that then dictates maximum device efficiencies. For core-only QDs in solution, $\eta_{PL}$ is typically reduced by one to two orders of magnitude when deposited as thin films [79]. Evidence suggests that this ‘self-quenching’ results from efficient non-radiative Förster Resonant Energy Transfer (FRET) of excitons within the inhomogeneous size distribution of QDs to non-luminescent sites [6,80–82], where they recombine non-radiatively [83]. It follows from the very strong inter-dot spacing dependence of FRET efficiency (it decreases as spacing increases) that QD ligand length and shell thickness can profoundly impact the degree of QD ‘self-quenching’. Thin films of core-shell CdSe-ZnS QDs with long oleic acid ligands, for example, typically retain $\eta_{PL}$ of 10-20 %, which directly affects the external quantum efficiency (EQE) of QD-LEDs containing those QD films. The EQE of a QD-LED is defined as the ratio of the number of photons emitted by the LED in the viewing direction to the number of electrons injected. It may be expressed as:

$$\text{EQE} = \eta_h \chi \eta_{PL} \eta_{oc}$$

(2.1)

where $\eta_h$ is the fraction of injected charges that form excitons in QDs, $\chi$ is the fraction of these excitons whose states have spin-allowed optical transitions, $\eta_{PL}$ is the QD PL quantum yield resulting from these transitions, and $\eta_{oc}$ is the fraction of the emitted photons which are coupled out of the device. The internal quantum efficiency (IQE) is the efficiency of the charge recombination process, independent of $\eta_{oc}$ (i.e. $\text{IQE} = \text{EQE}/\eta_{oc}$). A full description of how EQE is defined and measured in our experiments can be found in Appendix A, Section A.1.

It is also technologically significant that for CdSe QDs, for example, $\chi \approx 1$, identical to that of the most efficient organic phosphors, which are used in high-efficiency organic LEDs (OLEDs) [84]. In CdSe QDs, the high $\chi$ is a result of the small energetic separation ($<25$ meV) of the ‘bright’ and ‘dark’ band-edge excitonic states [85], which have spin-allowed and spin-forbidden transitions to the ground state, respectively. Thermal mixing at room temperature enables efficient crossing of
excitons from dark states to higher energy bright states, leading to a high effective $\chi$.

With $\chi \approx 1$, IQE is then limited by $\eta_r \eta_{PL}$. The greatest hurdle to achieving high efficiency QD-LEDs is the simultaneous maximisation of $\eta_r$ and $\eta_{PL}$. QD-LEDs have been reported that appear to demonstrate PL-normalised IQEs (that is, IQE/$\eta_{PL}$) approaching (at least within a factor of two) 100 %, and that are therefore limited only by $\eta_{PL}$ [6, 58, 63, 86, 87]. This motivates the focus of this thesis on understanding and controlling the quenching of QD PL in QD-LEDs.

2.1.3 Solution processable

QD surface ligands confer solubility in a variety of organic solvents. This enables the use of low cost QD deposition techniques such as spin-coating [88], mist coating [89], inkjet printing [90, 91], and microcontact printing [92, 93]. Ligands can also be chosen [50] (or cross-linked post-deposition [94, 95]) to enable the deposition of subsequent materials in orthogonal solvents. These methods have led to, for example: organic-QD hybrid structures [96]; molecular length-scale control of dot-to-dot separation [97]; QDs deposited on curved surfaces [98]; QD monolayers [88]; QD multilayer superstructures [99]; and one-dimensional chains [100].

2.1.4 Stable

It is commonly attested that the photostability of QDs exceeds that of organic chromophores, and that this advantages their application in LEDs. Yet oxidation of QDs has been seen to cause spectral diffusion (blue-shifting) and PL quenching in both single QDs [101, 102] and ensembles of QDs [103]. Exposure to light generally exacerbates these effects through photo-oxidation and photo-bleaching [102], though substantial photo-brightening (increased $\eta_{PL}$ following exposure to light) has also been observed [104–106]. Beyond the presence of oxygen, these phenomena have been found to be critically dependent on an array of factors including humidity [107, 108], QD film geometry [109], and the duration [103, 106], intensity, and wavelength [109] of illumination.
Nevertheless, QD shells markedly improve photostability \cite{102} by passivating surface traps, by confining excitons to QD cores, and by hindering the diffusion of oxygen, for example, into QD cores. Moreover, thick inorganic multishells \cite{110,111}, surface-passivating ligands \cite{112}, and radially graded alloyed shells \cite{113} have been shown to heavily attenuate, and even entirely suppress the PL intermittency phenomenon of CdSe QDs known as ‘blinking’. Reductions in blinking are relevant to QD-LEDs because they translate to higher ensemble $\eta_{\text{PL}}$ \cite{114}. Talapin \textit{et al.} recently synthesised QDs with inorganic molecular metal chalcogenide ligands \cite{115} and with metal-free ionic ligands \cite{116}, relieving QDs of instabilities associated with photo-damage of organic ligands \cite{110}. We caution that many of the above studies, however, are based on single-QD spectroscopy at cryogenic temperatures.

Overall, at least as bioanalytical labels, QDs are proving to be more photostable than organic dyes \cite{117}. Whether this comparison could hold good in LEDs, however, is yet unclear. Tremendous opportunities exist to better understand and improve the longevity of QDs in QD-LEDs by investigating the chemistry and photo-physics of films of QDs under operating conditions \cite{118}.

### 2.1.5 Cost competitive

From a manufacturing standpoint, QD-LEDs may be approximated as QD-enhanced OLEDs. The manufacturing cost of QD-LEDs can be broadly divided into the cost of raw materials and the fabrication costs of processing these materials. The similarity of the constituent materials of QD-LEDs and OLEDs means that they are fabricated using a similar toolbox of thin-film processing techniques, so that QD-LED commercialisation would benefit from the manufacturing infrastructure and expertise developed for OLED production. Aside from the QDs themselves, the materials typically employed in QD-LEDs (metals, metal oxides and organic small molecules) are also very similar to those found in OLEDs. Their materials costs should therefore be commensurate with those that are enabling the growth of OLED markets, and would benefit from their economies of scale.

To estimate the materials costs of QDs typical in light-emitting applications when
produced in large quantities, we perform a quantitative analysis based on published small-scale synthetic procedures, which colleagues have previously used to assess the commercial viability of organic materials for photovoltaics [119]. We consider a few of the most common and promising QD-LED materials and synthetic preparations: red-emitting ‘legacy’ CdSe QDs [65], ‘modern’ CdSe QDs [120], ‘legacy’ CdSe-ZnS core-shell QDs [72], and ‘modern’ CdSe-CdS core-shell QDs [120] (all with trioctylphosphine oxide (TOPO) ligands); NIR-emitting PbS-CdS core-shell QDs (with oleic acid ligands); and, lastly, PbS QDs (with oleic acid ligands), which are not only commonly used in NIR QD-LEDs but have also garnered tremendous interest as an active material in QD-based solar cells. The ‘legacy’ and ‘modern’ labels refer to the synthetic recipe evaluated, as discussed below. As detailed in ref. [119], our cost analysis takes into account all of the material inputs to these procedures in order to estimate the total material costs for each type of QD (based on our assembled database of quotations from major chemical suppliers for each of the input materials). As an example, our model for the synthesis of PbS-CdS is represented graphically as a flowchart in Figure 2-3. The first box in the flowchart represents the starting material, lead (II) oxide. Red arrows indicate reagents, green arrows indicate solvents, and blue arrows indicate additional materials required for workup and purification (‘crash out’). The indicated quantities of input materials and waste are calculated to produce one kilogram of product.

The materials cost results from our models for each synthetic procedure are summarised in Table 2.1. We note that the materials costs that we consider represent only one component of the overall cost to produce these materials. In the case of pharmaceutical drugs, for example, materials only account for 20-45% of the cost of drug synthesis. The balance includes contributions for labor, capital, utilities, maintenance, waste treatment, taxes, insurance, and various overhead charges [119].

We find that the materials costs of visible-emitting ‘legacy’ CdSe QDs ($569-660 \text{ g}^{-1}$; lower value is without workup, upper value is with workup) exceed those of ‘modern’ CdSe QDs ($58-59 \text{ g}^{-1}$) by an order-of-magnitude as a consequence of similarly sizeable differences in the costs of reagents, solvents, and workup materials. This
Figure 2-3: Cost analysis for large-scale QD synthesis, example flowchart for synthesis of core-shell PbS-CdS QDs. The flowchart describes the synthesis of 1 kg of PbS-CdS core-shell QDs. The requisite quantities of (red arrow) reagent, (green arrow) solvents, and (blue arrow) workup (‘crash out’) materials are indicated for this single-step process. Note that a quantitative yield is assumed, as discussed in the caption of Table 2.1.

reflects the 20-year evolution in synthetic procedures that has led to the use of significantly smaller quantities of more economical input materials, notably a significantly cheaper and air-stable source of Cd (cadmium oxide replaces dimethyl cadmium). These advances carry forward to the ‘modern’ CdSe-CdS core-shell QDs ($61-65 \text{ g}^{-1}$), which cost only fractionally more than their core-only equivalents, again owing to the use of an economical source of Cd for the shell. In contrast, the ‘legacy’ CdSe-ZnS core-shell QDs ($1884-1996 \text{ g}^{-1}$) inherit the ten-fold higher costs of their starting CdSe QDs and require the use of an expensive source of zinc for their shell (replacing dimethyl zinc is key to lower costs). It is possible that reports of QD costs of up to $10,000 \text{ g}^{-1}$ (ref. [69]) may result from evaluation of antiquated ‘legacy’ syntheses rather than more economical state-of-the-art approaches. The materials costs of NIR-emitting QDs (PbS, Method 1: $18-29 \text{ g}^{-1}$; PbS, Method 2: $45-68 \text{ g}^{-1}$; and PbS-CdS:
$68-97 \text{ g}^{-1}$) are roughly commensurate with those of the ‘modern’ visible-emitting QDs.

Current target prices for QDs synthesised via scaled-up continuous processes are \( \sim \$10 \text{ g}^{-1} \) (ref. [121]). As a guide, the materials cost of Alq$_3$ - an archetypal organic dye used in OLEDs since the 1980s, and therefore subject to considerable economies of scale - is \( \sim \$4 \text{ g}^{-1} \) (ref. [119]). However, most heavy-metal-based phosphors found in high-performance OLEDs are considerably more expensive. A representative example is Ir(ppy)$_2$(acac) (ref. [122]), for which we calculate a materials cost of $658-1297 \text{ g}^{-1}$. Nevertheless, direct comparison of the materials costs of QDs with those of organic dyes is complicated by the specifics of a given application, which determine how much material is consumed. Considerations include whether it is used at a neat film or as a dopant dispersed in a host matrix, the thickness of such a film, and the wastefulness of the deposition technique employed. As is to be expected, the first QD-based products address optical down-conversion by using a compact edge-mounted geometry [70] that requires relatively small amounts of QDs (often dispersed to maximize $\eta_{\text{PL}}$).

One way to try to assess our results is to translate them into approximate materials costs-per-unit-area (Table 2.1). The per-area costs are based on the assumption that a typical QD-LED might comprise a 25 nm film of hexagonally close packed QDs separated by \( \sim 0.5 \text{ nm} \) due to their surrounding organic ligands. As expected, we obtain similar values for ‘modern’ CdSe ($3 \text{ m}^{-2}$) and CdSe-CdS ($4 \text{ m}^{-2}$) QDs as for PbS (Method 1: $1-2 \text{ m}^{-2}$; Method 2: $3-5 \text{ m}^{-2}$) and PbS-CdS ($4-6 \text{ m}^{-2}$) QDs. ‘Legacy’ CdSe and CdSe-ZnS QDs are significantly more expensive ($35-41 \text{ m}^{-2}$ and $90-95 \text{ m}^{-2}$, respectively). Especially given the likelihood that QD syntheses will be subject to some economies-of-scale [69], this is competitive, for example, with the DOE’s 2020 SSL target cost of organic materials of $10-15 \text{ m}^{-2}$ for OLEDs [123]. Moreover this is just one possible metric, which does not necessarily reflect the higher materials costs that luxury items such as displays might be able to shoulder.

One significant assumption that has so far been made, however, is that we can deposit QDs with 100% efficiency. In reality, the spin-casting technique (and therefore microcontact printing, which in published studies involves a spin-casting step) that
has so far dominated laboratory demonstrations of QD-LEDs wastes \(\sim 95\%\) of the starting solution [124]. Unless the QD waste is recyclable, the associated 20-fold increase in QD materials costs could render some applications economically unviable. This points to the importance of developing low-waste QD-deposition techniques. For example, as mentioned earlier, inkjet printing of multi-coloured pixel arrays of QDs for both down-conversion [125] and RGB QD-LED [124] technologies has been demonstrated, but further refinements in film quality and device performance are required.
Table 2.1: Calculated large-scale chemical synthesis costs for red- and near-infrared-emitting QDs and for two archetypal organic dyes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ref.</th>
<th>Steps</th>
<th>Reagents ($ g^{-1}$)</th>
<th>Solvent ($ g^{-1}$)</th>
<th>Workup ($ g^{-1}$)</th>
<th>Total (w/o workup) ($ g^{-1}$)</th>
<th>Total (w/ workup) ($ g^{-1}$)</th>
<th>Total (w/ workup) ($ m^{-2}$)</th>
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<tr>
<td>‘Legacy’ CdSe (TOPO) QD</td>
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<td>298.22</td>
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<td>90.82</td>
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<td>Alq$_3$</td>
<td>[127]</td>
<td>1</td>
<td>0.44</td>
<td>0.00</td>
<td>3.90</td>
<td>0.44</td>
<td>4.34</td>
<td></td>
</tr>
<tr>
<td>Ir(ppy)$_2$(acac)</td>
<td>[128]</td>
<td>1</td>
<td>621.66</td>
<td>35.86</td>
<td>639.26</td>
<td>657.52</td>
<td>1,296.78</td>
<td></td>
</tr>
</tbody>
</table>

Cost-per-gram for ‘legacy’ CdSe QDs (with trioctylphosphine oxide (TOPO) ligands); ‘modern’ CdSe QDs (TOPO ligands; wurtzite-CdSe synthesis); ‘legacy’ CdSe-ZnS core-shell QDs (TOPO ligands); ‘modern’ CdSe-CdS core-shell QDs (TOPO ligands; wurtzite-CdSe synthesis); PbS (via two methods) and PbS-CdS core-shell QDs (oleic acid ligands); fluorescent dye, tris(8-hydroxyquinolinato) aluminium (Alq$_3$); and phosphorescent dye, acetylacetonatobis(2-phenylpyridine) iridium (Ir(ppy)$_2$(acac)). The cost analysis accounts for all material inputs (reagents, solvents, and workup ['crash out']), yielding total costs-per-gram both without and with workup. For the QDs, these have been converted into costs-per-area assuming a QD film of 25 nm thickness, as detailed in the text. *In the absence of literature yields, we assume quantitative yields; although this is clearly a slight overestimate, it is a reasonable approximation given the synthetic refinements and waste recycling that will surely accompany scale-ups in QD synthesis.
2.2 Quantum-dot light emitting devices

A typical electrically driven colloidal QD-LED comprises two electrodes, which inject charge into a series of active layers sandwiched between them (see Fig. 3a, for example). Since their invention in 1994 [48], their performance has improved dramatically. Fig. 2-4 summarizes this progress for the case of orange/red-emitting (almost always CdSe-based) QD-LEDs in terms of two metrics: (a) peak EQE; and (b) peak brightness. EQE is directly proportional to power conversion efficiency, a key metric for SSL and displays, and brightness values of $10^3 - 10^4$ cd m\(^{-2}\) and $10^2 - 10^3$ cd m\(^{-2}\) are required for SSL and display applications, respectively.

These achievements have in part been a result of evolutions in device architecture, which in two recent reviews of the field, we classified into the four device ‘types’ depicted in the inset of Fig. 2-4a [1,2]. It can be seen that these four types have evolved roughly chronologically. Despite the scattered data, we observe steady increases in both EQE and brightness, with values approaching those of (phosphorescent) OLEDs. In the following sections, we outline the distinguishing features of each type of QD-LED.

2.2.1 Evolution of QD-LEDs

Type-I: QD-LEDs with polymer charge transport layers

These earliest QD-LEDs, pioneered in the early 1990s, were a natural progression from polymer LEDs (PLEDs). Devices comprised a CdSe core-only QD-polymer bilayer or blend [130], sandwiched between two electrodes. QD electroluminescence (EL) was achieved but EQEs were extremely low (<0.01 % EQE, ~100 cd m\(^{-2}\)), in part due to the low $\eta_{PL}$ of QDs without shells (10 % in solution). The low brightness was a consequence of the very low current densities that could be reached while using insulating QDs as both charge transport and emissive materials. Core-shell CdSe QDs were later employed in type-I structures to take advantage of their higher $\eta_{PL}$ [131], and EQEs of up to 0.22 % (max. 600 cd m\(^{-2}\)) were reported using CdS shells [132]. However, these devices still exhibited significant parasitic polymer EL, indicative of
Figure 2-4: Progression of orange/red-emitting QD-LED performance over time in terms of peak EQE and peak brightness. a, Peak EQE. b, Peak brightness. QD-LEDs (a substantial but non-exhaustive selection from the literature) are classified into one of four ‘types’, as described in the text, and are compared with selected orange/red-emitting (phosphorescent) OLEDs. Solid lines connect new record values. Data for a are taken from references: (type-I) [129–132]; (type-II) [47, 58, 59, 87, 88, 133–136]; (type-III) [49, 137, 138]; (type-IV) [60, 61, 86, 94, 139–142]; and (OLEDs) [84, 93, 118, 143–146]. Data for b are taken from references: (type-I) [48, 89, 129, 131, 132]; (type-II) [47, 62, 88, 135, 136]; (type-III) [137, 147]; (type-IV) [6, 60, 61, 86, 93, 94, 139–142]; and (OLEDs) [145, 148–150].
inefficient exciton formation in QDs.

