

Incorporation of Quantum Dots into Optoelectronic Devices: Ligands as Charge Brigands

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Submitted in total fulfilment of the requirements of the degree of
Doctor of Philosophy

December 2019

Abstract

With their tunable and almost monochromatic emission over the whole visible spectrum, colloidal II-VI semiconductor quantum dots (QDs) are attracting significant interest as novel electroluminescent materials in light-emitting diodes (LEDs). Being processable in solution allows the deposition of large-scale films at low cost and brings QDs in a competitive position to their organic counterparts.

Organic ligands capping QDs are used to maintain colloidal stability during synthesis and provide passivation in solution. While ligands remain invisible under optical characterisation, this thesis provides insights into the mechanisms by which ligands impact charge carrier dynamics within a light-emitting diode. In doing so, robust and bright QDs emitting at 410 nm are synthesized, passivated with ligands of various lengths and electrical conductivity and incorporated into an LED architecture.

Based on Impedance Spectroscopy measurements ligands have been identified as a major obstacle for charges transiting to the QD to produce light: ligands act as brigands in trapping charges and prevent efficient charge recombination. A novel capacitance behaviour is described and attributed to the accumulation of charge carriers within the ligands during operation. Together with an inductive response in the impedance plane changes in capacitance can be used as a diagnostic tool to determine the recombination efficiency in a quantum dot light-emitting diode (QLED). By driving a QLED with a rectangular pulse accumulated charges lead to a delayed luminescence peak when the bias is turned off and can thereby be visualised. When a 5 nm thick aluminium layer is added into the hole transport layers, trapped charges can open a memory window and add a new device functionality to a QLED. This thesis concludes with ideas to overcome the ligand-dependent charge accumulation and suggests a novel type of QDs for a more efficient device performance.

Declaration

This is to certify that

1. the thesis comprises only my original work towards the PhD,
2. due acknowledgement has been made in the text to all other material used,
3. the thesis is less than 100,000 words in length, exclusive of tables, maps, bibliographies and appendices.

Christian Blauth, December 2019

Acknowledgements

Writing this PhD has been a challenging exercise and without a great network of friends and colleagues it would have not been possible.

First and foremost, I would like to thank my supervisors Professor Paul Mulvaney and Dr Tadahiko Hirai for the opportunity to undertake this PhD. The freedom and support to pursue my own ideas as well as their guidance and constructive feedback have been significant contributions in developing a scientific mindset. Dr Kazunori Ueno's mentoring has greatly impacted my work, and I am grateful to him for his input into my project. I would further like to thank Dr Anthony Chesman for valuable discussions and his quick and detailed feedback on my work. I would also like to express my gratitude to my panel members Dr Wallace Wong and Prof. Ken Ghiggino.

My PhD was split between the Nanoscience Lab at Melbourne University and CSIRO's Flexible Electronics Lab where I met amazing people. Just to name a few, Susi, Régine, Cameron, Hanbo, Ben, Nick, Calum, Eser, Arun, Heyou - I would like to thank you all for the banter and support in making lab work fun.

Most of the ideas for this thesis were developed over a strong cup of coffee during a train ride from Richmond to Clayton. I would, therefore, like to thank Sloane Ranger for sophisticated coffee and Public Transport Victoria for providing an inspirational atmosphere and an occasional service on time.

Finally, I would like to thank my family back home for their encouragement and support for my studies. My time in Melbourne would have not been the same without Niki and Ros, who adopted me into their family. Thanks for making Australia my home away from home.

Preface

During the course of this Ph.D. project, three peer-reviewed publications have been made which is based on the work presented in Chapters 4, 6 and 7. They are listed here for reference in the actual publication status:

Blauth, Christian, Paul Mulvaney, and Tadahiko Hirai. "Negative capacitance as a diagnostic tool for recombination in purple quantum dot LEDs." *Journal of Applied Physics* 125.19 (**2019**): 195501.

Blauth, Christian, Paul Mulvaney, and Tadahiko Hirai. "Transient overshoot and storage of charge carriers on ligands in quantum dot LEDs." *Journal of Applied Physics* 126.7 (**2019**): 075501.

Blauth, Christian, Paul Mulvaney, and Tadahiko Hirai. "Ligand Memory Effect in Purple Quantum Dot LEDs" *Applied Physics Letters* 115 (17) (**2019**): 173505.

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Chapter 1

Introduction

The discovery of semiconductors fundamentally changed human existence, and has underpinned many advances in modern science. Shockley *et al.* [1] found that two gold electrodes connected to a germanium crystal led to an amplified output signal larger than its input. This discovery of the three-point transistor marked the beginning of an electronics revolution that was recognised with the Nobel Prize in Physics in 1956 [2, 3].

Semiconductor crystals, typically made of silicon, are widely used in high performance electronics, ranging from simple transistors to computers and display applications. Today, electronic devices are ubiquitous in daily life and are made from a great range of materials. Semiconductors are also used over a broad length scale, spanning from nanometers to square meters, from computer chips to light harvesting and light emitting purposes in solar cells and smart displays [4–6]. With more sophisticated device architectures and the development of new materials, bottom-up fabrication processes for semiconductors have become more prominent. These have enabled non-traditional deposition techniques, with solution-processed nano-semiconductors the best known example. With the shift from bulk semiconductors to their nanoscale counterparts, more complex device architectures can be achieved at the cost of reduced simplicity of the device. However, solution-processing enables mass production of devices at low cost.

Besides cheaper production costs, semiconductors in optoelectronic devices offer the potential to produce light at a higher efficiency than conventional incandescent lamps, thereby reducing the running costs of lighting. In 2009 more than one fifth of the electricity produced in the United States was used for artificial lighting [7], and consequently, new light emitting concepts could not only reduce costs but also limit greenhouse gas emissions. When semiconductors are used in a lighting application they are typically integrated into a light-emitting diode (LED) architecture. If all

the white-light sources around the world were exchanged for energy efficient LEDs, 1000 TWh/yr , which equals over 200 500-MW coal plants, could be decommissioned and more than 200 million tons of carbon dioxide saved [8]. With light emitting devices becoming more essential in portable electronic devices, such as smartphones and tablets, new concepts for efficient, stable and sustainable lighting are needed to meet the increasing demand.

With their bright and spectrally narrow emission, semiconductor nanocrystals (NC) or quantum dots (QDs) are alternative emitters for lighting and display applications [5, 9–13]. Currently, QDs are mainly used as downconverters for white background lights in TV applications, but their optoelectronic properties can also be harnessed to create a true emitter that does not need any background light. However, before a true QD display will be commercially available, several obstacles, particularly for blue-emitting QDs [10, 14–16], have to be overcome. Compared to organic emitters, which have already benefitted from decades of academic and industrial research, QDs face stability and life time issues. Overcoming these limitations will require an understanding of the chemical and electro-physical properties within a device.

This thesis examines the integration of deep-blue-emitting quantum dots into optoelectronic devices and addresses the fundamental questions about how current produces light. A critical problem that is limiting the stable and efficient operation of QLEDs is identified and described from several angles.

With a stable, colour saturated and almost monochromatic blue QD emitter, smartphone displays could not only be more efficient and last longer, but could also show hyper realistic images: this could particularly help patients in rural areas where a photograph could save a life or encourage the journey to the nearest hospital. A new blue could not only cure winter depression, enhance alertness and memory function in humans, but can also cure diseases like jaundice in just minutes. What if we got the blues right, fig 1.1 ?



Figure 1.1: When you get the blues...

1.1 Semiconductor Quantum Dots

Semiconductor Quantum Dots (QD) are a group of semiconductor nanocrystals (NC) with a diameter of 2-15 nm that show size and shape dependent optoelectronic properties. Each QD consists of hundreds or thousands of atoms and is typically comprised of III-V, II-VI or IV-VI semiconductors [17–19]. A crystallographic model is shown in figure 1.3b. Due to their size, QDs occupy the space between molecules that have discrete energy levels and bulk semiconductors that have large densities of ionically or covalently bonded atoms that form conduction and valence band states separated by the band gap [4]. Instead, QDs develop discrete energy states that depend on the size and shape of the nanocrystal. With decreasing QD size, the energy gap between the lowest unoccupied and the highest occupied energy state increases. Therefore, the size of the QD corresponds to the colour it produces, with small CdSe QDs emitting in the blue, bigger ones in the green and even bigger ones in the red part of the spectrum. [20–22]. Figure 1.2 describes the evolution from a bulk semiconductor to a QD decreasing in size and finally a single atom.

When changes in the absorption spectra of QDs dispersed in a glass matrix [22, 23] or in aqueous solutions [24] led to the discovery of the quantum size effect in size-dependent nanocrystals, QDs garnered more attention within the academic world.

In the following, steps for the synthesis of QDs that are uniform in size and shape are described. Furthermore, surface passivation procedures, such as the epitaxial growth

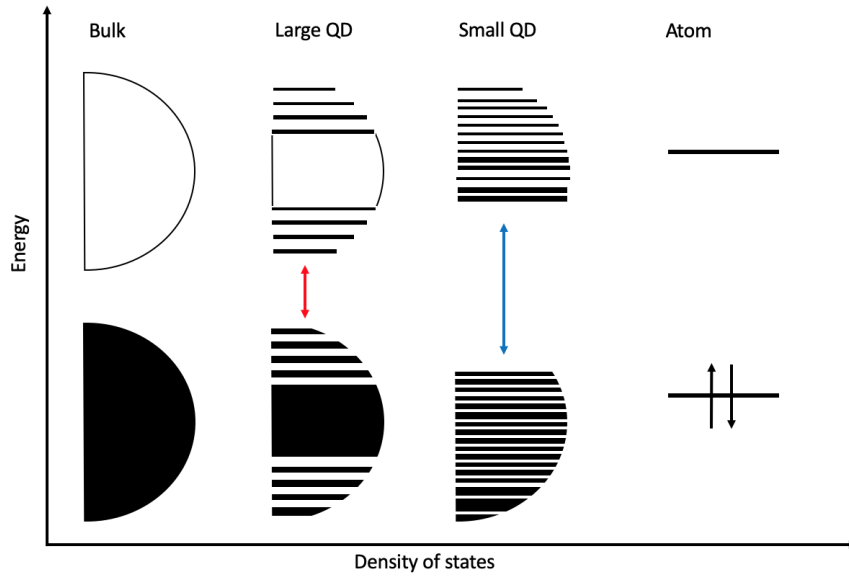


Figure 1.2: Electronic structure of a bulk semiconductor compared to a QD of different size, reproduced from [17].

of shells around QD cores and ligand passivation, are outlined. High quality QDs are the basis for their incorporation into optoelectronic devices. The operational principle of a solution-processed light emitting diode (LED) and a resistive change leading to a memory effect are summarised.

1.1.1 QD synthesis: Nucleation and Growth

Until the introduction of the hot-injection synthesis by Murray *et al.* [25] the fabrication of homogeneous and size-dependent nanocrystals with tunable chemical and optoelectronic properties was challenging. Subsequently, over the last 30 years, many synthetic pathways towards high quality metal nanocrystals have been described from mechanical fabrication, such as high energy ball milling [26] and laser ablation [27], or chemical routes through the liquid [28], the liquid-gas [29] or the gas phase [30]. However, these techniques are beyond the scope of this thesis.

In a modern, surfactant-assisted liquid phase synthesis, the growth of QDs is initiated in non-polar, high-boiling point organic solvents, fig. 1.3a. Typically long-chain ligands, such as alkylphosphines, alkylphosphine oxides or alkylamines, adhere to the surface of the growing NC and determine its growth conditions [31]. The capping ligands act as the template for the crystal growth and a highly reactive molecular precursor determines the final material composition of the NC. It can consist of organophosphine-chalcogenides for II-VI NCs where the metal alkyls are reacted with

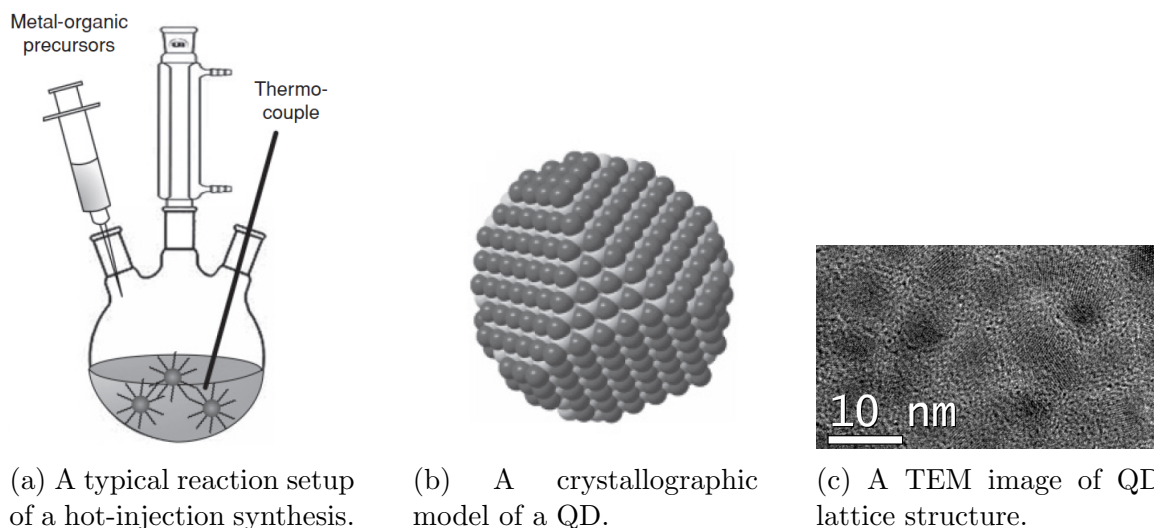


Figure 1.3: Colloidal Quantum Dots: A schematic illustration of surfactant assistant synthesis, 1.3a a), that produces homogeneous QDs. A crystalline model, 1.3b and a TEM image illustrate the QD. Adapted from [32].

organophosphine chalcogenides and is typically swiftly injected into a reaction solution. A typical reaction setup is shown in figure 1.3a. Figure 1.3c shows a TEM image of the as synthesised QDs and illustrates the lattice structure of the nanocrystals.

According to a theoretical model developed by LaMer and Dinegar [33], fig. 1.4, the temporally discrete injection initiates the strong growth rate of monomers, reaction I, and then leads to the homogeneous and controlled growth of the exciting nuclei of the NCs (reaction II) [32–35]. In this first growth phase, the size distribution of the crystals depends strongly on the reaction temperature and time over which the nuclei is formed and grown. In order to prevent the non-uniform growth of nanocrystals, the initial growth rate should be higher than the subsequent growth of nanocrystals [34, 36]. Typically, a second growth step is seen in the formation of nanocrystals, which is called Ostwald ripening (reaction III). There the comparably large surface energy of small crystals leads to their dissolution and instead supports the growth of even bigger nanocrystals [34, 37, 38]. As a result, the mean particle size increases over the course of the reaction, the particle concentration decreases, and the size distribution becomes more homogeneous [39].

In order to achieve high quality QDs with a homogeneous size distribution, balancing the reactivity of precursors during the first step of nucleation is crucial [35]. Homogeneous nucleation occurs when nuclei are formed uniformly throughout the

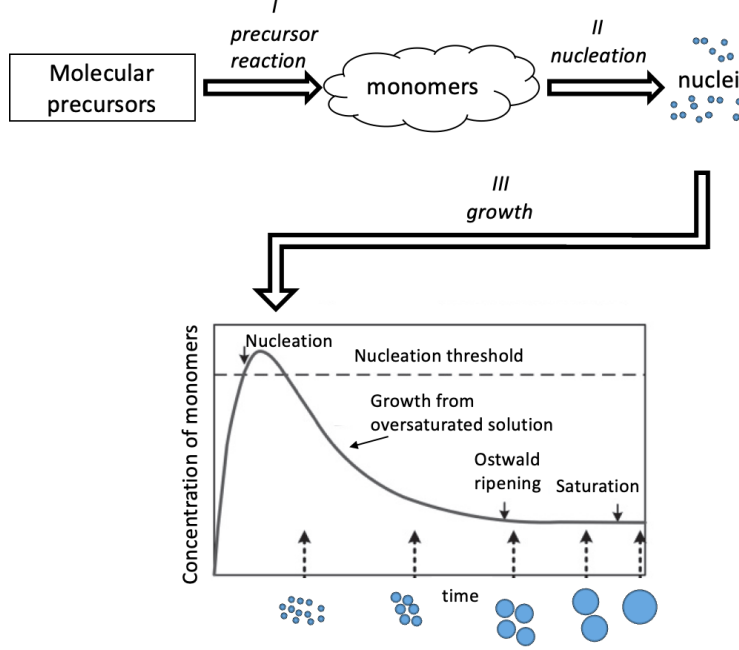


Figure 1.4: Main steps in the synthesis of colloidal QDs: a precursor reaction initiates the formation of monomers leads to the the growth of QDs. A detailed illustration of the growth mechanism is shown on, adapted from [32].

solution, figure 1.4 [35]. In the growth phase, the surfactants regulate the kinetics of nucleation: kinetically well balanced reaction conditions prevent too slow or too fast nucleation rates with respect to the growth rates, which will then lead to either bulky crystals or molecular clusters [31]. Under such heterogeneous nucleation conditions, the structural inhomogeneities, such as impurities, grain boundaries or dislocations, reduce the quality of the particles. In the liquid phase, homogeneous reaction conditions are much easier to achieve, since a stable nucleating surface is already present [31, 35]. A homogeneous nuclei formation is strongly dependent of the thermodynamics of the growth reaction [40].

The total free energy ΔG of a colloidal nanoparticle of radius r can be understood as the sum of the surface free energy γ and the bulk free energy ΔG_v , equation 1.1.

$$\Delta G = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 \Delta G_v \quad (1.1)$$

With the surface free energy always positive and the crystal free energy always negative, a maximum free energy can be determined which a nucleus has to pass through in order to form a stable and non-dissolving nucleus, by differentiating ΔG with respect to r and through setting it to zero, $\frac{\partial \Delta G}{\partial r} = 0$, which gives a critical free energy

depending on the critical radius r_{crit} , equation 1.2 [35].

$$\Delta G_{crit} = \frac{4}{3}\gamma\pi r_{crit}^2 \quad (1.2)$$

The nucleation rate for N particles during time t at a reaction temperature T can be described through equation 1.3, where A is a pre-exponential factor and k_B the Boltzmann constant.

$$\frac{\partial N}{\partial t} = A \exp \left\{ -\frac{\Delta G_{crit}}{k_B T} \right\} \quad (1.3)$$

With equation 1.3 the importance of a high nucleation rate in a very short time period (typically during the first 0.1-10 s) at the beginning of the nanocrystals' growth becomes evident.

Usually, the growth of NCs is initiated at high temperatures, over $300^\circ C$, to form highly crystalline particles and also to anneal and cure defects in the crystalline lattice [41]. The growth conditions not only determine the size but also the shape of the nanocrystal. Typically, shape control is achieved through the choice of capping molecules that selectively tune the growth kinetics and lead to NCs with various morphologies [42]: cubes [43], rods [28] or wells [44]. Furthermore, Shevchenko *et al.* [41] have shown that the precursors and surfactants can modify the crystalline phase of the nanoparticle, whereby three different polymorphs of cobalt NCs were grown by simply adjusting the reaction and growth conditions [31].

In particular, when several thousand QDs are deposited in a thin film, a homogeneous size and shape distribution across all particles is important as it ensures equal and smooth conditions across the whole QD layer.

1.1.2 The surface of a Quantum Dot

As already pointed out in section 1.1.1, the surfactant ligands have a great impact on the size and shape of the QD during the actual synthesis, but remain adherent and provide chemical and colloidal stability post-growth. Surface ligands not only determine the solubility of particles in solvents, but also their inter-particle interaction. Due to the high surface-to-volume ratio of QDs, the capping ligands have a strong influence on the physical properties, ranging from optical [45] to charge transport in thin films [46] and even magnetic properties [47]. Therefore, the choice of the ligand can strongly determine the performance of a QD in any given device architecture.

Figure 1.5 summarises the binding procedure of ligands to QDs. Typically, long-chain organic hydrocarbon ligands offer great flexibility during synthesis and contribute to their inter-particle interactions, as well as determine the packing density between

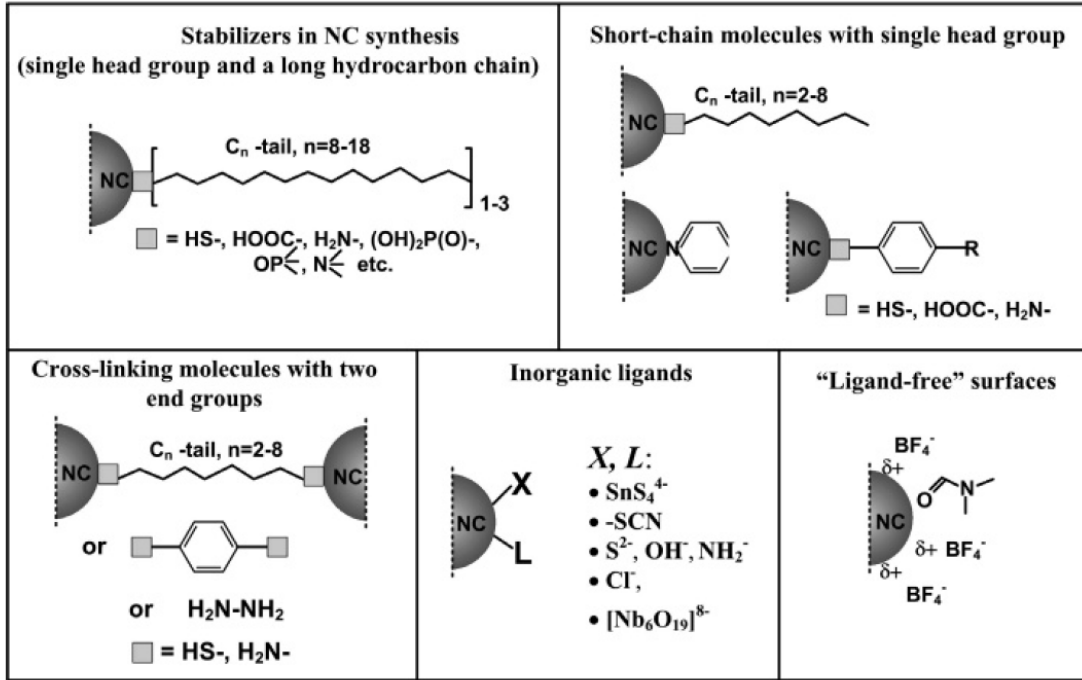


Figure 1.5: Overview of commonly used surface chemistries of QDs, including organic and inorganic ligands, [32]

neighbouring QDs in both short-and long-range films [31]. Long-chained ligands show an electrical conductivity of $\sigma \approx 10^{-11} - 10^{-14} \frac{S}{cm}$ and act as a charge injection and charge transport barrier [48]. The complete removal of organic ligands themselves has proven to be challenging. It often produces multiple surface dangling bonds which act as carrier traps in semiconductor NCs [31, 45]. Annealing of QD films above the boiling point of the respective ligand can partly remove some of the organic ligands but often leads to unwanted sintering of the QDs [49] or other side products damaging the QD, such as carbonaceous ligand pyrolysis [50]. Therefore, most adjustments to the surface and the ligands capping the QD use mild chemical ligand-removal techniques or ligand-exchange reactions, such as replacement of the initial ligand with shorter and more conducting ligands.