In these initial QD-LEDs, QD EL has been speculated to be driven by direct charge injection [49] (Fig. 2-5b), FRET (Fig. 2-5c), or both, with the relative contribution of these mechanisms remaining unclear [61,129,151,152]. In the case of direct charge injection, an electron and a hole are injected from charge transport layers (CTLs) into a QD, forming an exciton, which subsequently recombines via emission of a photon. FRET is also a viable mechanism, unique to devices having luminescent species, such as emissive polymers [153], small molecule organics [154], or inorganic semiconductors [155,156], in close proximity to the QDs. In this scheme, an exciton is first formed on a luminescent CTL. Thereafter, the exciton energy is non-radiatively transferred to a QD via dipole-dipole coupling (Fig. 2-5f, blue arrows). The relative contribution of these mechanisms, in all four types of QD-LEDs in fact, remains unclear and a better understanding of their roles, for example as a function of QD-LED architecture, will be essential in designing more efficient and brighter devices.

**Type-II: QD-LEDs with organic small molecule charge transport layers**

Type-II QD-LEDs were first introduced by Coe *et al.* in 2002 and instead comprise a monolayer of QDs at the interface of a bilayer OLED [47] (Fig. 2-6). These devices demonstrated record EQEs of 0.5%; an efficiency that has been augmented by an additional factor-of-ten through optimisations. The enhanced performance was attributed to the use of a single monolayer of QDs (enabled by the development of spin-coating [47] and microcontact printing [92,157,158] techniques), which decouples the luminescence process in the QDs from charge transport through the organic layers [47,49,133,154,155,158].

Using the microcontact printing method, Anikeeva *et al.* showed a series of QD-LEDs with emission tunable across the entire visible spectrum by varying the composition of QDs sandwiched between two organic CTLs (Fig. 2-6c) [58]. A maximum EQE of 2.7 % was achieved for orange emission. The spectral purity and tunability of the QD-LEDs reported in this work clearly demonstrates the potential that QD-LEDs hold for EL displays. It has also been demonstrated that white-emitting QD-LEDs
Chapter 2. Quantum-Dots as Luminophores

Figure 2-5: **QD Excitation mechanisms.** There are four routes by which to generate excitons in QDs that have been used in QD-LEDs. 

- **a,** Optical excitation: an exciton is formed in a QD by absorbing a high-energy photon.
- **b,** Charge injection: an exciton is formed by injection of an electron and a hole from neighboring charge transport layers.
- **c,** Energy transfer: an exciton is transferred to a QD via FRET from a nearby donor molecule.
- **d,** Ionisation: a large electric field ionises an electron from one QD to another, thereby generating a hole. When these ionisation events occur throughout a QD film, generated electrons and holes can meet on the same QD, forming excitons.
- **e,** Energy band diagram of a typical type-II QD-LED that outlines the two suspected QD excitation mechanisms: charge injection and energy transfer.

These excitons can be fabricated by simply mixing different compositions [134] or sizes [159] of QDs. A CRI of 86 was achieved by mixing red, green, and blue QDs. As shown in Fig. 2-2a, even higher CRIs should be achievable through the mixing of a greater variety of colours of QDs, suggesting the realisability of white QD-LEDs as SSL sources. Furthermore, compatibility of type-II QD-LEDs with flexible substrates is exemplified by the flexible white-light-emitting QD-LED shown in Fig. 2-7c.

Studies in our group have indicated that, at least in certain type-II QD-LED geometries, FRET is the dominant QD excitation mechanism [133]. Yet, for example, the achievement of EQEs >2% in QD monolayer-based devices comprising organic donor materials with very low $\eta_{PL}$ [135] challenges the universality of the FRET model.

Combining an OLED architecture with a monolayer of QDs was, nevertheless, a significant step forward in demonstrating efficient QD-LEDs. These devices boast all of the advantages of OLEDs, with the added benefits of enhanced spectral purity.
and tunability, as illustrated by the tunable EL shown in Fig. 2-6b, c. However, the use of organic layers introduces device instabilities upon air exposure [160,161]. As with OLEDs, commercialised QD-LEDs would then require protective encapsulation, which adds to manufacturing costs and hinders certain applications, such as flexible technologies. Furthermore, the relatively insulating nature of organic semiconductors can limit the current densities achievable in QD-LEDs prior to device failure, therefore limiting their brightness.

**Type-III: QD-LEDs with inorganic charge transport layers**

Replacing the organic CTLs of type-II QD-LEDs with inorganic CTLs could lead to greater device stability in air [160,161], and could enable the passage of higher current densities and therefore brighter emission.

One such all-inorganic QD-LED (apart from the organic ligands) was made by Mueller et al. by sandwiching a monolayer of QDs between epitaxially grown n- and p-type GaN (ref. [49]). QD EL was observed, though at very limited efficiencies (EQE <0.01 %). The epitaxial growth of GaN, however, diminishes the advantage of using colloidal QDs to inexpensively fabricate large area devices. This necessitates alternative approaches to developing QD-LEDs with inorganic CTLs.

One such alternative is to use sputtered metal oxides as CTLs. Like organic materials, metal oxide and chalcogenide thin films can be deposited at room temperature by sputtering. The broad variety of metal oxide and chalcogenide compositions enables fine-tuning of their energy bands, as needed for the optimal operation of QD-LEDs. In addition, metal oxides can be more conductive than their organic counterparts, with the conductivity of metal oxides tunable by controlling oxygen partial pressure during thin film growth. Caruge et al. applied this technique in QD-LEDs comprising zinc tin oxide and NiO as n- and p-type CTLs, respectively [137]. As expected, these devices were able to pass higher current densities (up to 4 A cm$^{-2}$) but the EQE was less than 0.1 %.

This inefficiency was attributed to the damage of QDs during sputtering of the overlying oxide layer, to carrier imbalance (due to a large hole injection barrier be-
between the p-type metal oxide and the QDs), and to quenching of QD PL by the surrounding conductive metal oxide [162]. To our knowledge, there has not been a report of a type-III QD-LED with efficiencies comparable to those of type-II devices. Aside from these DC-driven QD-LEDs, another sort of all-inorganic QD-LED that operates by an altogether different excitation mechanism has emerged over the past few years. These are capacitive structures consisting of two contacts sandwiching a film of dielectric material, with a layer of QDs at its centre [162, 163]. High AC voltages drive these devices, resulting in operation by field-assisted ionisation of QDs to generate free carriers (Fig. 2-5d) [164]. This architecture eliminates the need for CTLs and energy band alignment between different semiconductors.

**Type-IV: QD-LEDs with hybrid organic-inorganic charge transport layers**

The hybrid structure of type-IV QD-LEDs offers a compromise between type-II and type-III QD-LEDs, often comprising an inorganic metal oxide electron transport layer (notably solution processed ZnO [60, 61]) and an organic small molecule hole transport layer [50, 60, 61, 139, 142]. A typical device structure and its corresponding EL are shown in Fig. 2-6a, b. Significant efficiency gains have resulted, with recent visible-emitting QD-LEDs reaching EQEs as high as 20 % [140, 142] (Fig. 2-4a and 2-6a); approaching those of commercially mature phosphorescent OLEDs [118] as well as the outcoupling-limited ceiling of \( \sim 20-25 \% \) [165]. The brightness of type-IV QD-LEDs has also reached record levels of 218,800 cd m\(^{-2}\) (ref. [60]).

Type-IV devices can, if desired, be solution processed using colloidal metal oxide nanoparticles as the electron transport layer [60, 61]. In particular, Qian et al. have demonstrated red, green, and blue solution-processed (excluding electrodes) QD-LEDs. The EQEs of these devices were 1.7 %, 1.8 %, and 0.22 %, with maximum brightness values of 31,000 cd m\(^{-2}\), 68,000 cd m\(^{-2}\), and 4,200 cd m\(^{-2}\) for red, green, and blue devices, respectively. These brightness values are within range of the highest reported [61].

High-resolution microcontact printing of QD films (>1000 pixels per inch, 25 \( \mu \)m
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50

Figure 2-6: Modern QD-LED architecture and operation. a, Inverted hybrid organic-QD-inorganic type-IV QD-LED structure that has risen to prominence owing to its record efficiencies and brightness. It typically comprises a few monolayers of QDs sandwiched between an inorganic metal oxide electron transport layer and an organic hole transport layer. Photographs of tunable electroluminescence (EL) colours from: b, type-IV [2]; and c, type-II QD-LEDs (together with respective EL spectra) [58].

The energy transfer scheme that is suspected to dominate QD excitation in type-II QD-LEDs requires migration of one carrier type through the close-packed QDs of a monolayer film, so as to form excitons in an adjacent donor material (Figure 2-5e) [133]. Since type-III and type-IV QD-LEDs, in contrast with type-II QD-LEDs, employ QD films thicker than one monolayer (up to ~50 nm), the working mechanism of type-IV QD-LEDs is more compatible with a charge injection model.

2.2.2 Beyond Cd-based QDs: infrared and non-toxic QD-LEDs

The paucity of high-$\eta_{PL}$ NIR molecular and polymeric dyes provides a compelling impetus to extend the EL of QD-LEDs from the visible into the NIR range (780-
As EQEs of OLED and polymer LEDs emitting at $\lambda > 1 \mu m$ remain less than 0.3 % [166], NIR-emitting QD-LEDs boast unique potential. For example, one can envision solution-processable (potentially Si-compatible) sources of EL in the 1.3-1.55 $\mu m$ telecommunications band, which can be deposited on any substrate and at lower cost than existing (usually epitaxially grown) IR-emitters, finding application in optical telecommunications and computing [63, 77, 167–170]. Utilising biological transparency windows between 800 nm and 1700 nm (ref. [171]), one can also imagine deep tissue biomedical imaging and optical diagnostic [77, 171] applications, as well as on-chip bio(sensing) and spectroscopy usages [55, 77, 172] (for example, low cost NIR QD-LEDs in microfluidic point-of-care devices [173]). Night-vision-readable displays [174], night-time surveillance, and other security applications also present themselves.

Extension of the wet chemical methods previously discussed has readily enabled the synthesis of a variety of efficient NIR-emitting colloidal QDs, which in the telecommunications band include PbE (E=S, Se, Te), InAs, and HgTe, as well as core-shell QDs such as PbE-CdS and InAs-ZnSe. In many cases, high $\eta_{PL}$ have been achieved ($\geq 50$ %). There are a number of in-depth reviews [74, 76, 77, 177] for the interested reader.

Most NIR QD-LEDs have been based largely on type-I architectures and core-only NIR (lead chalcogenide) QDs [64, 151, 168, 169, 178, 179], with EQEs of up to $\sim 2$ % reported [64] (Fig. 2b). At QD Vision, Inc., NIR QD-LEDs with active areas of up to 4 cm$^2$ (Fig. 2b, inset) and radiances of up to 18.3 W sr$^{-1}$ m$^{-2}$ have been achieved; comparable to commercial IR LEDs and sufficient to serve as large-area IR illuminators (Fig. 2-7d). In this thesis, we describe the realisation of devices with efficiencies exceeding 4 % [15] - more than double the previous record - by transitioning to a type-IV device structure and exploiting the enhanced passivation of core-shell NIR QDs. Just as with visible-emitting QD-LEDs, it has been argued that electrical excitation of QDs in these NIR devices occurs either by FRET [63, 170] or by direct charge injection [168, 169, 180–182]; a balance between the two is likely in most cases.

Recently, Cheng et al. described the first Si QD-based LEDs, with very high EQEs of 0.6 % (type-I) [180] and 8.6 % (type-II) [183], though with rather blue NIR
Figure 2-7: **State-of-the-art QD-LEDs.** a, EQE versus applied voltage for very high performance (peak EQE of 18 %) red-emitting QD-LEDs (photograph in inset) [175]. b, The first demonstration of red-green-blue electroluminescence from (type-II) QD-LED pixels, patterned using microcontact printing [92]. c, Flexible white-emitting type-II QD-LED [176]. d, Large-area infrared illumination by an infrared-emitting QD-LED, as seen through an infrared camera [2].
EL of \( \sim 850 \) nm. Although emission at wavelengths beyond 1 \( \mu \)m may be difficult to achieve with Si QDs (efficient blue and green emitters have also not yet been demonstrated), this new breed of heavy-metal-free QD-LEDs nevertheless addresses growing concerns regarding the risks that cations such as cadmium, lead, and mercury pose to our health and to the environment [1]. The European Union’s Restriction of Hazardous Substances Directive, for example, severely limits the use of these materials in consumer electronics. Therefore, the likelihood of commercial success of QD-LEDs will be greatly increased if these devices can be fabricated using heavy-metal-free QDs.

As an aside though, we ask, how much cadmium (Cd) is actually in a QD-LED? We can estimate this by assuming that a typical QD-LED might comprise a 5 cm \( \times \) 5 cm film, 25 nm thick, of hexagonally close-packed CdSe-CdS core-shell QDs separated by \( \sim 0.5 \) nm due to their surrounding organic ligands. Then, the effective density of CdSe-CdS QDs with a diameter of 4 nm and a shell thickness of 2 nm is 3.5 g cm\(^{-3}\), which translates to a mass of 0.16 mg of CdSe-ZnS and therefore 63 \( \mu \)g of Cd. This is comparable to one’s daily Cd intake: the age-weighted mean Cd intake for males in the United States is 0.35 \( \mu \)g kg\(^{-1}\) day\(^{-1}\), or 24.5 \( \mu \)g day\(^{-1}\) for a 70 kg male [184].

All the same, the commercial demand for novel down-converters in single-chip white LEDs has specifically led to QDs being identified as likely candidate ‘phosphors’, yet concerns over Cd compliance issues threaten to inhibit their use [40]. There are therefore strong incentives to develop Cd-free QDs competitive with their traditional counterparts.
Chapter 3

Colloidal Quantum-Dots

3.1 Colloidal versus epitaxial QDs

Quantum-dots (QDs) may be categorised by their synthetic route as either ‘colloidal’ or ‘epitaxial’ (or ‘self-assembled’). Whereas the latter derive from relatively high-energy-input ‘dry’ methods of epitaxial growth from the vapour phase [185], colloidal QDs are synthesised by ‘wet’ chemical approaches [74] and are the focus of this thesis. The precise size and shape control, as well as the high monodispersity, spectral purity and $\eta_{PL}$ afforded by the chemical synthesis of QDs, are unmatched by epitaxial techniques. Colloidal QDs are freestanding and therefore amenable to a plethora of chemical post-processing and thin-film assembly steps, in contrast to epitaxial QDs, which are substrate-bound [99]. Additionally, the relatively inexpensive, facile, and scalable solution-based conditions necessary for the synthesis of nearly defect-free colloidal QDs have an impurity tolerance far exceeding that of the ultra-high vacuum environments required for epitaxial growth. Moreover, only weak quantum-confinement effects are observed in epitaxial QDs [186] owing to their relatively large lateral dimensions (typically >10 nm) and difficulties in size control. This is in stark contrast to the size-tunable emission of colloidal QDs, which are therefore favourable as luminophores in LEDs [187].
3.2 Colloidal QD synthesis

The benchmark preparation of colloidal quantum-dots (QDs, throughout), yielding high quality and monodisperse (size variation $< 4\%$ r.m.s.) nanoparticles, involves pyrolysis of organometallic precursors (such as dimethyl cadmium and trioctylphosphine selenium for CdSe and, in this thesis, lead (II) oleate and hexamethyldisilathiane for PbS) injected into a hot organic coordinating solvent (at temperatures of 120 to 360 °C) [65,74,188]. The experimental procedure is shown schematically in Fig. 3-1. Thermally activated nucleation and growth of small crystallites from the precursors ensues until arrested by cooling. Fine control of QD size (for example, from 1.5 nm to 12 nm for CdSe QDs [65]) and size dispersion can thus be achieved through control of reaction time and temperature, as well as precursor and surfactant concentrations. QD size is monitored by measuring absorption spectra of aliquots extracted from the growth solution during synthesis. Overcoating CdSe core-only QDs with ZnS shells has been shown to enhance QD stability and brightness [71,72]. This is usually achieved by injecting organometallic precursors to the shell material into a flask containing the cores. The resulting QDs are dressed with organic ligands, which confer solubility in a diversity of common non-polar solvents. Commercial red-emitting QDs used in this thesis were obtained from QD Vision, Inc.

Post-synthesis size-selective precipitation can further increase monodispersity in
colloidal QD solutions. Typically, prior to use in devices, QDs are precipitated and redissolved at least twice in order to eliminate excess ligands, then recast in a suitable solvent for solution-based deposition, such as spin-casting. For QDs with oleic acid capping ligands, as the case in this thesis, we precipitate our QD starting solution using butanol and then methanol (roughly 1 part butanol and 8 parts methanol to 1 part QD solution, by volume), redisperse is hexane, precipitate a second time, and finally redisperse the QDs in chloroform. Each round of precipitation is accelerated by centrifuging the solution at 3,500 rpm for 5 minutes.