Typically, ligand families with single anchoring groups, such as thio-, amino-, carboxylic-, phosphonato-, sulfonato- or an alkyl ($C_{12} - C_{18}$) or aromatic tail group are used during the synthesis of QDs and provide solubility in polar solvents. Due to the lack of direct observation of the atomic surface of the QD, a complete understanding of the binding functionality at the QD-ligand interface is yet to be achieved [32].

For the ligand exchange, QDs are exposed to a large excess of the new ligand, lead-

ing to the partial or complete exchange of surface ligands [51, 52]. The new ligand may have the same for an exchange between the ligands of the same head group, or a higher bonding affinity than the original ligand. Mild heating, as well as repetitive ligand exchange processes, can provide the desired degree of exchange. Whereas the exchange of the initial ligand for longer ones is rather easy, the exchange for very short-chain ligands such as methylamine, ethylamine or butylamine is challenging and often leads to poor colloidal stability and nanoparticle aggregation in both solution and a thin film [31]. For these shorter ligands, it can be beneficial to deposit a thin film with the original ligand which is then exposed to the new capping ligand.

1.1.2.1 Amines as Ligands

In particular for II-VI semiconducting QDs, amines have proved to be suitable surfactants [53]. High emission quantum yields of over 60% have been reported for CdSe QD cores stabilised with primary long-chain amines [54]. A study by Meulenberg *et al.* [55] has measured the surface strain of CdSe QDs and showed that capping with tri-n-octylphosphine oxide (TOPO) causes tensile stress whereas an amine capping leads to a compressive stress - another indicator of the superior performance of amine capped II-VI QDs. In 2006 Bullen and Mulvaney [56] reported that primary amines increase the emission of CdSe QDs whereas their secondary and tertiary counterparts only marginally impacted on the emission of the particles. The addition of a primary amine to CdSe cores typically leads to a slight blue shift and a shrinking of the QDs due to an additional electronic contribution of the capping ligand.

Due to the dense ligand packing on the QD surface, a theoretically almost 100% surface coverage and the ligand-assisted passivation of surface defects, in particular with regards to lattice contraction, leads to the enhancement of the emissive properties of amine-capped QDs [57, 58]. A dense surface coverage can further reduce gaps that can act as diffusion channels for oxygen. Oxidation of the surface can introduce traps and thereby decrease the emissive properties of the QDs [59].

CdSe has been the workhorse for most of the II-VI QD research but considering the concept of amine binding to the QD is independent of the actual material composition of a II-VI semiconductor nanocrystals. Therefore, amine binding techniques are translatable to all II-VI QDs. Puzder *et al.* [60] have calculated the binding energy of amines to the CdSe surface and found similar (0.91 eV for Cd (0001) compared to 1.05 eV for Se (000 $\bar{1}$) but slightly more preferential binding of the amine to the selenium side. The exact bonding mechanism is still unclear, however, it has been suggested

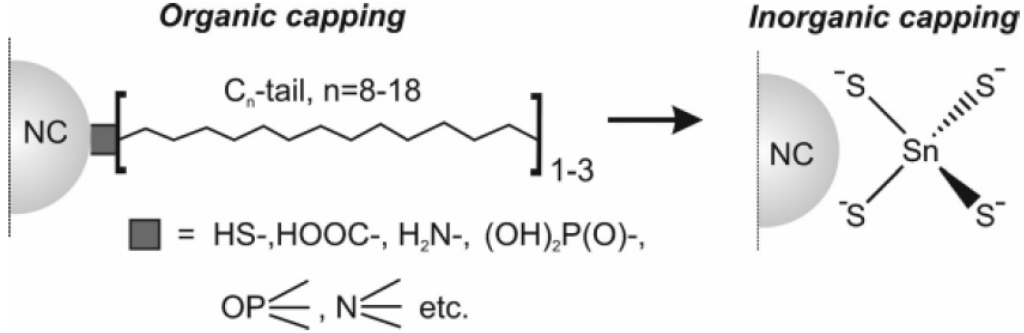


Figure 1.6: Overview of commonly used surface chemistries of QDs including organic and inorganic ligands [32].

that the bonding is achieved through the lone electron pair on the nitrogen atom of the amine then binds almost equally to the Cd and the Se [53]. The acidic protons of the NH₂ could coordinate to the metal sites of the NC and create the bond [61]. The coordination of the amine to the QD surface may occur through a combination of the lone electron pair as well as through the acidic protons [53].

1.1.2.2 Inorganic Ligands

In 2009 Kovalenko *et al.* [62] reported metal chalcogenide complexes (MCC), such as SnS₄⁴⁻, SnTe₄⁴⁻, Sn₂S₆⁴⁻, etc. as capping ligands and introduced an all-inorganic surface passivation for QDs.

Figure 1.6 illustrates the surface chemistry of QDs and the binding procedure of inorganic ligands to QDs. Just like their organic counterparts, these metal complexes maintain the colloidal stability, the size and the shape of the QDs. Changes in photophysical characteristics with regards to an inorganic ligand have not been reported. With good luminescence properties, the MCC ligands passivate dangling bonds, serving to maintain and possibly to improve the electronic characteristics of the QD. Furthermore, MCC complexes are typically soluble in common polar solvents such as water and can thereby provide a pathway for greener, less toxic production of thin QD films. Compared to organic ligands, their inorganic counterparts show superior performance for their incorporation into electronic devices: With a typical band-like charge transport and mobilities of up to $400 \frac{cm^2}{Vs}$, charge transport comparable to a

crystalline silicon-based transistor have been reported [63]. The thermal decomposition of the ligands at high temperatures decreases the distance between the particles in a film and creates a conductive path between the QDs [64]. MCC ligands no longer pose a charge injection and transport obstacle but instead encourage the transport of electrons and holes in transistors, increase the efficiency of ligand-passivated QD photovoltaics that exhibited 6% solar power-conversion efficiency [65], and are promising exchangers to link quantum dots onto photoanodes in quantum dot sensitized solar cells [66]. The incorporation of MCC-capped QDs in a light emitting diode architecture has not been reported. One reason might be that MCC ligands can trap holes and thereby quench the photo-luminescence of QDs [67].

1.1.2.3 Ligand-Free Quantum Dots

Quantum dots free of any capping light might sounds ideal for some applications, however, their synthesis is difficult and typically comes at the cost of aggregation, sintering or contamination. Dong *et al.* [68] have reported nitrosonium tetrafluoroborate (NOBF_4) to replace all original organic ligands capping a QD surface without aggregation or precipitation, and instead achieved positively charged QDs soluble in various polar solvents. With its oxidation properties NOBF_4 is only applicable to certain metal oxide and fluoride QDs [32]. Due to protonation, strong acids such as HBF_4 can remove ligands [69] but are also prone to etching other inorganic compounds. Furthermore, ammonium sulfide, $(\text{NH}_4)_2\text{S}$, has been shown to be able to strip all surfactant ligands in seconds and convert a metal-rich QD shell film into metal sulfides [70]. The removal of the ligands comes at the cost of a modified, sulphur rich shell which may impact the performance of the QD itself.

1.1.2.4 Core-Shell Quantum Dots

Besides passivating QD surfaces through ligands, the QD core can be covered by another semiconducting material shell that is epitaxially grown around it. Typically, two configurations are possible and are shown in figure 1.7:

in type I the shell material has a larger band gap than the QD core. Thereby, the QD is protected from energy loss to the environment and the wavefunctions for electrons and holes are physically separated from the dangling bonds which are considered a major pathway for charge trapping and non-luminescent recombination [42, 71, 72]. In a type II heterostructure, a shelling material with a smaller band gap than the QD core allows for the separation of one charge carrier in the core and the other in the shell. Such partial separation of electrons and holes decreases the overlap of

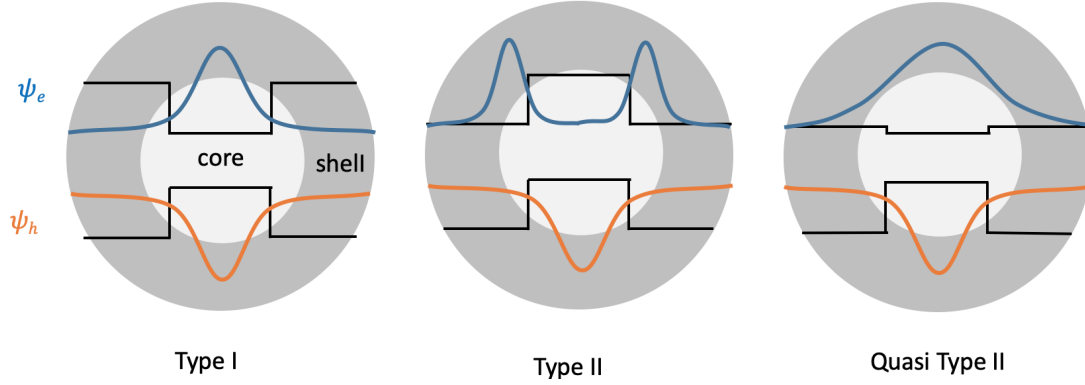


Figure 1.7: Schematic illustration of the most common core/shell QD heterostructure.

the charge carrier wave functions and increases the carrier lifetime, by decreasing the luminescence recombination rate [4, 73].

In particular, for the incorporation of QDs into bright optoelectronic devices, type I core/shell QDs are preferred, as non-luminescent recombination pathways are suppressed and a high photoluminescence is achieved. For devices that require a charge separation, such as photodetectors or solar cells, type II QD configurations can be beneficial [4].