As shall be the focus of Chapter 6, NIR-emitting QDs such PbSe and PbS are relatively unstable and prone to oxidation and PL quenching, and accordingly, display relatively low $\eta_{\text{PL}}$. Pietryga et al. have demonstrated a partial cation exchange method to controllably overcoat lead chalcogenide cores to form more stable core-shell QDs such as PbSe-CdSe, PbSe-CdSe-ZnS, and PbS-CdS [75]. As compared to the conventional shell growth approach mentioned above, cation exchange relies on the lability of Pb ions, which are susceptible to exchange with Cd ions when immersed in a highly concentrated solution of cadmium oleate. Gyuweon Hwang in Moungi Bawendi’s group used this technique to synthesise stable PbS-CdS QDs with $\eta_{\text{PL}}$ in solution of up to 53 % and emission peaks from 1.1 to 1.4 $\mu$m. Synthesis conditions were tailored to allow slower shell growth than normal by lowering the reaction temperature to 80-100 °C and reducing the Cd-precursor concentration [189]. Fig. 3-2a shows PL spectra at various times throughout the cation exchange reaction of two batches of starting PbS QDs. The gradual blue-shifting of PL peaks during the reaction reflects the in-growth of the CdS shell during Pb-to-Cd cation exchange, effectively shrinking the confining PbS core. Fig. 3-2b plots $\eta_{\text{PL}}$ as a function of shell thickness for the second batch. The 72 % rise in $\eta_{\text{PL}}$ upon addition of a shell attests to the passivation of surface traps on PbS cores. However, this initial increase (corresponding to a shell thickness of $\sim$2.5 monolayers) is followed by a gradual decline in $\eta_{\text{PL}}$ as shell thickness increases further, attributable to a rise in defect density resulting from lattice mismatch-induced stress [189].

Scaling up these synthesis techniques so as to reduce the cost of QDs is a pre-
requisite for the commercialisation of QD technologies, and increases in yield, from milligrams to kilograms per week, have been reported [121, 190].

3.3 Optical properties of QDs

The size-tunable colour of QD PL and absorption spectra is arguably their most unique and important property, and is governed by the quantum size effect. See, for example, ref. [191–193] for in-depth discussions. The intrinsic material constituting the QD confers a bulk crystal band-gap, but in a QD, electrons and holes are subject to quantum confinement effects that quantise these bulk energy levels, resulting in atomic absorption- and emission-like spectra [192]. When the radius of a QD is less than the material’s Bohr radius \( a_B = \hbar^2 \kappa/\mu e^2 \), where \( \kappa \) is the dielectric constant of the semiconductor and \( \mu \) is the effective mass of the electron-hole pair) the energy levels of a QD can be analytically approximated by modeling the QD as a particle-in-a-sphere with infinite potential walls. This applies, for example, to PbS QDs, whose exciton Bohr radius is approximately 18 nm [9], versus typical QD radii diameters of 2-5 nm. This gives a confinement energy of,

\[
E_{e,h}^{e,h} = \frac{\hbar^2 \phi_{l,n}^2}{2m_{e,h}a^2}
\]

where \( \phi_{l,n} \) is the \( n \)th root of the spherical Bessel function of order \( l \), \( j_l(\phi_{l,n}) = 0 \), and \( m_{e,h} \) is the effective mass of the electron or hole. This can be viewed as the kinetic energy of a free particle, but with quantised wave vectors, \( k_{l,n} \). Since QDs are typically larger than the lattice constant of their constituent material, one can apply the effective mass approximation, modeling the conduction and valence bands as parabolic and describing particle wavefunctions as linear combinations of Bloch functions. It is then possible to derive the energy of the electron-hole pair states,

\[
E = E_g + E^h(a) + E^e(a) - 1.8 \frac{e^2}{\kappa a}
\]

The first term on the right-hand side of the equation is the fundamental band-gap of
Figure 3-2: Photoluminescence spectra and quantum yield during PbS-CdS QD cation exchange reaction. a, PL spectra of aliquots collected at representative times with increasing CdS shell thickness (right to left) throughout two separate cation exchange reactions. First reaction batch (dashed) shell thicknesses and reaction times: 0 nm (i.e. PbS cores); 0.57 nm (5 min); 0.75 nm (30 min); and 0.89 nm (2 h). Second reaction batch (solid) shell thicknesses and reaction times: 0 nm (i.e. PbS cores); 0.18 nm (5 min, 80 °C); 0.21 nm (5 min, 100 °C); 0.69 nm (2 h); 0.8 nm; and 0.9 nm. The red-side of the red-most spectrum is clipped because of the spectral responsivity limit of the InGaAs array detector used to collect the data. b, PL quantum yield as a function of CdS shell thickness for the second batch (which we make use of in Chapter 6) of QDs in chloroform solution.
Chapter 3. Colloidal Quantum-Dots

The quantum confinement effect derived from the simple parabolic band approximation is elegantly manifested in spectral absorption measurements of QDs, wherein the absorption band edges move to higher energies as QDs are reduced in size (Fig. 3-3). It also accounts for the correlation between QD size and PL energy. However, given our focus in this thesis on QD PL, it is worth noting that a more detailed multi-band effective mass approximation is in fact required to explain some of the intricacies of QD PL spectra. These include their red Stokes shift with respect to their first absorption peak and their unusually long radiative lifetimes (roughly an order of magnitude longer than in the bulk [194]). These are explained by the fact that, as mentioned in Section 2.1.2, the lowest energy exciton state of a QD is in fact an optically inactive "Dark Exciton" state, which sits at lower energy than an optically active "Bright Exciton" state [194]. Their splitting energy is on the order of $k_B T$ and is therefore overcome at room temperature, effectively rendering QDs ‘phosphors’ at this temperature.
Figure 3-3: Absorption spectra of PbSe QDs as a function of nanocrystal diameter. Reproduced from ref. [9]
Chapter 4

Origin of efficiency roll-off in QD-LEDs

4.1 Role of QD luminescence in QD-LED efficiency

Much of the focus of QD-LED research over the past two decades has been on understanding and improving the efficiency of free carrier recombination in these devices, \( \eta_r \). This is reflected in the engineering of the multiple generations of QD-LED architectures described in Chapter 2, and is of course motivated by the direct dependence of EQE on \( \eta_r \) by way of Eq. 2.1. This expression also shows that EQE is directly proportional to the photoluminescence (PL) quantum yield (\( \eta_{PL} \)) of our QDs, yet this factor has received less attention. In particular, while there have been substantial efforts to elucidate the mechanisms of PL quenching in experimentally isolated QDs (for example, single QDs or QD ensembles) and QDs under very specific experimental conditions (for example, in electrochemical cells), much less scrutiny has been paid to QD PL quenching in operational QD-LEDs; accounting for their unique \textit{in situ} environment, which includes neighbouring conductive layers, large electric fields, charge current flow, and the associated device heating. We therefore begin by looking to the earlier literature of isolated QDs to identify the different processes that may be suspected to dictate the probability of QD PL in QD-LEDs. In this chapter and the next, we limit our scope to the bias dependence of QD-LED efficiency and investigate
the contribution of QD PL quenching on this behaviour. Zero-bias (occurring even at zero bias) contributions to PL quenching will be the focus of Chapter 6.

### 4.2 Overview

Even casual inspection of the typical EQE-versus-current density (or voltage) plot of a QD-LED reveals a pronounced decline in EQE (Fig. 4-1c): from its maximum value at relatively low currents (∼0.01 to 0.1 A cm$^{-2}$ at ∼2 V) to roughly half this value as current increases to ∼1 A cm$^{-2}$ at ∼8 V. This so-called efficiency ‘roll-off’ or ‘droop’ in fact plagues all LED technologies to date, yet until now, it has not been studied in QD-LEDs. Understanding its cause is essential to developing high-brightness, high-efficiency devices. Does a bias-driven reduction in QD $\eta_{PL}$ account for this efficiency roll-off in QD-LEDs? If so, what mechanism(s) are responsible for this quenching? These are the questions we set out to address in this chapter and the next.

### 4.3 Introduction

Nitride-based LEDs find wide and growing commercial application, and OLEDs and QD-LEDs have the potential to capitalise on the vast solid state lighting (SSL) and display markets. For all lighting technologies, however, efficiency roll-off presents a considerable challenge. Indeed, roll-off is among the most significant and enduring hurdles facing GaN-based LEDs and SSL, severely limiting the efficiencies achievable with high-brightness devices. Today’s commercial blue GaInN LEDs, for example, often suffer more than a 40% loss in EQE at desired high current densities (∼35 A cm$^{-2}$) compared to their peak EQEs at <10 A cm$^{-2}$ [195] (Fig. 4-1a). Roll-off raises SSL costs by requiring the use of multiple LEDs in a single lamp to keep efficiencies high. It adds constraints on optics and design, and it increases thermal loads [196]. All major LED companies reportedly have active ongoing research into roll-off effects [197]. According to the U.S. DOE’s latest assessment, addressing roll-off is among the highest priorities for LED-based lighting R&D [31]. Roll-off has also
been the topic of substantial investigation in efficient phosphor-based OLEDs over the past two decades. Like QD-LEDs, OLED efficiencies fall rapidly beyond \( \sim 0.01 \) to 0.1 A cm\(^{-2} \) (Fig. 4-1b). In a comprehensive review of white OLEDs, Reineke et al. recently proposed that the largest improvement factor needed for enhancing the efficiencies of this technology may come from reducing roll-off [198]. Importantly, the exciton annihilation processes that have been found to be responsible for roll-off in OLEDs (outlined briefly below) may also be a source of material degradation, because the associated high excitation energies may break the chemical bonds conferring functionality to some organic materials [199].

Despite all of this, confirming the origins of efficiency roll-off in GaN-based LEDs continues to be an active area of experiment and theory. Various mechanisms have been proposed, most prominently thermionic electron leakage from the light-emitting active region and Auger recombination (described in the next chapter) within this region, but also carrier delocalisation and poor hole injection [31,195,202]. Meanwhile, efficiency roll-off in OLEDs has been attributed to mechanisms including triplet-triplet annihilation, triplet-polaron quenching, and electric field-induced exciton dissociation [198,203,204]. Among these three, the first two (especially the former) are considered to play larger roles [201].

Surprisingly, efficiency roll-off and its origins have never previously been investigated closely in QD-LEDs. To do so, we begin by reexamining the expression for EQE in Eq. 2.1. Based on our physical understanding of each term in the equation, as well as inspection of the commonly cited mechanisms in the GaN and OLED literature, discussed above, we expect only two of the terms, \( \eta_{PL} \) and \( \eta_r \), to have a strong bias-dependence (we neglect outcoupling efficiency, which may strictly also have some bias dependence, for example due to dipole reorientation under applied electric fields). That is, \( \text{EQE} (V) = \eta_r (V) \chi \eta_{PL} (V) \eta_{oc} \propto \eta_r \eta_{PL} \). Efficiency roll-off can therefore be approximated as attributable to the bias dependence of \( \eta_{PL} \), of \( \eta_r \), or of some combination of the two. Falling \( \eta_{PL} \) would signify changes to the QD emitter itself, and the numerous potential mechanisms responsible for bias-driven QD PL quenching will be discussed in Chapter 5. In contrast, a reduction in \( \eta_r \) would re-
Figure 4-1: **Efficiency roll-off in different LED technologies.** External quantum efficiency (EQE) is seen to fall dramatically at high current densities in: a, GaN-based LEDs [200]; b, OLEDs [201]; and c, QD-LEDs (a typical red-emitting device fabricated in our laboratory and investigated in this thesis). Note that a exhibits roll-off due to both current density and thermal stress, a distinction discussed briefly in Chapter 5.
result from one or more forms of carrier leakage, such as those for GaN-based LEDs above, whereby electrons and/or holes are not confined to the QD region and leak through their respective blocking layers in a QD-LED. Unsurprisingly, distinguishing between $\eta_{PL}$ and $\eta_r$ as the origin of EQE bias-dependence in GaN-based LEDs and OLEDs has been key to uncovering the mechanisms discussed above. For example, in GaInN/GaN multi-quantum well (MQW) LEDs, Kim et al. measured EQE and PL as a function of excitation power and found no correlation, concluding that roll-off must be due to recombination outside of the MQWs [205]. They deduced that electron leakage was instead the dominant cause of roll-off. In contrast, Reineke et al. [204] and Kalinowski et al. [206] both observed good correlations between EL and PL in OLEDs, leading to the advancement of models for roll-off based on PL quenching via triplet-triplet annihilation. In this chapter, we take a similar approach to quantifying the contribution of PL quenching (versus carrier leakage) to roll-off in QD-LEDs.

4.4 Methods

The device structure we investigate is a type-IV QD-LED (see Section 2.2) with organic-inorganic hybrid charge transport layers that has recently attracted attention owing to its record high EQEs and brightness [2]. This red-emitting QD-LED is also more conveniently compatible with the visible-wavelength spectroscopic tools at our disposal, which we make use of in this chapter and the next. The device was fabricated on a glass substrate coated with indium tin oxide (ITO) and has the structure: ITO (150 nm) / zinc oxide (ZnO) (50 nm) / QDs (50 nm) / 4, 4-bis(carbazole-9-yl) biphenyl (CBP) (100 nm) / molybdenum oxide (MoO$_3$) (10 nm) / aluminium (Al) (100 nm). ZnO was radio-frequency sputtered, QDs were spin-cast out of chloroform, and CBP, MoO$_3$, and Al were thermally evaporated. We used CdSe-ZnCdS core-shell QDs with a peak PL wavelength of 610 nm, provided by QD Vision, Inc. The energy band diagram of the device is shown in the inset of Fig. 4-4 and is based on literature values [58, 93, 207, 208].

Based on our discussion in the previous section, the decrease in EQE at high
biases may be the result of either charge carriers leaking out of the QD layer or a reduction in QD luminescence efficiency. To identify which of these two mechanisms dominates, we perform a simultaneous EL-PL experiment and monitor the relative PL efficiency of the QDs as the device bias is swept. The experimental setup is shown in Fig. 4-2. To isolate the PL contribution from total luminescence, we modulate the PL excitation source ($\lambda = 530$ nm LED) at 1 kHz and send the combined EL-PL signal (collected using a Si photodiode and a current preamplifier) to a lock-in amplifier. The PL intensity is intentionally kept low (PL/EL <0.001 % at 13 V) to avoid significantly increasing the charge density within the QD layer. An excitation wavelength of 530 nm ensures that the QD layer is excited without exciting the surrounding wider band gap charge transport layers, as absorption spectra of the QD-LEDs constituent materials confirm (Fig. 4-3).

4.5 Results and discussion

Current density and normalised EQE measured for a typical device as described above are shown in Fig. 4-4a. The EQE peaks at 2 % for 4 V applied bias and rolls off by 50 % by 8 V, quite typical of a modern QD-LED. The results of the simultaneous EL-PL experiment are shown in Fig. 4-4b, with EQE and QD PL intensity normalised at 4 V applied bias. Below 4 V, the PL intensity remains constant (voltage independent). In contrast, above 4 V, the PL intensity decreases monotonically with increasing bias, tracking the decrease in EQE of the QD-LED. The correspondence between the decreasing PL intensities and EQE with applied bias identifies the change in the QD $\eta_{PL}$ to be sufficient to explain the QD-LED roll-off behavior. Importantly, this is the first time it has been demonstrated that efficiency roll-off in QD-LEDs can be ascribed to the QD emitters themselves, allowing us to discount extrinsic charge leakage effects as the cause, and to focus our investigation specifically on bias-driven QD PL quenching mechanisms.

To verify that the optically generated excitons used to probe our QD-LED do not interfere with the device’s intrinsic exciton dynamics, we conduct the same PL
Figure 4-2: **Simultaneous EL-PL measurement setup.** Relative EL intensity is collected by a photodetector mounted in front of the biased QD-LED. Simultaneously, QD PL is induced by excitation of the QD-LED with 530 nm light from an LED pulsed at 1 kHz passed through a microscope objective. The resulting combined EL and PL signal is collected by another photodetector and fed into a lock-in amplifier that separates the EL (d.c.) and PL (a.c.) components, enabling relative PL intensity to be isolated.
Chapter 4. Origin of efficiency roll-off in QD-LEDs

Figure 4-3: **Absorption spectra of QD-LED components.** Absorption spectra of CdSe-ZnCdS QDs (red), CBP (dark blue), and ZnO (light blue) confirm that at the excitation wavelength of 530 nm, only the QDs absorb significantly.

measurements at multiple excitation intensities, from 15.6 $\mu$W to 44.5 $\mu$W (Fig. 4-5). Normalising each PL signal by its excitation intensity, we confirm that the PL quenching trend is independent of this variable.

In the context of the discussion in Section 4.3, unlike some GaN-based LEDs but similarly to some OLEDs, we therefore conclude that we can neglect charge leakage effects in accounting for efficiency roll-off in QD-LEDs. We note that another possibility - that roll-off could be ascribed to permanent or semi-permanent thermal degradation of our device - can be neglected given the reproducibility of the above experiment when repeated on a one second timescale. In the next chapter, we probe the mechanistic origins of the bias-driven QD PL quenching deduced here.
Chapter 4. Origin of efficiency roll-off in QD-LEDs

Figure 4-4: EQE roll-off in a QD-LED and correlation with QD PL. a, Current density-voltage and EQE-voltage characteristics of the QD-LED under investigation. Inset: Energy band diagram of the device, with indicated energy values referenced to the vacuum level. b, Simultaneous EQE and QD PL intensity of the QD-LED (normalised at 4 V, when the peak EQE is 2 %) as a function of voltage. Roll-off of the EQE above 4 V is seen to reflect reduced QD PL efficiency at high biases.
Figure 4-5: Bias-induced QD PL quenching, normalised by optical excitation intensity. Relative QD PL intensities under 530 nm excitation at multiple intensities confirms the excitation probe does not disturb the device’s intrinsic exciton dynamics: (black) 15.6 $\mu$W; (dark grey) 33.4 $\mu$W; (light grey) 44.5 $\mu$W.
Chapter 5

Bias-driven QD luminescence quenching in QD-LEDs

Our measurements of visible-emitting QD-LEDs in Chapter 4 have identified bias-driven QD photoluminescence (PL) quenching to be responsible for the roll-off in efficiency of our QD-LEDs at high current densities. In this chapter, we conduct in situ measurements of QD-LED electroluminescence (EL) and PL spectra, and by comparing the two, reveal that strong electric fields are responsible for the reduced QD PL quantum yield ($\eta_{\text{PL}}$). The quantum confined Stark effect is found to consistently explain the observed phenomena.