1.1.3 Optical Properties of Quantum Dots

When a semiconductor is exposed to light of an energy that equals or exceeds its band gap, free carriers are generated. Thereby, an electron is excited from the valence band to the conduction band and leaves a positively charged hole behind. In a bulk semiconductor, and compared to the thermal energy at room temperature, the high dielectric constant prevents the formation of a strong Coulomb binding energy. In a QD semiconductor, the quantum confinement leads to a strong absorption response. Discrete electronic states in the conduction and valence bands produce electron-hole pairs with large binding energies that can create single and multiple excitons [4, 17].

Excited electron-hole pairs recombine in a bulk direct band gap semiconductor typically through luminescent band-to-band transitions. In a direct band gap colloidal QD, the recombination between discrete energy states produces near-monochromatic colours with large oscillator strengths, fig. 1.8 a. As already mentioned in chapter 1.1.2, dangling bonds and insufficient passivation of QDs can cause unintentional trapping charges, typically with trap state in the band gap, fig. 1.8 b. Thereby the

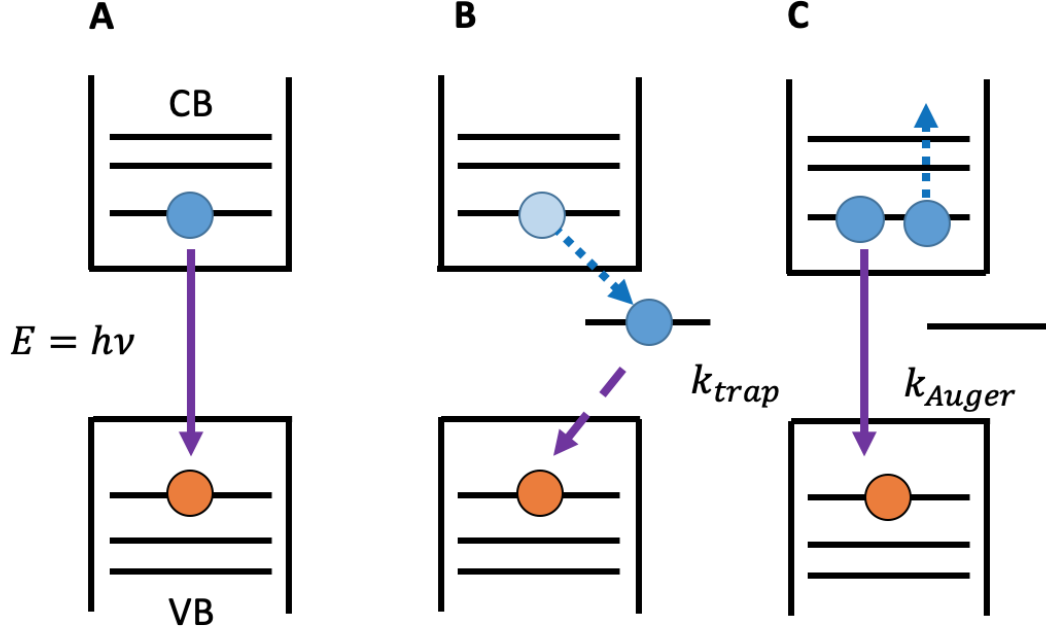


Figure 1.8: Schematic illustration of absorption and emission processes in QDs. Luminescent and non-luminescent processes such as Auger recombination are shown.

luminescent recombination rate is reduced. Despite efforts to passivate the surface of QDs, non-luminescent recombination pathways of excitons can occur. Among those, Auger recombination is the most dominant where the electron-hole recombination energy is transferred to a neighbouring third hot electron or hole. Figure 1.8b, shows the recombination of an excited electron hole pair that converts its energy to a neighbouring electron. The probability of Auger recombination is enhanced with an increased number of excited electron-hole pairs. In QDs with their strong spatial confinement, Auger recombination is more efficient than radiative recombination and happens at faster time scales [74]. Auger processes typically interact with subsequent excitations and promote the formation of a charged exciton [4].

1.2 Quantum Dot Devices

The greatest asset of QDs for light-emitting applications is their tunable bandgap. Due to their efficient, spectrally pure emission, that can be excited optically, chapter 1.1.3 and electrically tuned, colloidal quantum dots have emerged as a competitive choice for the emissive component in light-emitting devices. With their ligand based solution processability, the low-cost and potentially large scale deposition of QDs is easily facilitated, allowing for their incorporation into everyday applications. Furthermore, ligands not only passivate the QD but can be selected to enable the deposition of subsequent layers with orthogonal solvents [75], or enhance the film stability through crosslinking [76]. QDs also offer a substantial benefit over organic and polymer light emitting materials because the emission of QDs is spectrally narrow and can be extended beyond the visible spectrum and into the near-infrared.

In the following, the operational principle of QD light emitting diodes is described and challenges in both manufacturing and operation are outlined.

1.2.1 QD Light Emitting diodes (QLEDs)

In the simplest case, a QLED consists of two electrodes (1.9a), which are responsible for the injection of charge carriers, and an emissive layer (EML), where charges recombine with photon emission. Prior to recombination, electrons and holes have to be separated: through the injection of holes, electrons are removed from the valence band of the semiconductor, whereas the injection of electrons corresponds to the addition of charges to the conduction band [77]. Typically, for energy minimisation purposes, electrons and holes sit close to the band gap of the semiconductor, meaning that electrons move to lower energy levels within the conduction band, whereas holes occupy higher energetic states in the valence band [78, 79]. Therefore, for ideal charge injection, the work function of the cathode, the hole injecting electrode, has to be the same or smaller than the electron affinity of the quantum dot. Consequently, for the injection of electrons, the work function of the anode has to fit or exceed the ionisation potential of the semiconductor QD [80]. Figure 1.9b shows the energy diagram of a simplified Quantum Dot LED when 0V is applied. At this stage, the vacuum levels are flat, the Fermi levels are not aligned and charges cannot flow.

When a bias $V > 0$ is applied, charge carriers flow from one electrode through the QD layer to the other, the potential differences between the electrodes equilibrates and finally the Fermi levels align. Thereby, the vacuum energy shifts and the conduction

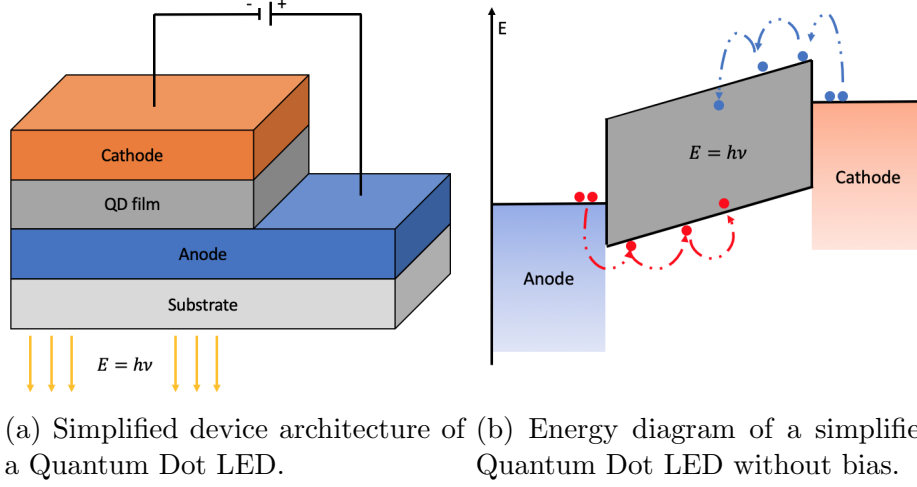


Figure 1.9: Figure A shows a simplified device architecture: On a substrate, typically glass or plastic, a light emitting quantum dot film is sandwiched between a transparent anode and a cathode. Figure B shows an energy diagram where holes are injected from the anode and transported to the cathode. Electrons are conversely injected from the cathode and transported to the anode. When an electron and a hole are bound, energy is released through recombination pathways.

and valence bands of the semiconductor film tilt. Since the electrodes surrounding the QD film have different work functions, a built-in potential V_{bi} occurs. It can be described (equation 1.4) as the potential difference of the the work functions divided by the elementary charge e and the thickness L of the semiconductor film [81, 82].

$$V_{bi} = \frac{1}{eL} \Delta\Phi = \frac{1}{eL} (\Phi_{anode} - \Phi_{cathode}) \quad (1.4)$$

When a potential $V < V_{bi}$ is applied, charges cannot overcome the potential barrier and therefore classically are not injected into the semiconductor. For simplicity, tunnelling of charge carriers is omitted. When the applied bias is increased to $V = V_{bi}$, the built-in potential can be compensated, which equals to a flat band structure within the semiconductor film. With further increases to the applied potential, the band structure tilts and electrons and holes are injected into the QD film.

1.2.1.1 Electrodes

For a light out-coupling device, such as a QLED, at least one electrode has to be transparent at the emission wavelength. Despite the existence of both top [83] - or bottom [13] - emitting and semi-transparent QLEDs [84, 85], the working principle equals those of bottom emitters, which are described further. Besides the transmittance window, the work function is crucial for the device design. As described before,

the work functions of the electrodes should match the energy levels of the QDs in order to achieve efficient injection of charge carriers into the device.

By far, the most common transparent anode for solution processed quantum dot devices is indium tin oxide (ITO). The n-doped semiconductor is usually 100 nm thick, has a work function of 4.9eV and shows a relatively low resistance, typically several $100\ \mu\Omega\text{cm}$ [86] while maintaining good transmittance over the visible spectrum. Milliron *et al.* [87] have shown that an oxygen plasma treatment can shift both work function and electron affinity by $\sim 0.5\text{eV}$ and thereby enhance the injection of holes. Due to the use of the rare metal indium and the energy intensive manufacturing processes required, as well as the subsequent high economic cost, ITO has been identified as a bottleneck for this technology [88]. Alternatives could be ultrathin aluminium in combination with a buffer layer of MoO_3 doped perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) [89], aluminium-doped zinc oxide (AZO) [90–92], or a multilayer of tungsten trioxide WO_3 /silver/ WO_3 [93]. Graphene based anodes [94–96] also act as efficient semitransparent anodes in organic LEDs and solar cells. A conductive polymer mix, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has been widely used as a transparent and printable electrode [94, 97, 98].

Despite its rather low work function, in particular for ultra-wide band gap emitters, (emitting deep blue or even purple EL), ITO can still create an injection barrier for holes. Therefore, a hole-injecting layer is introduced between the electrode and the QD. Organic semiconductors [99], metal oxides [100] or even the previously mentioned PEDOT:PSS [101] can increase the conductivity and facilitate the injection of holes. With a slightly higher work function than ITO, PEDOT:PSS can facilitate the injection of holes, particularly into small QDs [102]. Besides reducing the injection barrier and improving charge transport to the particle, PEDOT:PSS can further act as an electron barrier in a QLED and improve the device performance. Transition metal oxides (TMO), such as molybdenum tri-oxide (MoO_3), vanadium pentoxide (V_2O_5) and tungsten trioxide (WO_3), have been extensively studied because of their exceptional electronic properties for charge injection and extraction in organic electronic devices. Their introduction into an optoelectronic device could advance the device structure and performance in organic and quantum dot electronics [103].