5.1 Bias-dependent QD quenching mechanisms

Potential mechanisms responsible for bias-dependent QD PL quenching are encapsulated by Eq. 5.1, which expresses QD $\eta_{\text{PL}}$ (and therefore external quantum efficiency, EQE) in terms of radiative ($k_r$) and non-radiative ($k_{nr}$) recombination rates:

$$\text{EQE}(V) \propto \eta_{\text{PL}}(V) = \frac{k_r(V)}{k_r(V) + k_{nr}(V)}$$  \hspace{1cm} (5.1)

We have explicitly reflected the potential bias-dependence (V) of each term. First consider $k_{nr}$. As we shall see in Chapter 6, one contribution to the non-radiative
recombination rate comes from surface traps and the local environment (Fig. 5-2, left). But trap-assisted quenching may also be exacerbated under bias as the device heats up, for example due to thermally-activated charge transfer from a QD core to a defect state. Heat-induced PL quenching can be seen by monitoring the PL spectrum of a film of our QDs on a temperature-controlled substrate. As plotted in Fig. 5-1, a temperature rise of just a few tens of degrees Celsius is enough to cause QD $\eta_{PL}$ to begin to fall. Indeed, the impact of thermal efficiency droop on the EQE of GaN-based LEDs can be as detrimental as that of current density-related efficiency droop [200] (Fig. 4-1a).

Studies of single QDs and QD ensembles also demonstrate another bias-dependent contribution to $k_{nr}$; namely, free charge carriers (Fig. 5-2, middle). For example, with current densities in QD-LEDs routinely exceeding the order of 1 A cm$^{-2}$, imbalanced charge injection can lead to charge accumulation on a QD, increasing Auger non-radiative recombination, whereby an exciton dissipates its recombination energy as
kinetic energy to a third charge rather than as a photon \([6,12,67,87,136,138,209]\). Because the rate of Auger recombination is orders of magnitude faster than the rate of radiative recombination (few to hundreds of picoseconds, versus nanoseconds), PL is completely quenched in charged QDs. Over the years, numerous specific mechanisms by which Auger recombination proceeds in QDs have been shown. These include coupling between an exciton and a carrier that is in a QD \([12,209]\), on its surface \([12]\), or in a deep trap state \([210]\), coupling between multiple charge-neutral excitons, such as biexcitons and triexcitons \([209]\), and coupling between a carrier and an exciton with one of its charges in a deep trap state \([211]\).

Application of bias in a QD-LED also imposes an electric field across the QD film on the order of 1 MV cm\(^{-1}\), providing the third mechanism for PL quenching shown in Fig. 5-2. The electric field spatially polarises the electron and hole wavefunctions of the exciton, \(|\psi_e\rangle\) and \(|\psi_h\rangle\), respectively, to opposite hemispheres of the QD, reducing their overlap integral. As a result, \(k_r\), which is proportional to the optical matrix element of the electron and hole states (\(k_r \propto |\langle \psi_e | p | \psi_h \rangle|^2\), where \(p\) is the momentum operator), is reduced by the field \([11]\). From Eq. 5.1, a decrease in \(k_r\) can therefore reduce \(\eta_{PL}\) and with it, EQE. These polarisation effects are also seen, for example, in InGaN LEDs, where piezoelectric and spontaneous polarisation leads to large electrostatic fields (>1 MV cm\(^{-1}\)) in the quantum well active regions, spatially separating electron and hole wavefunctions and reducing \(k_r\). Interestingly though, this is not thought to be the cause of efficiency roll-off, but rather is suspected as (partly) responsible for the ‘green-yellow gap’ in LED efficiencies \([39,41]\). Additionally in QDs, the shift of the electron and hole wave functions from the QD’s center breaks its local neutrality and increases the exciton’s interaction with polar optical phonons. This interaction leads to significant phonon broadening of the PL line \([213]\). A closely related characteristic of the electric field’s effect is the quantum confined Stark Effect (QCSE) \([214]\), which is a shift in the bound state energies of the QD leading to a change in the effective band-gap of the material. Described in terms of second order perturbation theory, the shift in effective band-gap of a QD in the presence of an electric field, \(E\), is given by \([214]\),
Figure 5-2: **Zero-bias and bias-driven QD PL quenching mechanisms.** Schematic of an archetypal QD-LED under bias, with an electric field across the QD film and free charge carriers present. Even at zero bias, excitons in QDs are exposed to PL quenching pathways such as (box, leftmost) relaxation via surface defect states and (box, second from left) energy or charge transfer to/from neighbouring trap states (represented by the blue arrow), for example in conductive charge transport layer materials. As bias increases, PL quenching by free charge carriers also becomes possible via Auger recombination (box, second from right). In these three cases, QD $\eta_{\text{PL}}$ is reduced due to an increase in the non-radiate recombination rate, $k_{\text{nr}}$. However, according to Eq. 5.1, $\eta_{\text{PL}}$ can also be reduced due to a decrease in $k_r$, and this can occur under exposure to an electric field that polarises the exciton (box, rightmost). Alternative processes due to an electric field could include exciton dissociation, phonon coupling, or coupling with surface state defects. In these cases quenching would again occur, but due instead to an increase in $k_{\text{nr}}$. Adapted from ref. [212]
\[ \Delta E_n = \langle \psi_n | \mathbf{e}_r \cdot \mathbf{E} | \psi_n \rangle + \sum_{k \neq n} \frac{|\langle \psi_k | \mathbf{e}_r \cdot \mathbf{E} | \psi_n \rangle|^2}{E_n - E_k} \] (5.2)

or, in simplified form,

\[ \Delta E_n = \mu E + \frac{1}{2} \alpha E^2 \] (5.3)

where \( \mu \) is the projection of the dipole moment of the QD in the direction of the electric field, and \( \alpha \) is the QD’s polarisability in the same direction. In QD ensembles, \( \mu \) averages to zero and one observes a quadratic red-shift in QD PL with increasing electric field [214].

However, a reduction in QD \( \eta_{PL} \) by electric field is not necessarily dominated by the reduction in \( k_r \), described above [215]. An electric field may also reduce \( \eta_{PL} \) by enhancing phonon coupling [213], exciton coupling to surface trap states [12,216], or exciton dissociation [135,164,217–220]. In all three cases, \( \eta_{PL} \) is reduced by an increase in \( k_{nr} \). For example, the dissociation of excitons can occur when the Coulombic binding strength of the electron-hole pair is overcome by the polarising electric field, causing one of the charges to be ionised out of the QD [221]. The expected (roughly exponential) field-dependence of the exciton dissociation rate given by the Onsager-Braun model would result in a proportional increase in \( k_{nr} \) [11]. Analogously, one prominent explanation for roll-off in nitride-based LEDs is that polarisation fields drive electron leakage out of the active region of these devices [39,205].

In this chapter, we seek to determine which of the three bias-dependent quenching mechanisms - heating, Auger recombination, or electric-field-inducing quenching - is primarily responsible for the QD PL quenching found to be responsible for EQE roll-off in the previous chapter.
5.2 Electric field-induced quenching in QD-LEDs

5.2.1 Introduction

As discussed above, reduction of PL efficiency in QD thin films has been previously measured when QDs are heated [222], charged (Auger recombination) [219], or placed under a strong electric field [216,217]. We preliminarily eliminate temperature effects on QD $\eta_{PL}$, as measurement of the operating temperature of our QD-LEDs with an infrared camera shows a change of no more than a few degrees ($\sim$5-6 °C rise over $\sim$10 seconds at 0.1 A cm$^{-2}$, corresponding to $\sim$8 V, as shown in Fig. 5-3). Consulting Fig. 5-1, this temperature rise is not sufficient to affect $\eta_{PL}$ enough to explain the roll-off, especially on the short timescales (on the order of a second) of each of our measurements. In QD-LEDs, like in OLEDs, the device temperature will likely rise by several tens of degrees Celsius, but this temperature rise has a time constant on the order of tens to hundreds of seconds [223] - incompatible with the fast, repeatable nature of our measurements. Tentatively speaking, charging effects also seem less than likely because QDs generally have long charge retention times (on the order of minutes to hours [219]), whereas the efficiency roll-off curve (Fig. 4-4) is measured within seconds and was reproduced multiple times successively, with the peak EQE unchanged. Moreover, we consistently observe a red-shift in EL with increasing biases applied to our QD-LEDs (Fig. 5-4), qualitatively consistent with the red-shift one would expect from a QCSE. From these observations, we hypothesise that it is the electric field associated with the applied bias that is quenching the QD PL at high voltages and set about testing this hypothesis.

5.2.2 Methods

To characterize the QCSE in our QD-LED structure, we first measure the PL spectra of the QD films in our devices under reverse bias. The experimental setup is shown in Fig. 5-5b. Reverse biasing allows the effect of electric field on the QDs in the QD-LED to be studied in situ, in absence of any charge injection. To avoid damaging
Figure 5-3: **Thermal image of QD-LED under constant current bias.** Collected with an infrared camera, the thermal image shows the temperature distribution across a half-inch substrate (delineated by a large grey box) resulting from biasing of a single QD-LED pixel (1.21 mm$^2$, small grey box) at 0.1 A cm$^{-2}$ for $\sim$10 seconds.

Figure 5-4: **QD-LED EL spectra.** Normalised spectra of QD-LED EL biased at: (black) 2 V; (orange) 5 V; and (red) 8 V exhibit a gradual red-shift, qualitatively consistent with the quantum confined Stark Effect.
the device by prolonged reverse biasing, we apply sawtooth-like voltage waveforms (Fig. 5-5a) with a 500 Hz repetition rate. The sawtooth amplitude peaks at -18 V and is followed by a duration of positive voltage (1.6 V) to reduce stress on the device by minimising the average net applied voltage, but without turning on EL. QD PL is induced by a 530 nm wavelength LED emitting 100 $\mu$s long pulses synchronised with the voltage waveform and QD PL spectra are collected with a spectrometer. By sweeping the time delay (phase shift) between the voltage waveform and the illumination pulse, PL spectra of the QDs under different electric-field strengths can be collected while keeping all other conditions unchanged. To assess the degree to which the QCSE occurs while the QD-LED is in operation, EL spectra are monitored as the device is forward biased, again with all other experimental variables held constant. The experimental setup for this measurement is shown in Fig. 5-6. This combined approach allows the study of QD PL and EL from the same active device structure.

5.2.3 Results and discussion

The resulting PL and EL spectra are normalized and their peak emission energies are compared. Fig. 5-7 shows EL spectra obtained at 5, 11.6, and 13.8 V overlaid with PL spectra with coincident peak energies (PL at 1.6, -8.6, and -16 V, respectively). Both PL and EL spectra are approximately Gaussians at low biases and redshift at higher biases. However, EL does not exhibit the same spectral broadening that is observed in the PL. In particular, a shoulder begins to appear on the low energy side of the PL spectra. The inset of each panel in Fig. 5-7 shows a double-Gaussian fit to each asymmetrically broadened PL spectrum. We attribute the double-Gaussian profile to emission from QD subpopulations that are subject to two different environments; for example, a layer of QDs next to ZnO and a layer of QDs away from ZnO. QDs placed adjacent to the ZnO are expected to exhibit energy levels that differ from that of QDs placed adjacent to the CBP, which has a lower dielectric constant [224]. The difference between EL and PL spectra (even when the peaks are matched) can be explained by the fact that the electric-field distribution is generally different between
Figure 5-5: **QD PL electric field-dependence measurement technique.** Reverse biasing our QD-LED allows measurement of PL spectra of QDs *in situ* in our devices, exposed to varying electric fields in absence of charge injection. **a**, The relative timing (phase) of the 530nm LED optical excitation square wave pulse (green) and a reverse bias sawtooth-like voltage waveform (black), synchronised at 500 Hz repetition rate, determine the magnitude of the field at which each PL spectrum is recorded by the spectrometer setup shown in **b**.
Figure 5-6: **QD-LED EL measurement setup.** EL spectra from our QD-LED are measured as increasing increments of forward bias are applied.
forward and reverse biased diodes [225], thus affecting the two populations differently.

Each PL and EL spectrum is decomposed into two Gaussians, and their intensities and peak energies as a function of device voltage are shown in Figs. 5-8a and b, respectively. The black solid line in Fig. 5-8a is a fit to the PL intensity data assuming a simplified version of the model described in Ref. [216]. In Fig. 5-8b, PL and EL peak energies for both subpopulations redshift under high bias. In particular, the PL peaks of subpopulation A show a quadratic dependence on voltage (black fit), which is a signature of the QCSE. There is no clear fit for the EL peak shift because the distribution of the electric field inside the diode is voltage dependent. The peak energies are maximum when the device is slightly forward biased, indicating the presence of a built-in electric field, which is expected in a diode structure.

Assuming that the EQE of the QD-LED is predominantly governed by the QCSE at high forward biases, we should be able to predict the EQE by comparing the forward-bias EL to the reverse-bias PL from Fig. 5-8a and b. A QD film exposed to an electric field will undergo a QCSE, which is manifested as a shift in the QD PL or EL emission spectra and a concomitant decrease in its PL or EL efficiency. Because the emission spectrum is a function of the applied field, whenever the forward-bias QD EL emission spectrum of subpopulation A (subpopulation B) matches the reverse-bias QD PL spectrum of the same subpopulation, the QDs in subpopulation A (subpopulation B) are experiencing the same local electric field under those particular EL and PL biasing conditions. Therefore, for each subpopulation, the EL efficiency at each forward bias can be predicted by finding the corresponding PL spectrum in reverse bias with peak energy matching that of the EL peak, and assigning the PL efficiency at that electric field to the EL efficiency. We emphasise that the choice of physical model used to fit the data in Fig. 5-8a does not affect the predicted EQE, which is calculated directly from the PL and EL spectra and the corresponding PL intensities.

For example, subpopulation A (Fig. 5-8b, red) shows an EL peak shift from 1.990 to 1.984 eV between 5 and 10 V. This shift corresponds to a PL peak shift from -4.5 to -11.3 V and indicates that the luminous efficiency is reduced by about 37 % (Fig.
Figure 5-7: Comparison of QD PL spectra (black lines) and QD EL spectra (orange diamonds) at corresponding peak emission energies, for three different biases. At high biases, the PL spectra exhibit a red shoulder that is not observed at lower biases or in the EL spectra. Insets: PL spectra (black) are reconstructed (green) using two Gaussians, which correspond to emission from two QD subpopulations, A and B (red and blue, respectively).
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Figure 5-8: Electric field-dependence of QD-LED PL and EL. a, Relative intensities of subpopulations A (red) and B (blue). The PL data are fitted to a simplified version of the model presented in ref. [216]. b, Peak energies of subpopulation A (red) and subpopulation B (blue). Quadratic fits (black lines) to the PL data are made assuming that the shifts are due to the quantum confined Stark effect.
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Figure 5-9: Measured EQE and predicted EQE as a function of voltage. EQE is predicted through the comparison of PL and EL data (Fig. 5-8) as described in the text. The agreement between the data and the prediction shows that the quantum confined Stark effect can self-consistently account for the QD-LED efficiency roll-off.

5-8a) for subpopulation A as a result of the QCSE. The relative number of excitons formed on the two subpopulations (A and B) of QDs is calculated by dividing their EL intensities in Fig. 5-8a by their respective PL efficiencies. The overall EQE is then the weighted average of the PL efficiencies of the two subpopulations. This analysis is applied to EL data between 2.5 and 14 V and the resulting predicted EQE, which is scaled to match the maximum of the measured EQE, is shown in Fig. 5-9. Predicted and measured EQEs are in good agreement, with EQE rolling off by up to 40% at 13 V. The match between the EQE behavior predicted by the QCSE and the experimentally observed efficiency roll-off is evidence that the electric field strength alone - and not carrier leakage or QD charging (Auger recombination) - is sufficient to model the efficiency roll-off.

To further understand the effect of the electric field on the QD PL efficiency, we measured transient PL of the QDs in the QD-LED. Based on our discussion in Section 5.1, it may be possible to distinguish between different possible microscopic
mechanisms behind electric field-induced quenching in our QD-LEDs by observing whether the field causes an increase in $k_{nr}$ or a decrease in $k_r$. Reduction of QD $\eta_{PL}$ has previously been attributed to a decrease in radiative exciton recombination rate (e.g. reduced electron-hole wave function overlap [226, 227]), an increase in non-radiative exciton recombination rate (e.g. exciton dissociation [221, 228]), or a decrease in the probability of forming thermalized excitons (e.g. hot charge carrier trapping by QD surface traps [12, 13]).

We perform this measurement using the same reverse biasing scheme as in Fig. 5-5a, but with a 100 ps laser pulse train at 540 nm wavelength replacing the green excitation LED. PL was detected with a Si avalanche photodiode and timing information was obtained via a time-correlated single photon counting module. The resulting transient PL at four different voltages reveals a lifetime of 4 ns for all of the voltages applied while the initial intensity decreases with higher applied voltage (Fig. 5-10). The inset indicates the times at which the QD PL intensity $I$ has decreased from its initial value of $I_0$ so that $I/I_0 = e^{-1}$ and $I/I_0 = e^{-2}$ ($\tau_{e^{-1}}$ and $\tau_{e^{-2}}$, respectively). Because $\eta_{PL}$ of our QD film is 8%, PL lifetime is dominated by the non-radiative rate. Therefore, the voltage independent PL lifetime observed suggests that the cause is either a decrease in the radiative rate or a decrease in the thermalized-exciton formation efficiency.

5.2.4 Conclusion

In conclusion, we have identified the electric field-induced PL quenching of QDs to be responsible for the efficiency roll-off in QD-LEDs. We use the relationship between PL peak shifts and PL quenching of QDs subject to the QCSE - observed while reverse biasing a QD-LED - to predict the efficiency roll-off in forward bias. The roll-off predicted by this analysis is in excellent agreement with our experimental data and correctly traces an EQE reduction of nearly 50%. Transient PL measurements suggest that the reduced QD luminescence efficiency is not the result of an increased non-radiative recombination rate.

This was the first study offering detailed insights into the efficiency roll-off in
Figure 5-10: **Transient PL of QDs under electric fields in a QD-LED.** Time-resolved PL spectra of QDs in our QD-LED, reverse biased at 0, -8, -12, and -16 V. Time constants of the decays (inset) are independent of the applied voltage, suggesting that the non-radiative exciton recombination rate is independent of the electric field.
QD-LEDs - a must for designing high-brightness QD-LEDs. It demonstrated definitively the contribution of electric field-induced QD PL quenching on QD-LED EQE, a conclusion that has since been corroborated [11]. Subsequently, others have reported evidence of roll-off dominated instead by Auger recombination in their QD-LEDs [6,229,230]. While this apparent dichotomy has yet to be explicitly resolved in detail, we hypothesise that it can probably be broadly interpreted as a manifestation of variations in the electronic confinement of the QDs used in different experiments by different groups. By "electronic confinement", we mean the degree of spatial confinement of an exciton’s electron and hole wavefunctions within the QD’s core. It is dictated by the energy levels of the valence and conduction bands of the core relative to the shell. For example, whereas overcoating a CdSe core with a ZnS shell tightens an exciton’s confinement in the core, overcoating with a CdS shell reduces the confinement [231]. In the case of CdSe-ZnS QDs, the Type-I energy offset between CdSe and ZnS presents large barriers to both electrons and holes, confining both to the core. In contrast, the quasi-Type-II band diagram of CdSe-CdS constrains the hole to the CdSe core while presenting only a small energetic barrier to delocalisation of the electron into the shell.

It has been shown that PL quenching by multicarrier Auger recombination is very significant in highly confined QDs because strong spatial confinement promotes carrier-carrier interactions, and that it is reduced in less confined QDs [232,233]. As an analogous form of ‘confinement’, it has been seen experimentally [229,233] and theoretically [234] that ‘alloyed’ QDs (graded compositions of cores or of core-shell interfaces) negate Auger recombination due to a ‘smoothing’ of confinement potentials. These confinement effects were shown to affect the roll-off of some QD-LEDs [6,229,230]. But there is a tradeoff between mitigation of charge- and electric field-induced PL quenching in QDs. Lower confinement simultaneously enables electric fields to more easily polarise the exciton wavefunction [11], a phenomenon particularly evident along the long (low-confinement) axis of nanorods, which exhibit pronounced Stark shifts in electric fields [235–237]. This tradeoff is illustrated in Fig. 5-11, which organises the different QD PL quenching mechanisms discussed above in
Figure 5-11: **Influence of QD electronic confinement on bias-driven PL quenching mechanisms.** Schematic shows the qualitative dependence of electric field-induced quenching and Auger recombination on QD electronic confinement. The example band diagrams show that whereas confinement increases in the Type-I energy alignment of CdSe-ZnS QDs, it is decreased by the quasi-Type-II offsets in CdSe-CdS QDs. Adapted from ref. [212]

terms of the degree of electronic confinement. It is likely that this tradeoff may be responsible for the attribution of roll-off to electric field by some and to charging by others. For example, observations of charge-induced roll-off in QD-LEDs are often based on devices employing QDs with Type-I band alignments [6], which are therefore more susceptible to Auger recombination than electric field effects. This is not always the case [229], however. Additional, more systematic investigations to correlate QD chemistry (which may, without intention, vary subtly but importantly with synthesis procedures) with roll-off mechanisms are needed, as discussed in Section 7.2.
Chapter 6

Zero-Bias QD Luminescence
Quenching in Infrared QD-LEDs

Chapters 4 and 5 examined the effect on QD-LED performance of in situ QD photoluminescence (PL) quenching that occurs as a function of applied bias. In this chapter, we turn our attention instead to zero-bias (occurring even at zero bias) contributions to PL quenching and QD-LED performance. By chemically passivating the surface of near-infrared (NIR)-emitting QDs, we are able to significantly mitigate in situ PL quenching and realise devices of record efficiency.

6.1 Bias-independent QD quenching mechanisms

In the previous chapters, we have seen how bias can induce quenching both by a reduction in the radiative recombination rate of QDs \( k_r \) and by an increase in their non-radiative rate \( k_{nr} \), per Eq. 5.1. At zero bias, past QD spectroscopy work and a limited number of QD-LED studies suggest that the primary contribution to PL quenching is by way of an increase in \( k_{nr} \), via electronic trap states on QDs and their neighbouring environment (Fig. 5-2, left). For example, if a defect state exists on the surface of a QD, trap-assisted non-radiative recombination can occur, whereby either the electron or hole of an exciton relaxes to the trap state, before recombining with the other carrier without photon emission [238]. (One specific bias-dependent instance of
Chapter 6. Zero-Bias QD Luminescence Quenching in Infrared QD-LEDs

this, relevant to quenching in operating devices, is heat-assisted quenching, whereby heat excites a carrier out of the QD into a surface trap state [222, 239]. This was discussed in Section 5.1.) A diversity of non-radiative interactions between excitons in QDs and neighbouring materials is also possible in QD-LEDs. For example, non-radiative energy transfer of an exciton to surface plasmon modes or non-radiative mid-gap states in adjacent transport layers are possible quenching pathways that will increase $k_{nr}$ [139] (Fig. 5-2). Exciton dissociation at charge transport layer (CTL)/QD interfaces is another possibility [207, 240, 241]. We note that the presence of highly conducting substrates can result in zero-bias Auger recombination (discussed in Chapter 5) due to equilibrium charge transfer [242], but this is unlikely to occur with typical QD-LED materials.

In thinking about how materials engineering may help characterise and control PL quenching processes, it is instructive to think about the influence of QD composition [212]. In addition to the electronic confinement effects depicted in Fig. 5-11 in Section 5.2.4, we can also expect the extent of surface passivation of a QD to impact the degree of trap-assisted non-radiative recombination, represented by an additional axis in Fig. 6-1. By "surface passivation", we refer to both: the chemical passivation of QD surface defect states (for example, by treatment with passivating ligands); and the physical separation of an exciton in a QD core from surface trap states [71, 120] and from the QD’s neighbouring environment (again, using long-chain organic ligands and, for example, by overcoating QD cores with a shell material). Several chemical families of ligands have been tailored to reduce surface defect densities while improving charge transport through QD films [243], though the tradeoff between defects and transport is less severe in QD light emitting applications, which therefore tend to make use of insulating long-chain surfactants (8-18 carbons). The strict distance-dependence of the rate of Förster Resonant Energy Transfer from QD cores to neighbouring QDs [82] and adjacent layers means that long ligands and thick shells help reduce the quenching effect of local defect states on adjacent QDs (‘self-quenching’, see Section 2.1.2) and on transport layer materials. Likewise, the rate of QD-to-QD carrier tunneling has previously been shown to depend roughly exponentially on the width and height
Chapter 6. Zero-Bias QD Luminescence Quenching in Infrared QD-LEDs

Figure 6-1: Influence of QD surface passivation and electronic confinement on zero-bias and bias-driven PL quenching mechanisms. Schematic shows the qualitative dependence of trap-assisted quenching, electric field-induced quenching, and Auger recombination on both QD surface passivation and electronic confinement. The example shown is overgrowth of a CdSe core by a CdS or ZnS shell. Both shells confer passivation, but as the corresponding band diagrams show, whereas confinement increases in the Type-I energy alignment of CdSe-ZnS QDs, it is decreased by the quasi-Type-II offsets in CdSe-CdS QDs. Adapted from ref. [212]

\[
\left(\frac{\Delta E}{2}\right)
\]

of the potential barrier separating adjacent QDs [244], such that ligands and shells can also impede PL quenching via charge transfer to/from the QD [229]. Fig. 6-1 portrays the common practice of adding a wide band-gap shell of ZnS or CdS to a CdSe core-only QD. The passivating effect is experimentally reflected by an increase in \(\eta_{PL}\) of almost one order of magnitude compared to native CdSe cores [74]. Passivation is also evidenced by the recent advent of "giant" shelled CdSe QDs [110,245]; shell thicknesses more than double the diameter of cores confer resilience to PL quenching even upon removal of passivating ligands.

Fig. 6-1 delineates the two variables - confinement and passivation - and the quenching processes we postulate to dominate in each regime. We note that the
quenching mechanisms may be distinguished by their bias-dependence: whereas Auger recombination and electric field-induced quenching, by definition, require the application of a device bias (‘bias-driven’), trap-assisted recombination exists even in its absence (‘zero-bias’). They can also be distinguished by their contribution to PL quenching: either increasing $k_{ur}$ (trap states, Auger recombination, and electric-field induced phonon coupling, surface state coupling, or exciton dissociation) or decreasing $k_r$ (electric field-induced exciton polarisation).

In this chapter, we ask if improved QD passivation (left to right in Fig. 6-1) can indeed mitigate zero-bias PL quenching induced by surface trap states and the QDs’ local environment. Can this strategy be used to enhance the performance of infrared-emitting QD-LEDs, which until now have been based almost solely on core-only QDs?

6.2 Efficient infrared QD-LEDs using core-shell QDs

6.2.1 Overview

Near-infrared (NIR) light sources integrated at room temperature with any planar surface could be realised by harnessing the broad spectral tunability, high brightness and solution-processability of colloidal QDs. Yet the performance of NIR QD-LEDs has remained low compared with visible-emitting devices until now [1]. One notable difference to date is that while visible-emitting QD-LEDs have employed core-shell QDs (QD cores overcoated by a wider band-gap inorganic shell) almost since their inception [132, 246], NIR QD-LEDs have, with one exception [151, 179], been based solely on core-only QDs. As we have discussed above, the use of QDs without shells can compromise their intrinsic $\eta_{PL}$, increase their susceptibility to extrinsic (zero-bias) PL quenching processes, and also reduce their photostability [75]. In this chapter, we show that PbS-CdS core-shell QDs enhance the peak EQE of PbS core-only control devices by 50- to 100-fold, up to $4.3 \pm 0.3 \%$. ‘Turn-on’ voltages are lowered by $0.6 \pm 0.2$ V and per-amp radiant intensities are increased by up to 150 times. Peak EQEs and power conversion efficiencies are more than double those of previous QD-LEDs [64]
emitting at wavelengths beyond 1 μm, and are comparable with those of commercial NIR LEDs. We demonstrate that the primary origin of the performance enhancement is passivation of PbS cores by CdS shells against \textit{in situ} PL quenching, suggesting that core-shell QDs may become a mainstay of high-efficiency NIR QD-LEDs.

6.2.2 Introduction

Electrically-driven and wavelength-selectable NIR and shortwave infrared (SWIR) light sources that can be deposited on any substrate and at lower cost \cite{1,2} than existing (usually epitaxially grown) IR-emitters have the potential to enhance existing technologies and to trigger the development of new ones. Beneficiaries could include optical telecommunications and computing \cite{77,167}; bio-medical imaging \cite{77,171,247}; on-chip bio(sensing) and spectroscopy \cite{55,77,172}; and night-time surveillance and other security applications. Among the candidate large-area planar light-emitting technologies, colloidal QD-LEDs and organic LEDs (OLEDs) stand out, as they enable room-temperature processing and non-epitaxial deposition. Between them, QD-LEDs should perform better at wavelengths beyond $\lambda = 1$ μm because in this spectral range the luminescent organic dyes used in OLEDs exhibit lower $\eta_{PL} (<5\%)$ \cite{166}) than the colloidal QDs used in QD-LEDs. The PL emission wavelength of QDs can be precisely tuned through quantum-confinement effects, with high $\eta_{PL}$ maintained throughout the visible and NIR ($\eta_{PL} > 95\%$ \cite{120} and $\eta_{PL} > 50\%$, respectively, in solution). This can be appreciated directly in Fig. 6-2b, which is a false-colour InGaAs camera image of six different PbS QD samples emitting at evenly spaced wavelength intervals between 1.2 and 1.7 μm under ultraviolet illumination. Furthermore, solution processability of QDs enables their epitaxy-free integration with Si-electronics \cite{94}. NIR QD-LEDs with peak EQEs of 8.6 % at $\lambda > 1$ μm \cite{183} and 2 % at $\lambda > 1$ μm \cite{64} have so far been demonstrated, compared with 6.3 % \cite{174} and <0.3 % \cite{166} for OLEDs, respectively.

In this work, we significantly raise the performance of $\lambda > 1$ μm NIR QD-LEDs by adopting strategies used in visible-emitting QD-LEDs (which have demonstrated EQEs of over 20 % in the red \cite{140}). Based on the discussion above, our primary
Figure 6-2: Infrared QD PL, as seen by eye and with an infrared camera. Six vials of colloidal PbS QDs illuminated with an ultraviolet lamp (475 nm), as seen: a, by eye, captured with a regular camera; and b, with an infrared camera. The samples emit at roughly evenly spaced wavelengths intervals between 1.2 and 1.7 \( \mu \text{m} \). In b, three images were collected with an InGaAs camera (sensitive from 900-1700 nm): one with a 1300 nm bandpass filter; a second with a 1475 nm bandpass filter; a third with a 1600 nm bandpass filter. The three images were each assigned a different primary colour and then overlaid. Courtesy of Jessica Carr.
strategy is to emulate visible-emitting QD-LEDs in their use of QDs overcoated by wide band-gap shells [132, 246]. NIR QD-LEDs have, with one exception [151, 179], employed solely core-only QDs, exposing the QDs to the quenching pathways outlined above. Secondly, the use of ‘type-IV’ (organic-QD-inorganic hybrid) QD-LED architectures (as defined in Section 2.2), which have shown the highest EQEs, has heretofore been restricted almost exclusively to visible-emitting devices [1]. Here we report a novel NIR ‘type-IV’ QD-LED and demonstrate that the use of core-shell PbS-CdS QDs results in an enhancement of peak EQEs of one to two orders of magnitude over PbS core-only controls. This is shown to be a consequence of increased in situ QD $\eta_{PL}$ accrued by virtue of the passivating CdS shell. The peak EQEs and power conversion efficiencies obtained surpass those of any previously reported $\lambda > 1$ $\mu$m NIR QD-LED [64].

6.2.3 Methods summary

Core-only (control) oleic acid-capped PbS QDs are synthesised using the procedure described in Section 6.2.6 at the end of this chapter. The QDs are then subjected to a partial Pb$^{2+}$-to-Cd$^{2+}$ cation-exchange reaction [75] (Fig. 6-3a, Section 3.2, and Section 6.2.6), whereby the addition of a large excess of cadmium oleate yields core-shell PbS-CdS QDs, also capped with oleic acid. Growing wide band-gap shells like CdS on PbS cores by cation-exchange likely circumvents mismatch of crystal structures encountered in traditional shell growth techniques.

The core-only PbS QDs have a mean diameter of 4.0 nm, deduced by transmission electron microscopy and from the spectral position of the 1S excitonic absorption peak. This corresponds to a peak PL wavelength of $\lambda = 1315$ nm in solution. By cation-exchange we synthesised two types of thin-shelled PbS-CdS QDs and one type of thicker-shelled PbS-CdS QDs. The thin-shelled QDs have core diameters of 3.6 nm and shell thicknesses equivalent to 0.2 nm (assuming uniform shell coverage), but are distinguished by their synthesis injection temperatures of 80 °C (PbS-CdS(0.2 nm, Sample A)) and 100 °C (PbS-CdS(0.2 nm, Sample B)), respectively. The thicker-shelled PbS-CdS QDs have a core diameter of 2.6 nm and a shell thickness equivalent
Chapter 6. Zero-Bias QD Luminescence Quenching in Infrared QD-LEDs

Figure 6-3: **QD synthesis and QD-LED design.**  

- **a,** Schematic illustration of the cation-exchange reaction used to convert core-only PbS QDs into core-shell PbS-CdS QDs.  
- **b,** Device architecture (left) and cross-sectional scanning electron microscope (SEM) image (right) of the ‘type-IV’ QD-LED based on these QDs.  
- **c,** The QD-LED’s flat-band energy level diagram. Band energies are in eV (referenced to the vacuum level) and are taken from literature \[122, 248–253\]. Based on the model in ref. \[249\], the electron affinity of PbS is tuned from approximately 3.8 eV to 3.9 eV by the reduction in core size (from 4.0 nm to 3.6 nm) accompanying cation-exchange.
to 0.7 nm (PbS-CdS(0.7 nm)) (again assuming uniform shell coverage). These dimensions were determined by wavelength dispersive spectroscopy (see Section 6.2.6). $\eta_{PL}$ of these QDs, measured in chloroform solution, are shown in Fig. 3-2b.