A typical cathode has a rather low work function to efficiently inject electrons into the device. Metals with low work functions, such as calcium ($\Phi_{Ca} = 2.9\text{eV}$) or barium ($\Phi_{Ba} = 2.5\text{eV}$), are used. However, due to their high reactivity in air, the stability

of these electrodes is rather low [104, 105]. Usually a second metal, typically aluminium or silver with a higher work function ($\Phi_{Al,Ag} \approx 4.3\text{eV}$) is deposited on top of Ca or Ba to enhance the stability of the cathode. The highly reactive metals can be replaced by a very thin layer ($\leq 1\text{nm}$) of a metal salt such as lithium fluoride (LiF) or caesium fluoride (CsF) [106, 107]. Without a LiF buffer layer, the electron has to tunnel through the barrier, in which case the energy difference between the conduction band / lowest unoccupied molecular orbital (LUMO) of the emitter and the cathode's Fermi level are unchangeable and independent of the applied voltage. If a buffer layer is present, the voltage drop across the layer raises the cathode's Fermi level and thereby reduces the injection barrier for the electrons [108]. Another explanation could be a favourable dipole- or bias-induced re-alignment of the Fermi levels of the metal and the LUMO energy levels of the organic layers which could equally reduce the electron injection barrier [109]. Alternatively, metal oxides such as ZnO , TiO_2 , and SnO_2 nanoparticles have been shown to work as electron injection layers [75, 110–113]. Kirkwood *et al.* [112] have shown that the defect density and electron mobility of the ZnO nanoparticle electron-transport layer with a tunable mobility strongly affect QLED device efficiency and can be used to balance electron and hole injection into the QD layer. Mashford *et al.* [114] reported that the strong electronic coupling of quantum dots to an adjacent electron transport layer of ZnO nanocrystals facilitates charge transfer, which is responsible for both injecting electrons and maintaining an optimal charge balance for the quantum dot emitters.

1.2.2 Operational Principle of QLEDs

Highly luminescent QDs are typically made of a core/shell design and stabilised with long-chain organic ligands. Their electrical conductivity is very low and comparable to an electrical insulator which have mobilities of $\sigma \approx 10^{-11} - 10^{-14} \frac{\text{S}}{\text{cm}}$ [48]. Therefore, a QLED represents a P-I-N junction-type LED and requires additional charge transport layers to conduct electrical charges to the QDs. Furthermore, to improve charge injection, the QD film is very thin, typically one to two monolayers only.

The actual physical phenomena leading to electroluminescence (EL) is the formation of an exciton: It can be created through direct charge injection of charge carriers, fig 1.10B, from the charge transport layers into the QD or through Foerster resonant energy transfer (FRET) where a field-induced ionisation of a strong field drives electrons from one particle to another or from the charge transport layer to the QD, fig. 1.10D, E. Equally, a combination of several pathways is possible that subsequently lead to

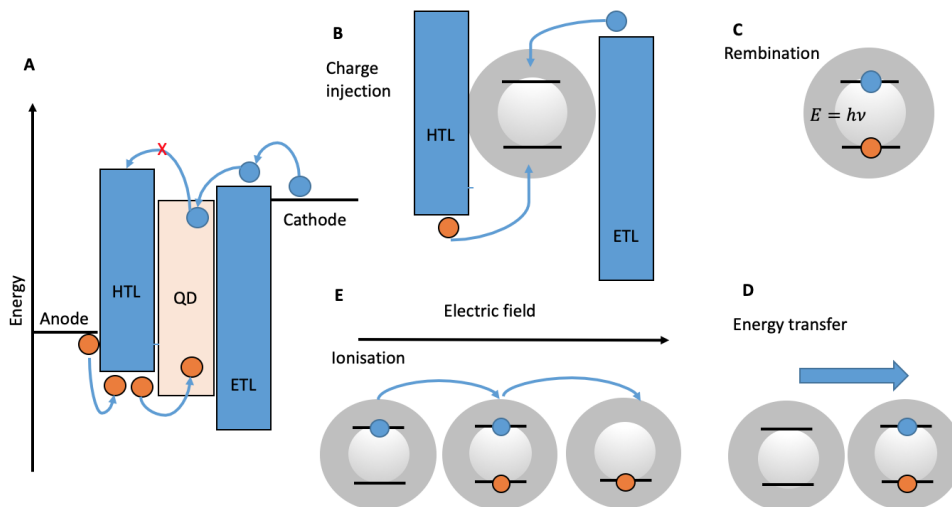


Figure 1.10: QD excitation in a device: A) Energy band diagram of a QD-LED showing two typical QD excitation mechanisms: charge injection and energy transfer, B) charge injection when electrons and holes are injected into the QD to form an exciton, C) recombination where an electron and a hole produce light, D) an exciton is transferred to a QD via FRET from a nearby donor molecule, E) ionisation: a large electric field ionises an electron from one QD to another and creates a hole. When these ionisation occurs throughout the QD film, generated electrons and holes pairs can meet on the same QD to form excitons, adapted from [115].

the emission of a photon. The exact mechanism of exciton formation is strongly dependent on the device architecture and choice of materials. A general and complete understanding for all devices still remains unclear [116–118]. Unfortunately, not all excitons recombine under the emission of light. Mechanisms of electroluminescence quenching are even less well understood. A description of common non-luminescent recombination pathways, such as Auger recombination and field induced quenching, is given in chapter 1.2.5.

1.2.3 Performance Indicators of QLEDs

For a fair comparison between different QLEDs, several standard indicators have been established to characterise QLEDs. They include the efficiency, the brightness and the colour of the light source.

The Internal Quantum Efficiency (IQE) is a measure of the conversion efficiency of injected charge carriers into photons and can be described as $IQE = \gamma\chi$. γ is the ratio of injected electrons to holes (or holes to electrons) from one electrode and is 1 for

a balanced injection, χ is the fraction of the emissive excitons and it is usually determined by the QD. Unfortunately, due to reabsorption, waveguide modes or reflection losses, not all emission can escape from the device. Therefore the external quantum efficiency (EQE) is measured which is related to the IQE via $EQE = \eta_{out} IQE$ where η_{out} describes the outcoupling efficiency of a device. The EQE describes the ratio of measured photons per second to injected carriers per second. The EQE is measured from the emitted optical power and device current and can be described as in equation 1.5.

$$EQE = \frac{P/h\nu}{I/e} \quad (1.5)$$

P describes the optical power emitted into free space, I is the injection current, and e is the elemental charge. For an ideal planar QLED with an IQE of 1, the EQE is still constrained within an efficiency ceiling of $\approx 20\%$ [119].

To characterise the emission from a QLED, both the electrical and optical characteristics should be considered. Maybe the most important feature of a light emitting device is its luminescence to the human eye. It is measured as the luminous intensity per unit area of light travelling in a given direction: The luminous flux Φ_ν describes the quantity of energy emitted by a light source per unit time and in all directions. It can be calculated via equation 1.6

$$\Phi_\nu = K_m \int_{380nm}^{780nm} \Phi_e(\lambda) V(\lambda) d\lambda \quad (1.6)$$

with $\Phi_e(\lambda)$ being the luminescent power distribution for each wavelength. $K_m = 683lm/W$ represents the luminous flux of light of 555 nm to which the human eye is most sensitive during daylight. $V(\lambda)$ represents the spectral sensitivity of the human eye and it becomes 0 beyond the visible range. The luminance itself is defined as the luminous intensity I_ν , which equals the luminous flux from a light source emitted in a given direction within a given angle θ , divided per unit area of light travelling in a given direction. It can therefore be calculated by equation 1.7 where A describes the area of the emitting surface, and ω is the solid angle. θ describes the angle between the emitting surface and the viewer [120].

$$L = \frac{\partial I_\nu}{\partial A \cdot \cos\theta} = \frac{\partial^2 \Phi_\nu}{\partial A \cdot \partial \omega \cdot \cos\theta} \quad (1.7)$$

Similarly to the EQE, the current efficiency is defined as the ratio of luminance to the driving current and is given in $\frac{cd}{m^2}$. Equally important is the turn-on voltage (V_{on}), the operational voltage at which the device switches on; within this work a device is considered to be on when its current efficiency exceeds more than $1 \frac{cd}{m^2}$.

1.2.4 Evolution of QLED Design

Typically, bright QDs are stabilised with long and bulky ligands and/or through a shell of a wider band gap semiconducting material. While maintaining good emissive properties, solid QD films show an electrically insulating behaviour and therefore present a charge injection obstacle [48, 121]. Consequently, the QD layer in an LED architecture is only several $10nm$ thick and is sandwiched between charge transport layers which conduct electrons and holes to the QD [122].

In an ideal case, the valence band of the hole injection and transport layer align with the energy level of the QD. Thereby, no additional energy barrier for holes is created. The confinement of charges within the active layer can be achieved if the hole transport layer can block electrons from transferring to the cathode. This is typically done by choosing a hole transport layer with a wider band gap than the emitter. Similarly, the electron transport layer is considered a hole blocking layer if its conduction band lies below the conduction band of the emitter, fig. 1.10A. A charge blocking function of the transport layers is not necessary; charge transport layers that match the energy levels of the emitter are sufficient - additional blocking layers on top of the charge transport layers can also be employed [123].

Since the first description of light-emitting diodes made from cadmium selenide nanocrystals in 1994, fig. 1.11A, their performance has improved significantly [124]. During their evolution four charge transporting architecture types have evolved, leading to a steady increase in brightness and device efficiency [115]. A summary of the evolution of typical QLED architectures is given in figure 1.11.