Using these QDs, we fabricate QD-LEDs comprising a zinc oxide (ZnO) sol-gel-derived, solution-processed electron-transport layer (ETL) and an organic small molecule hole-transport layer (HTL) of 4,4-bis(carbazole-9-yl)biphenyl (CBP), sandwiching a film of QDs in an inverted ‘type-IV’ device architecture (as defined in Section 2.2). Thin films of indium tin oxide (ITO), gold (Au), and molybdenum oxide (MoO$_3$) serve as cathode, anode, and hole-injection layers [253, 254], respectively. A schematic diagram of the QD-LED and a scanning electron microscope (SEM) image of its cross-section are shown in Fig. 6-3b. Its corresponding energy band-diagram is depicted in Fig. 6-3c. As previous reports have shown [254], MoO$_3$ plays the vital role of mediating efficient hole-injection from the Au anode into the deep highest occupied molecular orbital (HOMO) of CBP.

### 6.2.4 Results and discussion

Fig. 6-4a presents EL spectra for the PbS and PbS-CdS QD-LEDs described above. Their overall agreement with corresponding PL spectra from the same locations confirms pure NIR QD EL at a wavelength of $\sim$1.2 $\mu$m. In the absence of a QD layer, high voltages (>4 V) induce low-intensity visible EL characterized by two peaks at $\lambda = 400$ nm and $\lambda = 670$ nm (see Fig. 6-4a, Inset), resulting from CBP and/or ZnO emission. However, upon addition of a QD layer, this parasitic emission is entirely suppressed, indicative of efficient carrier recombination solely within the QDs. Fig. 6-4a shows that a blue-shift in EL and PL of more than 100 nm is achieved by adding a 0.7 nm CdS shell to core-only PbS. This is indicative of increased exciton confinement due to a reduction in core size during cation-exchange [75]. By fabricating similar devices with other batches of PbS and with thicker CdS shells, we have so far tuned EL peaks from PbS-CdS QDs between $\lambda = 1163$ nm and $\lambda = 1341$ nm. NIR EL and current-dependent brightness is visualized with an infrared camera (Fig. 6-4d, Inset; a corresponding video is available as online Supplementary material to the original
The effect of shell growth on NIR QD-LED performance is shown in Fig. 6-4b-d, which compare core-only PbS QDs with PbS-CdS(0.2 nm, Sample B) QDs. Results for the other core-shell QDs are summarised in Fig. 6-4b and in Appendix A, Fig. A-1 to A-4. Fig. 6-4b shows that the current density-voltage ($J-V$) behavior for both core-only and overcoated QDs is described by $J \propto V^{m+1}$, a signature of trap-limited space-charge conduction [94,255]. The corresponding radiance-voltage ($L-V$) plot (Fig. 6-4c) shows that replacing the PbS QDs with PbS-CdS(0.2 nm, Sample B) QDs results in a reduction in ‘turn-on’ voltage (measured at $3 \times 10^{-4}$ W sr$^{-1}$ m$^{-2}$) from $2.0 \pm 0.1$ V to $1.4 \pm 0.1$ V. This may be due to more efficient QD charge injection, suggested by the simultaneous reduction in ‘turn-on’ current density of more than an order of magnitude with increasing shell thickness [246] (Appendix A, Fig. A-5). Taken together, the $J-V$ and $L-V$ data yield an average peak power conversion efficiency of 2.4 %; more than double that of any previous $\lambda > 1 \mu$m NIR QD-LED [64] (Appendix A, Table A.1).

EQE-current density data is shown in Fig. 6-4d. Core-shell PbS-CdS(0.2 nm, Sample B) QD-LEDs exhibit average peak EQEs of $4.3 \pm 0.3 \%$. To our knowledge, this surpasses that of any previously reported $\lambda > 1 \mu$m NIR QD-LED [64] (Fig. 6-5 and Appendix A, Table A.1). This EQE is also commensurate with those typical of commercial NIR LEDs (3 % to 12 %) [256], though at significantly lower emission powers. In comparison, the average peak EQE of control core-only PbS QD-LEDs is approximately 50 to 100 times lower: $0.05\pm0.01 \%$; consistent with the performance of QD-LEDs previously reported using core-only PbS with similar long-chain carboxylic acid ligands [64]. As shown in Fig. 6-6b (black columns), EQE is sizably enhanced for all core-shell QDs investigated. A direct consequence of this is that radiant intensity efficiencies (radiant intensity per amp) are increased at all current densities above ‘turn-on’ by between 35 and 150 times by switching from core-only to core-shell QDs (Appendix A, Fig. A-5 and A-6). The grey columns in Fig. 6-6b represent the average peak EQEs observed from an anomalous (not included in any averaged performance data) ‘champion’ set of devices: up to $8.3 \pm 1.0 \%$ for PbS-CdS(0.2 nm, Sample B)
Figure 6-4: **QD-LED performance using core-only versus core-shell QDs.** 

- **a,** Normalised EL (solid, 3 V applied bias) and PL (dashed) spectra of QD-LEDs containing: (black) PbS; (red) PbS-CdS(0.2 nm, Sample A); (green) PbS-CdS(0.2 nm, Sample B); and (blue) PbS-CdS(0.7 nm) QDs. Inset: Normalised EL spectra of otherwise identical LEDs (with the structure shown in Fig. 6-3) with and without a film of QDs (8 V and 6 V applied biases, respectively).

- **b,** Average current density-voltage \((J-V)\) behavior of: (black) core-only PbS; and (green) core-shell PbS-CdS(0.2 nm, Sample B) QD-LEDs. The dashed grey lines are fits to \(J \propto V^{m+1}\), with \(m = 0\) and \(m > 1\) corresponding to Ohmic and trap-limited space-charge conduction regimes, respectively. The arrows indicate EL ‘turn-on’, which coincides with the upturn in slope of the \(J-V\) curves.

- **c,** Radiance-voltage characteristics of these devices. Solid lines represent average radiances and dotted lines correspond to minimum and maximum ‘turn-on’ voltages recorded for all measured devices.

- **d,** EQE-current density performance of these devices. Black and green error bars indicate experimental measurement errors while the standard deviation of device-to-device variations are shown in grey (Appendix A, Section A.1). Inset: photograph of an array of five QD-LEDs taken with an infrared camera, with the middle device turned on (active area of 1.21 mm\(^2\)) and emitting at a centre wavelength of \(\lambda = 1242\) nm.
Chapter 6. Zero-Bias QD Luminescence Quenching in Infrared QD-LEDs

Figure 6-5: Progression in efficiencies over time of visible- and near-infrared-emitting QD-LEDs, and comparison with this work and with commercial near-infrared LEDs. Visible-emitting QD-LED peak EQEs (a substantial but non-exhaustive selection from the literature, reproduced from our recent review [1]) are represented by filled black circles. Peak EQEs of near-infrared (NIR) QD-LEDs ($\lambda > 1 \mu m$), represented by filled green circles, are taken from Table A.1 in Appendix A. Solid lines connect new record values. The 4.3 % average peak EQE of the core-shell NIR QD-LEDs reported here is shown by a green star. The range of EQEs of typical commercially-available NIR LEDs are also indicated.

QD-LEDs (Appendix A, Fig. A-7). Repeated measurements of these ‘champion’ devices manifested persistently stable operation, suggesting that NIR QD-LEDs with EQE >10 % may be within reach.

Since the EQE of a QD-LED is proportional to $\eta_{PL}$ of its emitting QDs (Eq. 2.1), we can better understand the dramatic increase in EQE that comes from replacing core-only QDs with core-shell QDs by quantifying the correlation between changes in EQE and in $\eta_{PL}$ of the QDs in our devices. As we discussed in Section 6.1, even at zero-bias, $\eta_{PL}$ can be subject to in situ PL quenching mechanisms such as exciton energy transfer to conductive charge-transport layers (CTLs) [137, 257, 258], exciton dissociation at CTL/QD interfaces [207, 240, 241], and Auger recombination [242].

We therefore measure relative $\eta_{PL}$ of each type of QD in glass/ZnO/QD/CBP
and glass/ZnO/QD structures (Fig. 6-6b, Inset) that replicate the QDs’ *in situ* environment in our QD-LEDs. Relative $\eta_{PL}$ is quantified by comparing the integrated areas under the steady-state PL spectra of the QDs in these structures (see Section 6.2.6). The results for each type of QD are shown in Fig. 6-6b relative to $\eta_{PL}$ of core-only PbS, which has been normalised to unity. Whereas shell growth produces only a three-fold rise in $\eta_{PL}$ of QD-only (glass/QD) samples (blue in Fig. 6-6a,b) (and similarly when measured in solution, Fig. 3-2b), relative $\eta_{PL}$ of these QDs *in situ* (orange and green in Fig. 6-6b) increases by 30 to 100 times, indicating that the CdS shell significantly passivates PbS QDs against *in situ* non-radiative pathways. The similarity of the results for test structures with and without CBP (orange versus green in Fig. 6-6b) implies that ZnO is mostly responsible for the PL quenching. The generally good agreement between relative *in situ* $\eta_{PL}$ and average peak EQE (black columns) indicates that the shell-induced increases in $\eta_{PL}$ predominantly explain the efficiency enhancements achieved. This is further substantiated by the reproducibility of this correlation for EQE data corresponding to all measured current densities; examples at $\sim 10^{-4}$ A cm$^{-2}$ and $\sim 10^{-2}$ A cm$^{-2}$ are shown in Appendix A, Fig. A-8.

Time-resolved PL spectroscopy offers further insights into the shell-dependent QD PL quenching by ZnO. Fig. 6-7 shows the normalised transient QD PL decay curves for the glass/ZnO/QD samples. Compared with glass/QD samples (Appendix A, Fig. A-9), PL lifetimes are reduced for all of the QD types in the presence of ZnO, indicative of PL quenching; similar changes have previously been seen for PbS QDs with other metal oxides [259]. The longer PL lifetimes of core-shell versus core-only QDs (Appendix A, Table A.2) corroborate our conclusion that the former are more effective at mitigating PL quenching [242,259,260].

What specific mechanisms, symbolised by the blue arrow in the inset of Fig. 6-7, underpin the ZnO-induced QD PL quenching in our devices? Non-radiative energy transfer from visibly-coloured QDs to surface plasmon modes in conductive metal oxide CTLs of QD-LEDs has previously been postulated [137], but is unlikely here given the low carrier density of our undoped ZnO [261,262]. Indeed in general, energy transfer from PbS QDs to ZnO - for example, to ZnO mid-gap states - seems
Figure 6-6: Correlation of QD-LED EQE with QD PL quantum yields. a, Absolute PL quantum yields ($\eta_{PL}$) of drop-cast films of core-only (PbS) and core-shell (PbS-CdS) QDs on glass as a function of shell thickness, measured using an integrating sphere (described in Section 6.2.6). Cation-exchange serves as a facile post-synthesis approach to increasing $\eta_{PL}$ of NIR-emitting QDs to unprecedented values ($\eta_{PL} = 33\%$ in thin-film for a 0.7 nm shell). Error bars show standard deviations of the values measured at four locations per sample. b, Corresponding dependence of QD-LED average peak EQE on QD shell thickness is indicated by black columns. These EQEs correlate well with average relative in situ $\eta_{PL}$ of spin-cast films of these QDs ($\eta_{PL}$ of core-only QDs is normalised to unity) in: (green spots) glass/ZnO/QD; and (orange triangles) glass/ZnO/QD/CBP optical structures, depicted schematically in the inset. In contrast, relative intrinsic QD $\eta_{PL}$ (blue squares), taken from a, greatly underestimate the EQE enhancements. Average peak EQEs obtained from a ‘champion’ set of devices are shown as grey columns. The EQE error bars for the main devices (black columns) and the ‘champion’ devices (grey columns) indicate device-to-device variations (see Section 6.2.6 and Section A.1 for details). The QD $\eta_{PL}$ error bars show standard deviations between values measured at roughly five locations per sample.
Figure 6-7: Transient spectroscopy of shell-dependent QD PL quenching. Normalised time-dependent PL intensity of spin-cast films of: (black) PbS; (red) PbS-CdS(0.2 nm, Sample A); and (green) PbS-CdS(0.2 nm, Sample B) QDs, all on ZnO. Inset: Illustrations depicting the passivation by CdS shells of ZnO-induced PbS PL quenching (blue arrow).

at odds with the very low extinction coefficients reported for sol-gel ZnO in the NIR [262, 263]. Alternatively, electron transfer from PbS QDs to ZnO, which is widely observed in photovoltaics [207], could be responsible. As has been noted in the context of CdSe-CdS QD quenching by ZnO nanocrystals [142], however, the energetic favourability of the ZnO/QD dissociative interface for electron transfer is expected to be voltage-dependent (forward biasing mitigates electron transfer) whereas the ZnO-induced PL quenching that we observe is, at least in order-of-magnitude terms, voltage-independent (Appendix A, Fig. A-8). Hole transfer to ZnO mid-gap states [142] is therefore more plausible, yet the challenge in reconciling either energy or charge transfer models with the extremely short length scales on which PL quenching occurs (∼0.2 nm of CdS shell) points to a second possibility; quenching by defect states arising from the oxidation of PbS QDs by ZnO.

The roles of the QD core-shell structure and of the QD-LED ‘type-IV’ architec-
ture are inextricably linked. While the former largely explains the enhancement in EQEs observed, the latter is probably central to their high absolute magnitudes. The ‘type-IV’ design is conducive to efficient carrier recombination because it allows the processes of charge-transport and light-emission to be decoupled. Strikingly, the only two previously reported NIR QD-LEDs not possessing a ‘type-I’ structure (a more rudimentary architecture in which QDs play dual roles of CTL and emission centre, see Section 2.2) have also been the highest performing [64,183]. With the present demonstration we propose that together, cation-exchanged core-shell QDs and a ‘type-IV’ device architecture offer a new paradigm for the design of high-efficiency NIR QD-LEDs.

6.2.5 Conclusion

This work demonstrates that the efficiency of NIR QD-LEDs can be enhanced by up to 100 times by replacing NIR core-only QDs with core-shell QDs, as a result of a corresponding increase in \( \eta_{\text{PL}} \). As the demand for high brightness - and therefore high current density - QD-LEDs continues to necessitate the use of metal oxide charge-transport materials [162] (that commonly quench QD PL, even at zero bias), the use of core-shell QDs can serve as a general strategy by which to maximise the performance of future NIR QD-LEDs.

6.2.6 Detailed Experimental Methods

QD and zinc acetate synthesis and characterisation

Based on previously published procedures, core-only PbS QDs were synthesised using a large-scale method [264] and core-shell PbS-CdS QDs were synthesised by cation-exchange [75,265], as described below. QD shell thicknesses were deduced from elemental analysis of drop-cast films on glass substrates by wavelength dispersive spectroscopy [265].

**PbS:** A lead precursor is prepared by heating 30 mmol of lead acetate trihydrate
(Sigma Aldrich), 125 mL of octadecene (Sigma Aldrich), and 175 mL of oleic acid (TCI) in a round-bottomed flask for 12 hours under vacuum at 100 °C. A sulphur precursor is prepared by adding 15 mmol hexamethyldisilithiane (Fluka) to 150 mL of octadecene. The lead precursor is placed under nitrogen and heated to 150 °C before injection of the sulphur precursor. After cooling to room temperature, this solution is transferred into a nitrogen-filled glove box without air exposure. The synthesised PbS QDs are purified by adding methanol and 1-butanol until the solution is turbid, followed by centrifugation to precipitate the QDs. The supernatant is discarded and the QDs are redissolved in hexane [266].

**PbS-CdS:** PbS-CdS core-shell QDs are prepared by cation-exchange [75,265]. To control shell thickness, exchange is performed at 80 to 100 °C for between 5 min and 2 hours under nitrogen using an excess of cadmium oleate. Also see Section 3.2.

**Zinc acetate dihydrate solution:** The ZnO precursor is prepared according to a variant of well-established procedures [252,267], dissolving zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, Aldrich, 99.999 %, 12.56 g) and ethanolamine (NH₂CH₂CH₂OH, Aldrich, >99.5 %, 3.2 mL) in anhydrous 2-methoxyethanol (CH₃OCH₂CH₂OH, Aldrich, 99.8 %, 76.8 mL) under agitation in an ultrasonic bath for 4 hours. The solution was stored in a nitrogen-filled glovebox.

**QD-LED and optical sample fabrication**

Prior to device fabrication, the QDs undergo three rounds of precipitation and centrifugation with methanol and 1-butanol and are then redissolved in chloroform at 40 mg mL⁻¹ and filtered (0.45 μm PTFE). Devices are fabricated on glass substrates that are pre-patterned with a 150 nm thick film of indium-tin-oxide (ITO) (obtained from Thin Film Devices) and cleaned with solvent and oxygen-plasma. First, a zinc acetate dihydrate solution is spin-cast onto the ITO at 2000 rpm for 30 s in a nitrogen-filled glovebox. The xerogel is then sintered on a hot-plate at 300 °C for 5 min in the 10-20 % relative humidity environment of a glove-bag continuously flushed with dry...
air. This process results in the crystallisation of 55 ± 1 nm (by optical ellipsometry (Gaertner Scientific)) thick ZnO films and mitigates the sensitivity of ZnO to variations in atmospheric conditions. QD films are then deposited by spin-coating ∼ 40μL of ∼ 5 mg mL⁻¹ PbS (or PbS-CdS) QDs in chloroform at 1500 rpm for 60s; film thicknesses of 8 ± 1 nm are obtained, as determined by thickness-concentration calibration curves measured by profilometer (Tencor P-16) (Appendix A, Section A.2). This level of accuracy is necessary in order to allow the effect of shell thickness to be studied independently from the effects of QD film thickness. A 150 nm thick HTL of 4,4-bis(carbazole-9-yl)biphenyl (CBP) (purified before use via thermal gradient sublimation), a 10 nm thick hole-injection layer of molybdenum oxide (MoO₃), and a 100 nm thick Au anode (shadow masked) are then successively deposited via thermal evaporation at a rate of ∼0.1 nm s⁻¹ at a base pressure of 1 × 10⁻⁶ Torr. Overlap of anode and cathode defines active area pixels of 1.21 mm². The glass/ZnO/QD/CBP and glass/ZnO/QD structures are fabricated by the same methods as the QD-LEDs.