Following significant research into organic electronics, quantum dots were first incorporated between polymer charge transport layers, fig. 1.10A, [127]. Very early devices, made of CdSe cores, were proof-of-concept devices and exhibited poor performance both in brightness and efficiency. With more advanced passivation techniques and the incorporation of type I core-shell particles into a device, the efficiency of the devices increased continuously [128]. The exact pathway of exciton formation

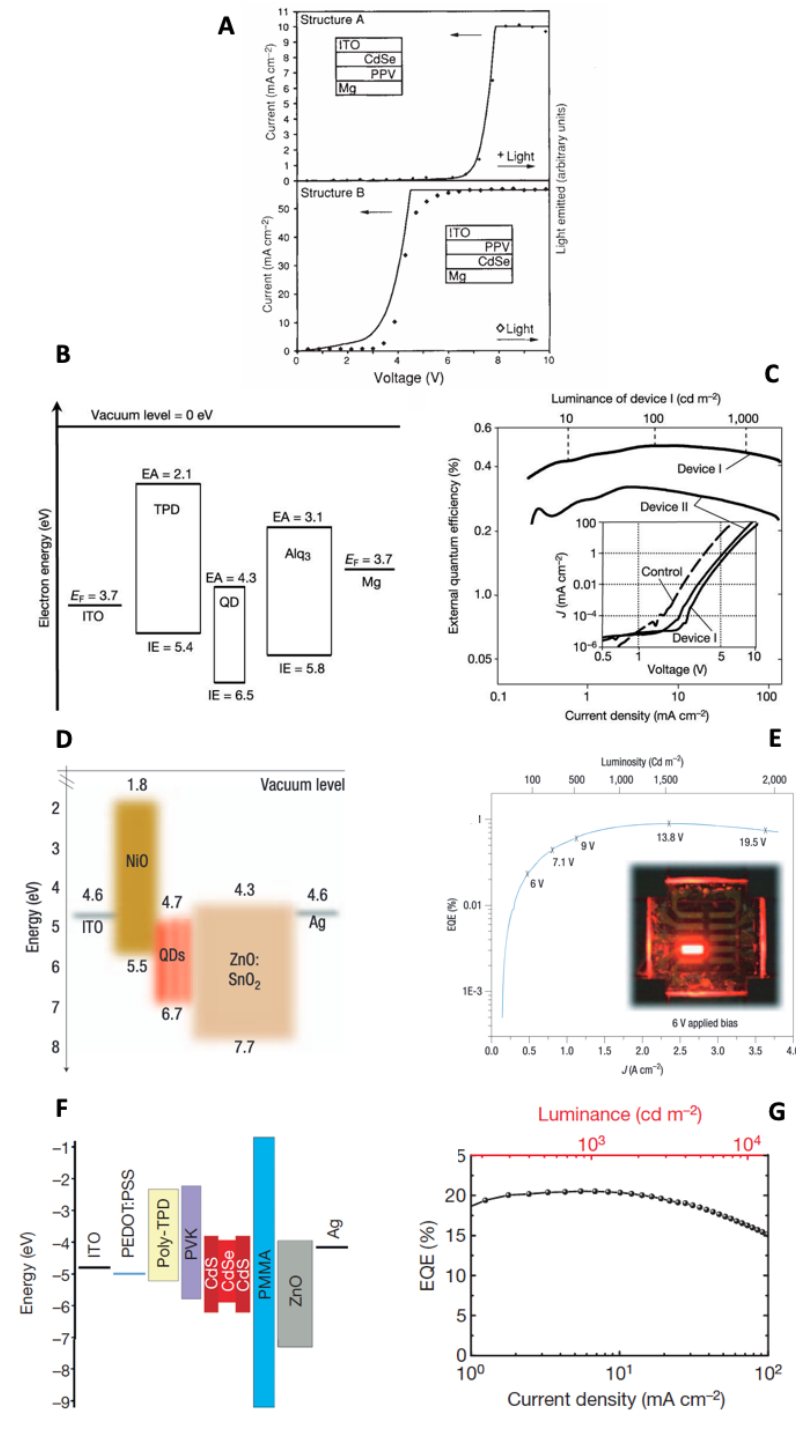


Figure 1.11: Evolution of the QLED design: Energy band diagram and electrical performance data are given. All figures are reproduced from cited publications. (a) first QLED design and J-V curves after Colvin *et al.* [124], (b) QLED with all-organic-charge transport layers after Coe *et al.* [125]. (c) EQE of the device from (b) as a function of current density. Device I contains a hole-blocking polymer, inset shows J-V curves. (d) All-inorganic device of Caruge *et al.* [126] (e) EQE characteristics of the all-inorganic device (c). (f) QLED with hybrid charge transport layers after Dai *et al.* [123] (g) Performance characteristics of (f)

remained unclear and it was suspected that a combination of direct injection and energy transfer was dominant.

In 2002 Coe *et al.* [125], fig.1.11b, demonstrated a hybrid light-emitting diode (LED) where an organic charge transport material was combined with a monolayer of type II QDs, resulting in a 25-fold improvement in luminescence efficiency over the best previous QLED results. Instead of incorporating a plain QD layer, a blend of QDs and organic charge transporting molecules was deposited onto a hole transport layer. Decoupling the luminescence process from charge transport was believed to enhance the luminescence and device efficiency. This work emphasised the importance and the practicality of closely packed QD films in QLEDs. By changing the location of an emissive QD layer within a QLED architecture, Anikeeva *et al.* [129] were able to show that, at least for type II core/shell QDs, FRET is the dominant excitation mechanism. Depositing a monolayer of QDs of various colours meant a significant improvement in the understanding of device functionality as well as efficiency [129–132]. The usually electrically insulating properties of organic semiconductors, as well as their instabilities towards air, can impact achievable current densities and limit the device stability.

Therefore, replacing organic charge transport layers with a more stable, inorganic layer could improve the lifetime of a device while maintaining higher current densities. In 2005 Mueller *et al.* [133] reported for the first time a QLED with an all-inorganic, nanocrystal-based architecture where the QDs are sandwiched between GaN injection layers. Through an energetic neutral atom beam lithography/epitaxy, a GaN matrix was deposited around the QDs without affecting either the nanocrystal integrity or its luminescence properties. Electroluminescence was reported however the current - luminescence efficiencies remained very low.

Metal oxides could be an alternative for charge transport as they can be deposited at room temperature by sputtering or even from solution [126], figure 1.11d. A great variety of metal oxides, such as nickel oxide (NiO) or tungsten oxide (WO₃) for hole and/or zinc oxide (ZnO) for electron transport [134–137] and chalcogenide compositions allow well-aligned energy bands and improve device operation. With a higher conductivity than most organic charge transport layers, metal oxides can increase the current densities up to 4 A/cm^2 in a device. Unfortunately, their luminescence efficiency is rather poor, mainly due to carrier imbalance within the active layer and QD damage during the deposition of the metal oxide. Attempts to dope metal oxide charge transport layers with another metal have increased the efficiency of a QLED

through reducing the exciton loss at the interface between the transport and the emission layer [137].

Hybrid architectures with an organic and an inorganic charge transport layer, typically an n-type metal oxide and a p-type organic semiconductor, have been described, fig. 1.11f [123]. Despite not being a new architecture, but owing to their high brightness and efficiency that competes with commercially mature phosphorescent OLEDs, these devices gained a lot of attention [114]. Their performance enabled the fabrication of full-colour 4-inch QLED displays [117].

In 2017, Zhang *et al.* [138] reported a tandem green QLED with an EQE over 23% and a high current efficiency over $100 \frac{cd}{A}$ making QLEDs highly competitive with phosphorescent organic LEDs. Four years earlier, red QLEDs with an external quantum efficiency (EQE) of 20.5% were reported [123]. Very recently, Wang *et al.* [139] incorporated $ZnCdS/Cd_xZn_{1-x}S/ZnS$ core/shell QDs emitting at 445 nm, with a photoluminescence quantum yield (PLQY) close to unity into a device and measured an EQE exceeding 18%, and a peak current efficiency of $3.4 \frac{cd}{A}$. Unfortunately, for deep blue and purple QLEDs, there is still a need to boost the efficiency.

1.2.5 Challenges

Before QLEDs can become a true commercial reality, several challenges must be addressed. Currently, their short lifespan, particularly for blue and purple emission, poor photon outcoupling efficiencies, as well as the quenching of photons within a device, are key issues to be solved. Addressing these requires a better understanding of operational mechanisms of QLEDs from both a chemical and device-physics perspective.

Despite many attempts to improve the device architecture, charge transport layers or inter-QD coupling, two crucial challenges remain: how to efficiently inject a balanced amount of charge carriers into the QD layer and once an exciton is formed, how to increase luminescent recombination while suppressing non-luminescent recombination pathways.

Monitoring the movements of charge carriers from the electrodes towards the active QD layer is typically done through a detailed analysis of capacitance. Typically, capacitance is measured through Impedance Spectroscopy (IS) where a DC voltage is superimposed with a small-amplitude AC signal. A detailed description of the measurement principle is given in chapter 2.5.2. From an IS measurement the real and

imaginary values of capacitance, resistivity and of the dielectric permittivity values can be achieved, respectively.

Changes in capacitance reflect the changes in density of charge carriers within the active layer and can be used to capture complex and unusual electrical responses with the phenomenon of negative capacitance (NC) being perhaps the most prominent example [140]. The NC effect has been reported in various electronic devices, such as crystalline and amorphous semiconductors, as well as in organic and nanoparticle devices spanning GaAs IR detectors, superconductors and OLEDs [141–150]. As fundamentally different as these devices are, so are the origins of NC, ranging from contact problems which cause parasitic resistances in series, [140, 151] to interface [142] and minority injection [152] problems. Many systems exhibiting NC consist of a conductor or a semiconductor sandwiched between two electrical contacts, with charge carriers stored and released from trap states when a sufficient bias and ac-voltage are applied. This phenomenon is enhanced in thin interface layers [149, 153] and is theoretically described by a positive-valued time derivative of the transient current response to a voltage step [140]. Uddin and Teo [154] have studied the differential capacitance of a hybrid QD/organic LED where the total capacitance of the device can drop below 0 based on the formation of a time-dependent transient current originating from the organic/QD interfacial states.

So far and with the multitude of various observations of NC in various device and material setups, no universal theory has been presented covering all physical aspects that can lead to capacitance dropping below 0.

From a theoretical point-of-view, negative capacitance NC has the same small-signal voltage and current relationship as positive inductance $L = j\omega L = -\frac{1}{j\omega C}$ [140]. However, the treatment of NC as an inductance is not meaningful, because a QLED does not produce a significant magnetic field nor does it display an inductance that increases with frequency. A more suitable numerical interpretation of a NC is based on an analysis of the transient current $\delta j(t)$ response to a voltage step. The total capacitance can then be described through equation 1.8, as the sum of $C_0 = C(\infty)$ as the geometric, frequency independent capacitance and a frequency trap state dependent capacitance. A decrease in capacitance occurs if the function $-\delta j(t)/dt$ is negative and monotonically increasing to 0, making $C(\omega)$ negative [140, 145].

$$C(\omega) = C_0 + \frac{1}{\Delta V} \int_0^\infty \delta j(t) \cos(\omega t) dt \quad (1.8)$$

For an optoelectronic device, such as a QLED, it can be assumed that capacitance depends on the accumulation and recombination of charge carriers. When electrons and holes are injected into the active layer and recombine at a finite rate, a finite volume exists where electrons and holes overlap, leading to a recombination current [145]. Therefore, a transient current response of positive and negative exponential components can be considered, using equation 1.9 [140].

$$\Delta j(t) = \Delta V \{a_1 \exp(-t/\tau_1) - (a_2 \exp(-t/\tau_2))\} \quad (1.9)$$

where a_1 is an arbitrary constant and τ_1 are the accumulation constant and the related time constant, respectively, whereas a_2 and τ_2 are the equivalent recombination constants. The capacitance corresponding to this transient is shown in equation 1.10.

$$\begin{aligned} C(\omega) &= C_0 + C_{acu} - C_{rec} \\ &= C_0 + \frac{a_1 \tau_1}{1 + (\omega \tau_1)^2} - \frac{a_2 \tau_2}{1 + (\omega \tau_2)^2} \end{aligned} \quad (1.10)$$

A detailed description on the impact of the accumulation capacitance with regards to NC is given in chapter 4.4.1.

Again, the physical origin of the transient current response to a voltage step, and its effect on the frequency dependent capacitance, can be broad. In a light-outcoupling device an accumulation of charge carriers and their recombination pathways appear to be connected to the formation of transient current and can thereby lead to NC.

Another issue challenging the development of novel QLEDs is its light-output. One way to assess the performance of a QLED is to measure its external quantum efficiency (EQE), which is the ratio of photons emitted over the amount of injected electrons. With a smaller and more accessible band gap for the injection of charge carriers, red and green QDs typically outperform their larger band gap counterparts [155].

When an exciton is present on the QD and recombines under the emission of light it contributes to the photoluminescence quantum yield (PLQY), relating the amount of photons injected over emitted by the QD. Typically, the PLQY of a QD is proportional to the EQE of a device and can be expressed through equation 1.11, where k_l represents the luminescent and k_{nl} the non-luminescent recombination rates. Obviously, k_{nl} is aimed to be as small as possible in order to maximise the efficiency of the device. In a device three main factors, shown in figure 1.12, can impact the

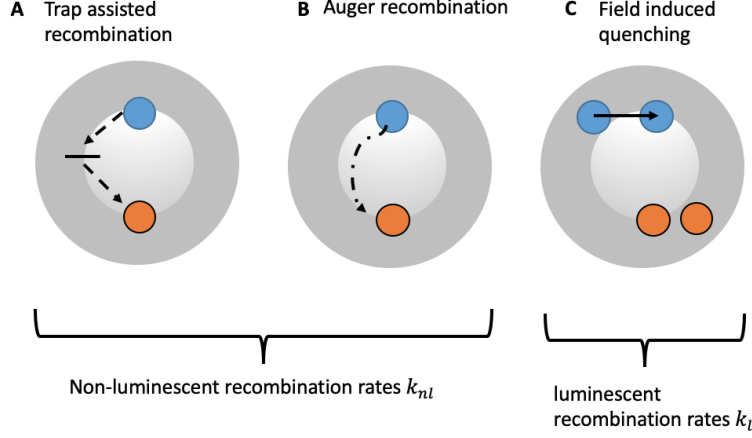


Figure 1.12: Effects for changing the recombination rates: (A) Trap assisted and (B) Auger recombination increase non-luminescent recombination k_{nl} while (C) the operational electric field can impact the luminescent recombination rate k_l , adapted from Bozyigit and Wood [156]

recombination rates k_{nl} and k_l .

$$EQE \propto PLQY = \frac{k_l}{k_r + k_{nl}} \quad (1.11)$$

In a QLED k_{nl} is mainly impacted by free charges and electronic traps between the electrode and QD core. A QD emitter with surface defects, such as through dangling bonds, contributes to trap-assisted recombination. Thereby, both charge carriers relax in a trap state and consequently recombine without the emission of light [156]. Equally, free charges on a QD impact the electron hole balance within the active layer and increase the probability of Auger recombination [157, 158]. Many devices with increased brightness and long time stability use inorganic, metal oxide, charge transport layers or a hybrid combination of organic and inorganic ones [13, 159–162]. Charged trap states within the oxide film are created through non-radiative energy transfer from excitons in the active layer and thereby reduce the EQE of the device further [163]. When a QLED is operated, the active layer is exposed to an electric field in the order of 1 MV/cm [156]. Bozyigit *et al.* [164] have shown that the QLED performance is significantly limited by the electric field which can induce a spatial separation between the electron and hole wave functions and thereby reduce the radiative rate of the exciton.

Typically, growing a shell around the QD core tends to improve passivation of the QD, but dependent on the energy levels of the shell material relative to those of the core, the shell itself can have a positive or negative impact k_{nl} [155, 156]. A

shell strongly confining both electron and hole wave functions on the QD core might passivate the QD and could suppress trap emission, but in reality the shell tends to promote carrier-carrier interactions and thereby increases the Auger recombination rate [74]. If the shell only confines the wave function of one charge carrier to the core, e.g. of the holes, and the wave function of the other carrier, electrons, extends into the shell, the carrier interactions are reduced and so is the Auger recombination rate [155, 156].

It may appear that thick shelled QDs, which offer the best passivation and suppress Auger based non-luminescent recombination, would be the ideal candidate for a QLED. However, "champion devices" did not show rather large shells. Instead, QLEDs with multilayered alloyed structures such as $ZnCdS/Cd_xZn_{1-x}S/ZnS$, $ZnCdS/ZnS$, $CdZnSe/CdZnS$, or $ZnCdSe$ produce the highest EQEs [126, 130, 156, 160]. These results suggest that the applied electric field impacts the luminescence efficiency strongly. With the electric field across QDs increasing, their luminescence decreases, exceeding a factor of 10 [164]. A study has shown that for many QLEDs field-induced luminescence quenching is responsible for an efficiency drop in EQE, whereas the current density plots maintains their performance [165]. A physical understanding of the origins of field-induced quenching in nanocrystals beyond the actual band structure of the QD has not yet been achieved. Time-dependent photoluminescence measurements revealed that the lifetime of the exciton on a QD is not changed in the presence of an electric field, suggesting that non-luminescent recombination rates are not effected either [164]. Hence a decreased electronic confinement of the electron and hole wave function increases field-induced electroluminescence quenching. The ideal QD for an optoelectronic device must therefore show a mediocre degree of exciton confinement: a minimally confined QD might not experience a low PLQY but field-induced luminescence quenching is likely. Conversely, a strongly confined QD might not suffer from quenching due to the presence of an electric field, but charging of a QD might decrease the efficiency of the device [155, 156]. Interestingly, the impact of ligands in a device has not yet achieved much attention: ligand-free QDs with stable electroluminescence have not been reported and such devices might allow a better understanding of QDs in an electric field or in a device architecture.

1.2.5.1 QLED Lifetime

The greatest technological obstacle preventing the commercialisation of electrically driven QLEDs is their operational lifetime. For a TV or smartphone application an initial brightness of $100 \frac{cd}{m^2}$ and a lifetime exceeding 10 000 h is required. The achieved operational lifetimes of red QLEDs have almost reached one hundred thousand hours, but the lifetime of blue QLEDs remains a challenge [117, 166]. State-of-the-art phosphorescent OLEDs with decades of industrial research have achieved lifetimes of over 70 000 h for blue [167] and 10^7 h for red [168] and thereby underline the importance of addressing the stability issues of QLEDs. As with OLEDs, advanced manufacturing and enhanced encapsulation techniques could address these lifetime issues.

Quantum dots themselves have been incorporated into TVs since 2016 when Samsung introduced their SUHD TVs. QDs were used in LCD TVs and convert a white backlight into coloured light, and thereby improving the resolution of the LCD displays. While applying a backlight to a QD-TV may not appear to be a genuine QD-based device, its brightness exceeds those of OLED TVs. With Samsung improving the backlight technology of its QD TVs in 2018, and only slightly increasing the luminous efficiency of its QDs, the commercial availability of a true QD TV with QDs lighting up individual pixels is still a long way off [169].

1.3 Memory Devices

Conventional memories can be split into two main categories: volatile memories, such as random access memories (RAMs), which lose their stored information once the power is switched off, and nonvolatile memories, such as hard disks, which keep stored information even if the power is turned off. Therefore, nonvolatile memory devices have attracted significant attention.

With conventional data storage technologies reaching their fundamental limits, new techniques to store information have become more popular. New memory devices with increased data densities, reduced production costs, potentially on flexible substrates, enhanced read/write cycles and lower power consumption, will be part of next-generation electronics. Those devices will employ light-weight materials, will be smaller and more easily integrated into a chip design, and can enable a more versatile approach to electronics. Hybrid architectures that can combine data storage with a second functionality, such as switching or light emission, have the potential to contribute to the electronics of tomorrow. Nonvolatile thin-film memory devices are great candidates for this aim.

As size and shape not only impact the optical emission but also control precisely the electric and magnetic properties, nanocrystals have been integrated into memory devices over the past decades [170–175]. In particular for low budget applications such as smart cards or wireless ID cards, the solution processability of nanocrystals can be a major advantage over conventional deposition techniques.

1.3.1 Operation of Memory Devices

A discrete memory device typically consists of a semiconducting bistable circuit that can store a binary code. The accessibility of the memory depends strongly on the switching speed of the semiconductor. Therefore, conventional nonvolatile memories are typically incorporated into a metal-oxide-semiconductor-field-effect-transistor (MOSFET) architecture with gate, source and drain electrodes. A floating and physically isolated semiconductor island is coupled to the channel of a field effect transistor and dependent on the applied bias, charges are stored or released from the channel [31].

Changing the electrical resistivity of a material can equally create a switching and charge storing capability. The appeal of such devices is their simplicity: a two terminal device achieves a low and a high resistance by changing the electrical pulse. In recent years, many organic and hybrid inorganic-organic material combinations

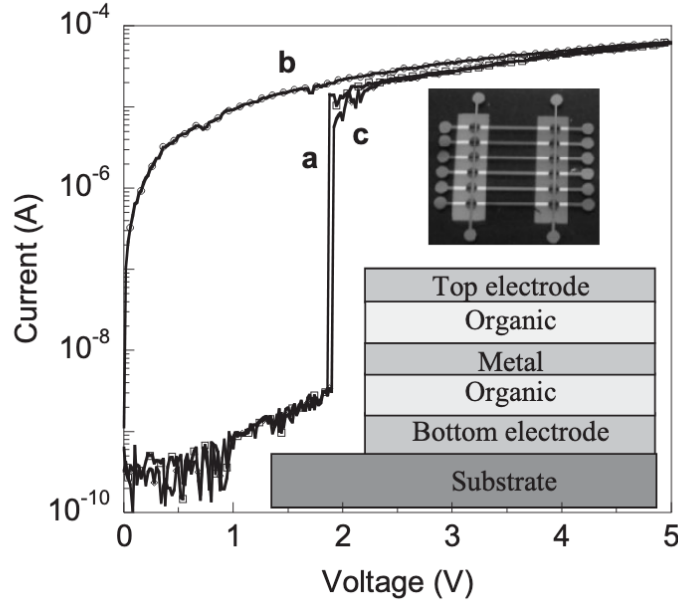


Figure 1.13: I-V characteristics of a memory device: a) and b) show the I-V characteristics of the first and second scan, respectively. Curve (c) is the I-V curve of the third scan after a reverse voltage pulse was applied [176]. The inset shows the design of the trilayer structure leading to the memory effect.

containing metal or semiconductor QDs are considered promising materials for next generation memory devices [31]. The general principle seen in the devices is the closely linked energy barrier within the active layer that prevents charges from recombining and instead stores charges, even after the bias is turned off. These can be trapped, physically separated or transferred to neighbouring layers [176]. Thereby, the materials become polarised and exhibit a low (OFF) and a high (ON) conductance state and qualify for a bistable operation. Furthermore, such bistable devices have been used beyond their memory functionality and could be in display applications as a switchable light emitting diode [177, 178].

Figure 1.13 shows the active layer of a bistable organic semiconductor consisting of organic/metal-nanocluster/organic trilayer structure sandwiched between an anode and a cathode [176].