**QD-LED characterisation**

Current density-voltage (J-V) characteristics are recorded in a nitrogen-filled glovebox using a computer-controlled Keithley 2636A current/voltage source meter. Simultaneously, front face EL power output through ITO is measured using a calibrated Newport 818-IR germanium photodiode and recorded with a computer-interfaced Newport Multi-Function Optical Meter 1835-C. The photodiode’s active area is aligned with the emissive pixel and a diaphragm between the two prevents collection of waveguided EL from the glass substrate. Total radiated power (from which radiance-voltage (L-V) characteristics and power efficiency are obtained) is then calculated by assuming Lambertian emission and by accounting for the wavelength dependence (weighted by the device’s EL spectrum) of the photodiode’s responsivity (Appendix A, Section A.1.2). EQE is calculated as the ratio of the number of forward-emitted photons to the number of injected electrons, per unit time (Appendix A, Section A.1). Power conversion efficiency is defined as the radiated optical power divided by the input electrical power. For each QD type, L-J-V and EQE data are taken from about
three pixels per device, and from devices fabricated on two to five separate runs; the only exceptions are the ‘champion devices’, for which data comes from three to five pixels on one ‘champion’ device (see Appendix A, Section A.1). In all cases, variations between data for a given QD type are referred to as "device-to-device" variations in this chapter.

Optical measurements

NIR EL and PL spectra, transient PL data, and $\eta_{\text{PL}}$ from the integrating sphere are collected in air, before which active sample areas are hermetically encapsulated by a glass coverslip in a nitrogen-filled glovebox using a solvent-free self-curing two-part epoxy (Torr Seal) rated to $10^{-9}$ Torr.

NIR EL and steady-state PL data are collected through a $\lambda = 850$ nm long-pass filter with a Princeton Instruments Spectra Pro 300i spectrometer coupled to a liquid nitrogen-cooled Princeton Instruments OMA V InGaAs CCD array detector. The excitation source for steady-state NIR PL is a $\lambda = 655$ nm diode laser (Thorlabs), which ensures that in the relative $\eta_{\text{PL}}$ measurement only the QDs, and not ZnO or CBP, are significantly excited. The fixed geometry of the setup maximises the comparability of relative PL intensities. A fiber-coupled Ocean Optics SD2000 spectrometer is used to monitor for visible EL.

Transient PL data is measured by exciting glass/ZnO/QD samples at $\lambda = 633$ nm and collecting resulting PL using superconducting nanowire single photon detectors, as previously reported [268].

For both steady-state and transient measurements of relative in situ QD $\eta_{\text{PL}}$, care was taken to record data in a low excitation-intensity regime (0.5 mW cm$^{-2}$ for the steady-state experiments) where PL intensity was not decaying with time (due to irreversible photobleaching), and at many sample locations to confirm homogeneity.

To extract relative $\eta_{\text{PL}}$, steady-state PL spectra were scaled to account for the spectral responsivity of the InGaAs CCD and for differences in relative absorbance between QD samples.

Absolute $\eta_{\text{PL}}$ measurements and calculations are performed using an integrating
sphere and calibrated reference detectors as described previously [266], except that here we account for the wavelength dependence (weighted by the PL spectra of the drop-cast QD films) of the photodiode’s responsivity using an approach analogous to that for calculating EQE and radiance (Appendix A, Section A.1). It was necessary to measure $\eta_{\text{PL}}$ for drop-cast (rather than spin-cast) films in order to detect sufficient signal. $\eta_{\text{PL}}$ is measured at four locations per sample, giving the means and standard deviations plotted in Fig. 6-6a.

NIR EL photographs are taken with a Xenics Xeva-2.5-320 HgCdTe short-wave infrared camera.
Chapter 7

Conclusion

7.1 Thesis summary

The mainstream commercialisation of colloidal QDs for light-emitting applications has already begun. Sony televisions emitting QD-enhanced colours have been on sale since 2013 [2], and optical down-conversion in QDs has been used to manufacture solid state light (SSL) bulbs with enhanced colour quality and reduced power consumption [1]. The bright and uniquely size-tunable colours of solution-processable semiconducting QDs also highlight the potential of electroluminescent QD-LEDs for use in energy-efficient, high-colour-quality thin-film display and SSL applications. Chapter 1 described how the threats of climate change and the drive for more sustainable global development create an imperative for improvements in society’s energy efficiency and carbon intensity, and explained why lighting technologies - including, potentially, QD-LEDs - have an important role to play. Chapter 2 discussed the key advantages of using QDs as luminophores in LEDs and outlined the two-decade evolution of four ‘types’ of QD-LEDs that have seen efficiencies rise from less than 0.01 % to more than 20 %. Indeed, the efficiencies of state-of-the-art electrically driven QD-LEDs now rival those of the most efficient molecular organic LEDs (OLEDs), and full-colour QD-LED displays have now been realised, foreshadowing QD technologies that will transcend the optically excited QD-enhanced products already available. A cost-analysis of industrial-scale QD synthesis was also conducted, showing that QD-
LEDs may be competitive with OLEDs in the SSL market. Chapter 3 provided an overview of the synthesis of colloidal QDs and the quantum confinement effects that dictate their remarkable size-tunable optical properties.

At the start of Chapter 4, we make the observation that whereas significant attention has been paid to engineering QD-LEDs with improved charge carrier recombination efficiencies, the influence of QD photoluminescence quantum yield ($\eta_{\text{PL}}$), which is also directly proportional to a device’s EQE, has not been carefully addressed. Subdividing QD PL quenching mechanisms into those that affect QD-LEDs even at zero bias and those that are bias-dependent, Chapter 4 then focuses on bias-driven QD PL quenching in QD-LEDs. We simultaneously measure the intensity of PL and EL as a function of applied bias, demonstrating that the roll-off in EQE observed in QD-LEDs at high biases can be fully explained by a commensurate reversible reduction in QD $\eta_{\text{PL}}$. This allows us to discount the possibility that roll-off results from charge leakage in our devices. For two decades, efficiency roll-off has been - and continues to be - one of the most persistent hurdles facing the realisation of high efficiencies at high brightness in all LED technologies. Ours is the first dedicated study of this effect in QD-LEDs, serving to narrow down the mechanisms that may be responsible.

Chapter 5 builds on the previous chapter by uncovering the specific process causing QD PL quenching, and therefore efficiency roll-off, in our QD-LEDs. Preliminarily ruling out heating and charge-induced Auger recombination in QDs, we hypothesise that electric field may be the primary quenching pathway and test that hypothesis. Using the shift in wavelength of QD PL from the quantum confined Stark effect as a proxy for the QDs’ local electric field, we measure QD PL under reverse bias (i.e. electric field without charge injection) to determine the field-dependent PL quenching. This allows us to predict the forward bias-induced EQE roll-off in our QD-LEDs. Excellent agreement with observed EQE confirms that electric field-induced quenching is indeed sufficient to account for roll-off in our QD-LEDs - an important guide to the engineering of future high efficiency, high brightness QD-LEDs.

In Chapter 6, we turn our attention to mitigating the influence of zero-bias quenching via electronic trap states on QDs and their local environment in QD-LEDs. We
choose to use NIR-emitting QD-LEDs as a testbed, since these devices boast unique potential. One can envision NIR light sources that can be deposited on any substrate and at lower cost than existing (usually epitaxially grown) IR-emitters finding application in optical telecommunications and computing (solution-processability may enable Si-compatibility), bio-medical imaging (utilising biological transparency windows between 800 nm and 1700 nm), on-chip bio(sensing) and spectroscopy, and night-time surveillance and other security applications. Yet to date, the performance of NIR-emitting QD-LEDs has trailed far behind their visible counterparts. By overcoating PbS core-only QDs with CdS shells via cation exchange, we demonstrate through in situ steady-state and transient PL spectroscopy that even atom-thickness surface passivation dramatically suppresses zero-bias PL quenching by the neighboring ZnO electron transport layer in our devices. $\eta_{PL}$ is enhanced by two orders of magnitude, yielding a record-performance NIR QD-LED with an average EQE of $\sim 4.3$ % and emission wavelengths in the technologically important $1.1-1.3 \, \mu m$ range.

### 7.2 Outlook

This thesis has been dedicated to understanding the role of QD PL quenching on QD-LED performance with and without bias. However, while our work on NIR QD-LEDs yielded a solution to overcoming some of these challenges at zero bias, we have not yet engineered a solution to the electric field-induced roll-off mechanism that we have identified. Indeed, further work is required to deepen our understanding of this process and its interplay with charge-induced Auger recombination in QD-LEDs, which has since been observed by others to sometimes also be involved. Moreover, based on our reviews of the QD-LED field and observation of its progress with respect to the SSL and display markets [1,2], key research hurdles facing QD-LEDs include better understanding and optimising blue emission, outcoupling, and device lifetime. We briefly discuss directions each of these topics could take.

- **Understanding QD-LED efficiency roll-off through QD composition:**
  
  Based on our discussion in Section 5.2.4, our understanding of the interplay
between electric field and Auger recombination in causing EQE roll-off in QD-LEDs may be tested by investigating the effect of QD composition - specifically electronic confinement - on roll-off. Klimov et al. have recently presented evidence of roll-off due to Auger recombination and its correlation with QD shell chemistry [6,229], yet similar efforts should be undertaken to better understand and mitigate electric field-induced roll-off in our devices. We observe that, for example, EQE roll-off is pronounced in our NIR-emitting QD-LEDs (Fig. 6-4) but, based on an initial review of the literature, is apparently less so in blue-emitting devices (Fig. 7-1). It is possible that the different conclusions we and others have arrived at as to the cause of roll-off in QD-LEDs (electric field versus charge) can be ascribed to subtle but systematic differences in the QDs used.

- **Mitigating QD-LED efficiency roll-off**: We propose three approaches to at least partly address roll-off in QD-LEDs, but there are surely others.
Firstly, one could investigate the use of QDs that are optimised to negate Auger recombination (for example, with an alloyed shell) \([229,233,234]\) but whose emission derives from a localised trap state that is less sensitive to the quantum confined Stark Effect. For example, QD-LEDs might employ QDs comprising a luminescent impurity like Mn\(^+\) [269–271] (note these QDs have already been successfully employed in a type-III QD-LED [162]).

Another approach, proposed by Bozyigit \textit{et al.} [212], is to reduce the electric field felt by the QDs in a QD-LED by embedding the QDs in a material of high dielectric constant. For example, atomic layer deposition might be used to in-fill the QD film. Simulations suggest that the use of a matrix material such as TiO\(_2\) (\(\varepsilon \geq 86\)) could reduce the effective electric field by a factor of 10 [212].

An alternative strategy could be to operate QD-LEDs in an altogether different way so as to avoid the deleterious effects of charge and field, and in fact use them to our advantage. For example, as we have previously proposed [272], emission from a light emitting device might be based on \textit{optical} excitation of QD PL (a "PL-LED"), with electric field (in absence of charge injection, by way of a capacitor structure, say) applied only to intentionally dim or turn off QD PL emission. Particularly for applications that do not require large ON-OFF ratios, this approach leverages the most invaluable properties of QDs - their optical ones - while avoiding the difficulties and challenges of exciting them electrically. Since thin dielectric films can then replace thicker, often absorbing charge transport layers, this opens the door to realising a transparent light-emitting technology.

- \textbf{Thermal efficiency roll-off in QD-LEDs:} Our thermal imaging experiments indicated insufficient short-term temperature rises to explain the roll-off in our QD-LEDs (Fig. 5-3). However, just as with OLEDs, prolonged operation may nevertheless lead to a substantial rise in temperature (many tens of degrees Celsius) in QD-LEDs, threatening both efficiency and material integrity. Sys-
tematic QD-LED junction temperature measurements as a function of current density, akin to those performed in OLEDs [223], may be informative of their commercial high-brightness performance limits.

- **Blue QD-LEDs:** The performance of blue-emitting QD-LEDs has improved dramatically over the past few years [273]. Fig. 7-1 shows the progression in record efficiencies of hybrid deep-blue (CIE $y < 0.1$) QD-LEDs, which are seen to be quickly approaching those of state-of-the-art OLEDs using phosphorescent and thermally-activated delayed fluorescence (TADF) emitters. As Fig. 7-1 also demonstrates, blue QD-LEDs exhibit much less severe efficiency roll-off at high biases compared to OLEDs, such that QD-LED and OLED EQEs are comparable at high brightness. While enabling true blue EL emission, these QD-LEDs have sub-bandgap turn-on voltages of 2.5-3 V [60, 61, 140, 141, 273] that are lower than those of corresponding OLEDs (3.3-5.4 V [274–276]); a key factor in ensuring small energy losses during electron-photon conversion, and therefore in achieving high power-efficiencies [277]. As we described in Section 1.2, efficient, stable blue-emission from OLEDs remains elusive, presenting an impediment to OLED commercialisation as a white light source.

Blue-emitting QD-LEDs have received limited attention to date compared with red-emitting devices, so we propose a course of research investigating the two limiting factors to the performance of blue QD-LEDs: efficiency and lifetime. By developing understanding in these two largely unexplored areas, it may be possible to develop efficient and stable blue QD-LEDs with the potential to enable a new generation of white SSL sources.

To our knowledge, there has been no systematic study to uncover the factors limiting EQEs and lifetimes in blue QD-LEDs. The substantial rise in efficiencies of blue QD-LEDs in just the last few years (Fig. 7-1) has been largely attributed to apparent advances in QD synthesis chemistry. At the same time, it is most frequently cited that blue QD-LEDs exhibit inferior performance to their red and green counterparts because of the larger hole injection barrier at
the QD/hole transport layer (HTL) interface resulting from the deeper highest occupied molecular orbital (HOMO) level of the higher-energy QDs [60, 273]. This argument is certainly plausible, but has not yet been validated by systematic investigation of the impacts of hole injection and charge balance on EQE. Building on successes with OLEDs [118, 278], and with the suspicion that excess electron injection may detrimentally impact today’s blue QD-LEDs, one might investigate the impact of charge (im)balance on device performance through the use of doped charge transport layers, conductive metal oxides, and charge blocking layers.

- **Outcoupling in QD-LEDs:** While many of the structural modifications successfully implemented in OLEDs and GaN-based LEDs to enhance the outcoupling of generated light may be translatable to QD-LEDs, it is emerging that many of the outcoupling strategies reported in the academic literature may not be compatible with commercial applications. Outcoupling techniques must be low cost, scalable to large area devices and manufacturing, compatible with OLED device architectures, and robust with respect to lifetime and environmental degradation [40]. For example, plasmon losses can most easily be mitigated by increasing the distance between the emissive layer and metal cathode, yet this can increase device operating voltages. Solutions to this specific tradeoff may include doped charge transport materials or unconventional transport materials such as perovskites. Interestingly, ongoing investigations of large QD PL enhancements (between \(\sim 2\)- and \(50\)-fold) through QD-metal nanostructure interactions suggest that carefully tailored plasmonic templates may be used to enhance the efficiency of QD-LEDs [93, 279].

- **Lifetimes of QD-LEDs:** Intrinsic QD PL lifetimes of >14,000 hours and respectable PL thermal stabilities (12% fall-off at 140 °C) are reported by QD Vision, Inc [280, 281]. These are comparable with inorganic phosphors and render QDs already commercially viable in many optical down conversion applications. However, lifetimes of electrically driven QD-LEDs remain relatively
short. QD-LED half-lives, $T_{50}$, from an initial luminance of 100 cd m$^{-2}$, are typically on the order of $10^2$-$10^4$ hours, compared to $10^5$-$10^7$ hours for today’s OLEDs, which have undergone more than a decade of rigorous commercial-scale refinement [282].

Fig. 7-2 depicts the evolution of QD-LED operational lifetimes, with all devices compared to the same initial luminance of 100 cd m$^{-2}$ [60–62, 93, 94, 131, 132, 140, 141, 140, 141, 281, 283]. Red-emitting QD-LEDs, which are the colour most commonly reported, clearly demonstrate a steady and substantial improvement in lifetimes over the past several years. In fact, encouragingly, people have recently reported red- and green-emitting QD-LEDs with half-lives of nearly $10^5$ hours when operated at 100 cd m$^{-2}$ initial brightness (see Fig. 7-2).

However, to date, discussion of the lifetime limitations of QD-LEDs has been sparse - in almost every case a side note to other kinds of device studies. Indeed, to our knowledge, there has been no systematic study of the degradation of statistically significant populations of QD-LEDs operating over extended periods of time in ambient room conditions; for example, no detailed characterisation of the physical parameters of degradation or attempts to assign specific mechanisms to this process. In contrast, in the more established field of OLEDs, substantial effort over the past 30 years has gone into discovering and overcoming their failures and degradation. Initial research topics in this area might include:

- Establishing consistent benchmarks and testing procedures for QD-LED lifetime measurement and reporting: device encapsulation, testing conditions, data fitting, and extrapolation are often not consistent between studies.

- Investigating whether QD-LED ambient stability is primarily limited by intrinsic or extrinsic degradation processes. In particular, are non-emissive ‘dark spots’ the dominant factor in short QD-LED lifetimes, as was previously found to be the case in OLEDs?
□ Studying whether colloidal QDs in fact confer additional stability compared to organic luminophores on overall light-emitting device performance, as is commonly supposed. Is QD-LED lifetime primarily limited by degradation of the QDs themselves, or by their surrounding materials?
Figure 7-2: **QD-LED operating lifetimes.** a, Progression in reported lifetimes ($T_{50}$) over time of electrically-driven visible-emitting QD-LEDs, all compared at the same initial luminance of 100 cd m$^{-2}$, driven by constant current. The red-emitting QD-LED reported in 2007 (hollow red triangle) was tested under low vacuum ($5 \times 10^{-3}$ Torr) [62], whereas all other devices were tested in ambient conditions. b, Required OLED/QD-LED luminance for certain applications. Overlaid are the reported lifetimes of several green phosphorescent OLEDs, which are compared to the long-lived green QD-LED developed by Yang *et al.* [141] (unfortunately this is the only instance in which QD-LED lifetimes have been measured for more than one initial brightness). In the cases where two lifetime data points are available, a straight line extrapolation offers a rough projection of the device half-life at low luminances, as previously shown [284]. It is widely accepted that for indoor display applications, the required brightness for individual pixels (depending on size, color, and device architecture) is about 200-600 cd m$^{-2}$ [285,286]. For other applications like outdoor display, lighting and window integrated transparent devices, higher brightness is required. The industrial community now demands a device lifetime as high as 20,000 h at 500 cd m$^{-2}$ for displays, where the lifetime is defined to reach 80 % ($T_{80}$) or even 95 % ($T_{95}$) of the initial brightness; that is, exhibiting a drop of only 20 % and 5 %, respectively, instead of the 50 % ($T_{50}$) metric typically reported by researchers.
Figure A-1: Raw EQE-current density data with measurement errors and device-to-device variations. EQEs of individual QD-LED pixels using: a, PbS; b, PbS-CdS(0.2 nm, Sample A); c, PbS-CdS(0.2 nm, Sample B); and d, PbS-CdS(0.7 nm) QDs are indicated by black lines, with blue dots showing their averages. Measurement errors and device-to-device variations are represented by blue and grey error bars, respectively.
Table A.1: **Summary of reported NIR QD-LED peak external quantum efficiencies and power efficiencies.** Peak performance metrics for a number of reported near-infrared QD-LEDs are tabulated in chronological order.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Year</th>
<th>Peak EQE (%)</th>
<th>Peak Power Conversion Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tessler <em>et al.</em> [179]</td>
<td>2000</td>
<td>0.5</td>
<td>0.02</td>
</tr>
<tr>
<td>Steckel <em>et al.</em> [170]</td>
<td>2003</td>
<td>0.001</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Koktysh <em>et al.</em> [181]</td>
<td>2004</td>
<td>&lt;0.001</td>
<td>-</td>
</tr>
<tr>
<td>Konstantatos <em>et al.</em> [63]</td>
<td>2005</td>
<td>0.27</td>
<td>0.01</td>
</tr>
<tr>
<td>O’Conner <em>et al.</em> [182]</td>
<td>2005</td>
<td>0.02</td>
<td>1.2 x 10^-4</td>
</tr>
<tr>
<td>Bourdakos <em>et al.</em> [168]</td>
<td>2008</td>
<td>1.15</td>
<td>0.66</td>
</tr>
<tr>
<td>Choudhury <em>et al.</em> [169]</td>
<td>2010</td>
<td>0.83</td>
<td>0.08</td>
</tr>
<tr>
<td>Cheng <em>et al.</em> [183] (λ &lt; 1μm)</td>
<td>2011</td>
<td>6.7 (3 nm QDs); 8.6 (5 nm QDs)</td>
<td>0.4 (3 nm QDs); 8 (5 nm QDs)</td>
</tr>
<tr>
<td>Sun <em>et al.</em> [64]</td>
<td>2012</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Ma <em>et al.</em> [95]</td>
<td>2012</td>
<td>0.72</td>
<td>0.11</td>
</tr>
<tr>
<td><strong>This work</strong> [15]</td>
<td>2014</td>
<td><strong>4.3</strong></td>
<td><strong>2.4</strong></td>
</tr>
</tbody>
</table>

All peak external quantum efficiencies (EQEs) are quoted directly from the references. Unless provided, peak power efficiencies are approximated by computing \( (P_{EL}/IV) \times 100\% \) as a function of \( I \) or \( V \). Here, \( P_{EL} \) is maximum emitted power, which, unless given, is approximated by extracting plotted data (Plot Digitizer) and computing \( P_{EL} = (I \cdot EQE \cdot hc)/(|e| \cdot \lambda) \) (where \( \lambda \) is peak emission wavelength) as a function of \( I \) or \( V \) so as to find its maximum. Dashes (-) indicate unknown values not calculable by these methods. Note that \( \lambda > 1\mu m \) for all references except Cheng *et al.*
Figure A-2: **Current density-voltage behavior.** Average performance of QD-LEDs based on: (black) PbS; (red) PbS-CdS(0.2 nm, Sample A); (green) PbS-CdS(0.2 nm, Sample B); and (blue) PbS-CdS(0.7 nm) QDs.
Figure A-3: **Test-to-test variations in peak EQE.** Peak EQEs of individual QD-LED pixels (arbitrarily numbered) tested multiple times using: a, PbS; b, PbS-CdS(0.2 nm, Sample A); c, PbS-CdS(0.2 nm, Sample B); and d, PbS-CdS(0.7 nm) QDs. Peak EQEs are shown after multiple test cycles: (black) Test 1; (red) Test 2; (green) Test 3; (blue) Test 4; and (turquoise) Test 5. Successive test cycles yield peak EQE values between 84 % and 104 % of the initial values for all pixels and all QD types.
Figure A-4: **Day-to-day variations in raw EQE-current density data.** EQEs for: (black and red) two pixels of PbS-CdS(0.2 nm, Sample A) QDs; and for (dark green, light green, blue) three pixels of PbS-CdS(0.2 nm, Sample B) QDs (all ‘champion’ devices). For each pixel, data was recorded one day after fabrication (Day 1, open circles) and again (solid lines) either two (Day 2) or four (Day 4) days after fabrication. We see that EQE either remains unchanged or increases slightly over the course of at least a few days.
Figure A-5: **Radiance-current density characteristics.** Average radiance for QD-LEDs based on: (black) PbS; (red) PbS-CdS(0.2 nm, Sample A); (green) PbS-CdS(0.2 nm, Sample B); and (blue) PbS-CdS(0.7 nm) QDs. Upon shell growth, ‘turn-on’ current densities (measured at $3 \times 10^{-4}$ W sr$^{-1}$ m$^{-2}$) are reduced by 8, 16 and 31 times for PbS-CdS(0.2 nm, Sample A), PbS-CdS(0.2 nm, Sample B), and PbS-CdS(0.7 nm) QDs, respectively. For any given current density above core-only QD-LED ‘turn-on’, the radiance of the core-shell QD-LEDs is between 35 and 150 times higher than that of the core-only QD-LEDs.
Figure A-6: **Enhancement in radiant intensity efficiency.** The enhancement in radiant intensity efficiency (radiant intensity per amp) compared with that of the control core-only PbS QD-LED is shown as a function of current density for QD-LEDs using: (red) PbS-CdS(0.2 nm, Sample A); (green) PbS-CdS(0.2 nm, Sample B); and (blue) PbS-CdS(0.7 nm) QDs. ‘Turn-on’ current densities are indicated by dashed lines. Once the core-only PbS QD-LED (black dashed line) has turned on, the enhancement is between 35 and 150 times for all core-shell devices.
Figure A-7: **EQE-current density characteristics of anomalous ‘champion’ QD-LEDs.** Record performance curves for one set of QD-LEDs using: (black) PbS; (red) PbS-CdS(0.2 nm, Sample A); (green) PbS-CdS(0.2 nm, Sample B); and (blue) PbS-CdS(0.7 nm) QDs. Peak EQEs are 1.7 %, 7.7 %, 9.4 % and 5.3 %, respectively, as plotted in Fig. 6-6b.
Figure A-8: **Dependence of QD-LED EQE-shell thickness correlation on current density.** Average EQE data measured at current densities of $\sim 10^{-4}$ A cm$^{-2}$ and $\sim 10^{-2}$ A cm$^{-2}$, extracted from Fig. A-1, are represented by green and blue columns, respectively, and compared with the average peak EQE data (black columns) shown in Fig. 6-6b. The error bars indicate device-to-device variations in EQE. For all data sets a similar correlation with shell-thickness is reproduced.
Table A.2: PL lifetimes of spin-cast films of core-only (PbS) and core-shell (PbS-CdS) QDs on ZnO, calculated from Fig. 6-7. \( \tau_{e-1} \) and \( \tau_{e-2} \) are the times at which QD PL intensity, \( I \), has decreased from its initial value of \( I_0 \) to \( I = I_0/e \) and \( I = I_0/e^2 \), respectively.

<table>
<thead>
<tr>
<th></th>
<th>PbS</th>
<th>PbS-CdS(0.2 nm, A)</th>
<th>PbS-CdS(0.2 nm, B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tau_{e-1} ) (ns)</td>
<td>0.4</td>
<td>1.2</td>
<td>3.6</td>
</tr>
<tr>
<td>( \tau_{e-2} ) (ns)</td>
<td>1.1</td>
<td>8.8</td>
<td>17.6</td>
</tr>
</tbody>
</table>

Figure A-9: **Transient photoluminescence of QDs on glass.** Normalised time-dependent PL intensity of spin-cast films of: (black) PbS; (red) PbS-CdS(0.2 nm, Sample A); and (green) PbS-CdS(0.2 nm, Sample B) QDs, all on glass.
A.1 Calculation and error estimate of EQE and radiance

A.1.1 EQE calculation

EQE is calculated as the ratio, per unit time, of the number of forward-emitted photons to the number of injected electrons, \( I(V)/|e| \), where \( I(V) \) is the current passing through the QD-LED at an applied bias, \( V \). We can express this as,

\[
\text{EQE}(V) \, [\%] = \frac{N_{\text{phot}}(V) |e|}{I(V)} \cdot g \cdot 100
\]  

(A.1)

where \( N_{\text{phot}}(V) \) is the number of forward-emitted photons actually collected by the photodiode, and the geometric factor, \( g \), accounts for the solid angle of the EL profile (assumed to be Lambertian) subtended by the photodiode, \( \Omega = \pi/g \):

\[
g = \frac{a^2 + L^2}{a^2}
\]  

(A.2)

Here \( a \) is the diameter of the active area of the photodiode and \( L \) is the distance between the emitting QD-LED pixel and this active area.

We calculate \( N_{\text{phot}}(V) \) from the current output (‘photocurrent’, \( I_{\text{pc}}^{\text{meas}} \)) of the photodiode in response to detected EL at each applied bias, accounting for the wavelength dependence (weighted by the device’s EL spectrum) of the photodiode’s responsivity, \( R(\lambda) \).

To do this, first note that the area below a wavelength-resolved EL spectrum measured from a QD-LED, \( EL(\lambda) \), is proportional to the number of photons emitted per unit time. Then, multiplying this by the energy per photon \( hc/\lambda \) and by \( R(\lambda) \, [\text{AW}^{-1}] \), we obtain values proportional to measured photocurrent,

\[
I_{\text{pc}}'(\lambda) = EL(\lambda) \cdot \frac{hc}{\lambda} \cdot R(\lambda)
\]  

(A.3)

Integrating between the wavelength limits of the EL spectrum (\( \lambda_i \) and \( \lambda_f \)), a figure proportional to total measured photocurrent is then given by,
\[ I_{pc}^{\text{prop}}(\lambda) = \int_{\lambda_i}^{\lambda_f} I_{pc}'(\lambda) d\lambda \]  

(A.4)

Scaling \( \text{EL}(\lambda) \) to satisfy the requirement that \( I_{pc}^{\text{prop}}(\lambda) \) equals \( I_{pc}^{\text{meas}} \) yields a revised EL spectrum, \( \text{EL}(\lambda)' \), the area below which is now \textit{equal} to the number of photons emitted per unit time.

\[ \text{EL}(\lambda)' = \text{EL}(\lambda) \cdot \frac{I_{pc}^{\text{meas}}}{I_{pc}^{\text{prop}}(\lambda)} \]  

(A.5)

Thus, \( N_{\text{phot}} = \int_{\lambda_i}^{\lambda_f} \text{EL}(\lambda)' d\lambda \)  

(A.6)

Repeating this procedure for all applied biases and substituting \( N_{\text{phot}} \) into Eq. A.1 gives voltage (or current density)-dependent EQE, as plotted in Fig. 6-4d. We note that in the limit - often assumed for relatively narrow QD EL spectra - that emission is monochromatic, with wavelength \( \lambda_0 \), Eq. A.6 simplifies to \( I_{pc}^{\text{meas}} \lambda_0/hcR(\lambda_0) \) and therefore Eq. A.1 can be rewritten as,

\[ \text{EQE}(V) \% = \frac{I_{pc}^{\text{meas}}}{R(\lambda_0)} \cdot \frac{\lambda_0}{hc} \cdot \frac{|e|}{I(V)} \cdot g \cdot 100 \]  

(A.7)

Eq. A.7 is the simplified expression for EQE often quoted [7].

A.1.2 Radiance calculation

Analogously, the ‘true’ emitted power is \( P_{\text{EL}} = \int_{\lambda_i}^{\lambda_f} \text{EL}(\lambda)' \cdot \frac{hc}{\lambda} d\lambda \), giving radiance as,

\[ L(V) = \frac{P_{\text{EL}}(V)}{A \cdot \Omega} \]  

(A.8)

where \( A \) is the QD-LED pixel area. Again, this is evaluated for all applied biases, leading to Fig. 6-4c.
A.1.3 EQE measurement error

Eq. A.1 indicates that EQE is subject to experimental measurement errors in $N_{\text{phot}}$, $I$ and $g$, namely $\sigma_{N_{\text{phot}}}$, $\sigma_I$, and $\sigma_g$, respectively. $\sigma_I$ results from Keithley 2636A equipment resolution and $\sigma_g$ from geometric errors in $a$ and $L$ in Eq. A.2. From Eq. A.6, $\sigma_{N_{\text{phot}}}$ in turn arises from errors in $I_{\text{pc}}^{\text{meas}}$, $EL(\lambda)$, and $R(\lambda)$, namely $\sigma_{I_{\text{pc}}^{\text{meas}}}$, $\sigma_{EL}$, and $\sigma_R$, respectively. $\sigma_R$ results from Newport 818-IR photodiode calibration error whereas $\sigma_{I_{\text{pc}}^{\text{meas}}}$ is due to background noise recorded by the photodiode/Newport Multi-Function Optical Meter 1835-C measurement setup. $\sigma_{EL}$ is taken to be negligible. Total measurement errors, represented by black and green error bars in Fig. 6-4d, are calculated by combining $\sigma_{I_{\text{pc}}^{\text{meas}}}$, $\sigma_R$, $\sigma_I$, and $\sigma_g$ in quadrature, accounting for multiplication factors implicit in Eq. A.1. Measurement errors for QD-LEDs based on all QD types are shown in Fig. A-1, indicated by blue error bars.

A.1.4 Device-to-device EQE variation

Fig. A-1 shows raw EQE-current density data (from about three pixels per device, and from devices fabricated on two to five separate runs) for QD-LEDs based on all QD types. These device-to-device variations strictly arise due to systematic errors because they exceed the measurement errors calculated above. However, as a useful guide, device-to-device variations are approximated by the standard deviations of raw data from their mean, shown as grey error bars in Figs. 6-4d, 6-6b, and A-1.

The EQE errors for the ‘champion’ QD-LEDs, indicated by grey error bars in Fig. 6-6b, represent the standard deviations in EQE of three to five pixels on single ‘champion’ devices.

A.2 QD film thickness calibration

In order to separate the effect of QD shell thickness from that of QD film thickness it is necessary to accurately control the latter. We do this by varying the concentration of the spin-cast QD chloroform solution. QD film thickness-concentration calibration
curves are determined for each QD batch by spin-coating QD solutions of known concentrations onto ZnO (prepared identically to that in the QD-LEDs) and measuring their film thicknesses with a profilometer. To do this, an edge of each QD film is wiped-off with a chloroform-moistened polyurethane swab (VWR). Because this procedure does not detectably affect ZnO film thickness, the step-height measured by profilometer corresponds to QD film thickness. Roughly 15 line-scans per sample (5 line scans (µm separation) at 3 positions (mm separation)) yield the data plotted in Fig. A-10. Orthogonal distance regressions, accounting for errors in both QD concentration and film thickness, are then used to calculate concentrations required for the 8 ± 1 nm films used in all QD-LEDs.
Figure A-10: **QD film thickness-concentration calibration curves on zinc oxide.** Black dots indicate average thicknesses (as measured by profilometer) of spin-cast films of QDs as a function of the QD solution’s concentration in chloroform for: 

- **a**, PbS;  
- **b**, PbS-CdS(0.2 nm, Sample A);  
- **c**, PbS-CdS(0.2 nm, Sample B); and  
- **d**, PbS-CdS(0.7 nm) QDs.  

Horizontal error bars indicate uncertainties in concentrations and vertical error bars show standard deviations in measured thicknesses from multiple locations per sample. Solid lines are orthogonal distance regressions (Igor Pro 6.1, WaveMetrics, Inc.) from which concentrations used in QD-LED fabrication were determined.
Bibliography


[34] Rogelj, J., Mccollum, D. L., & Riahi, K. The UN’s ‘Sustainable Energy for All’ initiative is compatible with a warming limit of 2 C. *Nature Climate Change* 3 (2013), 545.


Bibliography