A current-voltage (I-V) curve for an organic trilayer memory device is shown in figure 1.13. The first voltage scan, curve a, shows a strong increase in the current at about 2 V. If the bias is further increased, the device remains in this high-current state even after bias is switched off, shown in the second voltage scan shown in curve b. Curve c however shows the I-V curve once the device has been reset by applying a negative

bias and the I-V characteristics become nearly identical to curve a [176, 177].

A purely metallic middle layer leads to a nonfunctional memory device; the formation of metal nanoclusters are crucial for the memory effect. Therefore, the middle layer is typically only a few nanometers thick, usually < 10 nm. Electronically, and in a device under forward bias, these clusters can be described as an assembly of quantum wells close to each other. Due to the large band gap of the organic layers surrounding the metal cluster, opposite charges tunnel through the barrier, against the direction of the applied electric field, polarise the metal interlayer, with the charge stored, creating a memory window [179]. When the bias is further increased, holes are injected into the top organic layer and turn the device on by creating an ON state. Under reverse bias, the amount of injected charge decreases making the active layer resistive and forming an OFF, low- conductance state. In this manner, a nonvolatile, memory effect is created. The metal nanocluster interlayer is purely responsible for the storage of charges and exhibits fast, nanosecond switching [176].

Nanocrystals have been introduced into resistive switching devices by blending them with organics [176, 180]. Gold nanoparticles capped with saturated alkanethiols, an inert polymer such as polystyrene (PS) and a conjugated organic compound, 8-hydroxyquinoline (8HQ), were sandwiched between two metal electrodes. Their operational functionality equals those of a purely organic device; however the memory window, the difference between the ON and the OFF state, showed a huge current increase from 10^{-11} to 10^{-6} A [180]. By blending Au nanocrystals with an inert polymer, write-once-read-many times (WORM) electronic memory can be created. A WORM can not be reset to low conductance once it has reached a high conductance state by any positive or negative voltage [181].

Beyond metal nanoparticles, metal oxide particles have also been blended with organics. Electric field-induced charge transfer from organic molecules to oxide nanoparticles increases the amount of mobile charges within the active layer and thereby enhances the memory window [31]. In 2008, Das and Pal [182] measured I-V curves of a monolayer of four different QDs and were able to show electrical bistability, fig. 1.14.

Core/shell quantum dots of various material combinations have been shown to have a memory functionality [31]. Ghosh *et al.* [183] showed that the shell thickness of CdS/PbS core-shell QDs strongly impacts the bistability. They were able to show that a medium shell thickness leads to the strongest bistability, whereas overly thick or overly thin shells tend to decrease the memory window. Fischbein and Drndic [184]

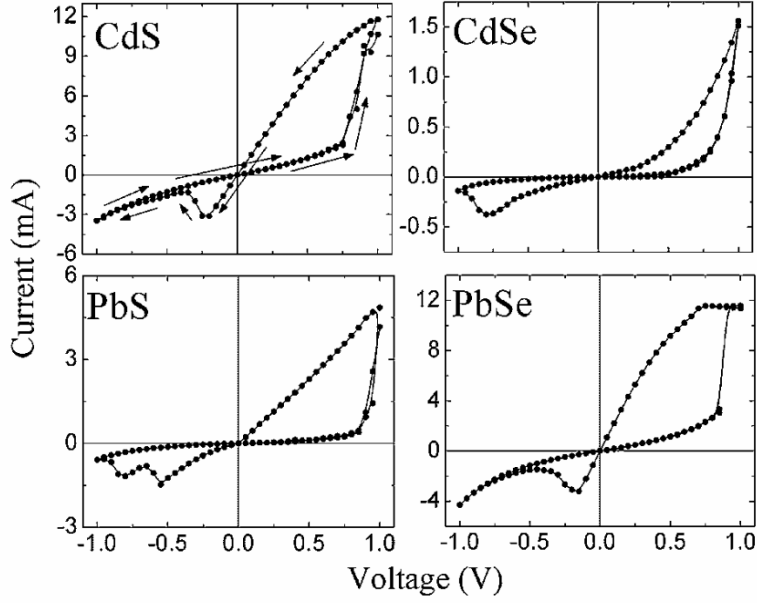


Figure 1.14: I-V characteristics of four different QDs showing a bistability in a voltage loop [182].

showed a CdSe nanocrystal quantum-dot array with a robust memory functionality. Their device can be reset with a voltage pulse but they further found that light can also be used to restore or even enhance the conduction. Upon oxidation of surface states, mid gap states in II-VI or IV-VI QDs can be created that can act as dopants in semiconductors and increase electrical conductivity [31, 185]. So far, a clear understanding about the bistability in nanocrystal solids has not yet been achieved.

1.4 Summary and Thesis Outline - Research Questions

The aim of this introductory chapter is to provide an overview over quantum dots spanning from their synthesis to surface passivation techniques, as well as their incorporation into light emitting diodes. Due to their almost monochromatic emission, QDs are ideal candidates for emitters in light emitting diodes (LED), however, several issues in particular in regards to lifetime and stability have to be overcome. The general principles of an LED and of a memory effect are outlined to create a solid foundation for the discussion of QDs in optoelectronic devices. While ligands are known to play a fundamental role in stabilising nanocrystal shape and size, and therefore the optical and electronic properties, of QDs, their impact in a device has not yet achieved much attention. With a set of five different ligands of various length and electrical conductivity, this thesis aims to better understand how charges travel from the electrodes via the ligands to the QD and finally recombine with the emission of light.

In chapters 4 and 5 impedance spectroscopy is applied to the devices to study how the charge population changes within the active layer. Chapter 4 looks at changes in capacitance of the devices and thereby relates recombination pathways of injected charge carriers. An equivalent circuit is fitted to the measured data in chapter 5. Based on a previously established model, resistive differences are explained and linked to a new capacitive phenomenon in QLEDs. Based on the capacitive and resistive responses, the ratio of luminescent and non-luminescent recombination in a device is outlined. In chapter 6 the light output of a device is studied when it is just turning on. By changing driving conditions of the QLED delayed recombination spike is seen after the bias has been turned off. In chapter 7, the device architecture is slightly changed and a new functionality is added to a quantum dot light emitting diode. The final chapter of this thesis, 8, looks at attempts to overcome the previously described problems and extends the work on blue QDs beyond organic surface protection in a device architecture.

In general, the application of QDs in light emitting diodes is elucidated and challenges and hurdles investigated.

The research described in this thesis aims to answer the following three questions:

- How do the ligands capping a QD influence its device performance ?
- How can charge accumulation on ligands be monitored in QLEDs - optically and electrically ?
- Can accumulated or stored charges contribute to a device functionality ?

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Chapter 2

Experimental methods

Throughout this thesis, a series of experimental techniques have been used to synthesise QDs and to characterise their optoelectronic properties and examine their potential use in LEDs. This chapter includes a description of the most commonly used techniques in this thesis, in order to avoid repetition in the following chapters. Techniques specific to an experiment are explained in the relevant experimental section of each chapter.

2.1 Chemicals

Cadmium oxide CdO (99.95%), zinc acetate dihydrate $Zn(acet)_2$ (>98%, reagent grade), 1-octadecene (ODE) (tech grade, 90%), oleic acid (OA) (tech grade, 90%), sulfur powder (99.98%), tributylphosphine (TBP) (97%), acetone, ethanol, butylamine (99%), octylamine (99%), oleylamine (70%, technical grade), aniline (>99.5%), triphenylamine (98%), PEDOT:PSS (Al 4083), poly(9-vinylcarbazole) (PVK) ($M_w > 20,000$ (GPC), N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)-2,2'-dimethylbenzidine (NPD) (> 99% (HPLC)), chlorobenzene, 3,3',5,5'-tetra[(m-pyridyl)-phen-3-yl]biphenyl (BP4mPy) (> 99% (HPLC)), lithium fluoride, aluminum

All chemicals were purchased from Sigma-Aldrich and were used without further purification. Acetone and ethanol were purchased as analytical grade reagents from Univar, toluene and chlorobenzene from ChemSupply, TBP from Capot Chemical Co. Ltd., PEDOT:PSS was purchased from Heraeus Clevios, PVK and BP4mPy from Luminescence Technology Corp.

2.2 Synthesis of CdS/ZnS Quantum Dots

Since the first report of colloiddally stable and monodisperse CdS nanoparticles both in shape and size, [1] much research has been dedicated to improving synthetic routes [2–5]. The hot-injection synthetic method was the first to reproducibly produce colloiddally stable, uniform nanoparticles with narrow luminescence emission bands. These are important material properties in many electronic devices. The nanoparticles used in this research project were synthesised following a protocol developed by Bae *et al.* [6] whereby 0.5 mmol of cadmium oxide CdO (99.95%), 5 mmol of zinc acetate dihydrate $Zn(acet)_2$ (>98%, reagent grade), 7 ml of 1-octadecene (ODE) (tech grade, 90%), and 3.5 mL of oleic acid (OA) (tech grade, 90%) were firstly placed in a 50 mL round bottom flask. The mixture was heated to 100°C and degassed under vacuum for 1h before it was heated to 310°C under N_2 to form a transparent solution of the metal oleates, $Cd(OA)_2$ and $Zn(OA)_2$. At this temperature, 3 mmol of sulfur powder (99.98%) dissolved in 3 mL of 1-ODE, which was heated to 150°C, was swiftly injected into the reaction flask to trigger the growth of $Cd_{1-x}Zn_xS$ cores. After 6 min, 4 mmol of sulfur powder dissolved in tributylphosphine (TBP) (97%) was introduced into the reactor to overcoat the existing $Cd_{1-x}Zn_xS$ cores with a ZnS shell. The reaction was stopped after 70 min and the flask cooled down to room temperature. The QDs were purified through 3 centrifuge steps: The crude solution was washed by adding acetone until the solution became turbid, usually by doubling the volume. The addition of small amounts of ethanol helped to quantitatively precipitate the particles. The precipitate was collected after centrifugation at 4000 rpm and redispersed in a minimal volume of toluene [3]. The batch was then split into 5 parts and a ligand exchange was performed: For the insulating ligands, (butylamine (99%), octylamine (99%) and oleylamine (70%, technical grade)) an excess of the appropriate amine was added to the QD solution while for the electrically conducting ligands (aniline (>99.5%) and triphenylamine (98%)) a 1 wt% to 10 wt% was added based on the ligand to QD mass ratio, as determined by UV-VIS absorption spectroscopy. All QDs were precipitated another 3 times to ensure that non-binding ligands were washed away. The particles were filtered through a Whatman PTFE filter.

2.3 Optical measurements

For absorbance and photoluminescence (PL) measurements diluted QD solutions with the appropriate ligands were filled into a quartz cuvette with a path length of 1 cm. UV-visible absorbance measurements were performed on an HP Agilent 8453 spectrophotometer where the sample was exposed to white light reaching into the infrared. Light that was not detected by the instrument was either absorbed or reflected. However, as losses were typically very small, the use of an integrating sphere for enhanced sensitivity was usually not necessary.

Fluorescence emission and excitation spectra were recorded on a Horiba Jobin Yvon Fluorolog-3 spectrometer. Electroluminescence spectra of the devices were obtained with a luminescence colour meter (Topcon MB-7A) (integration time 600 *ms*).

TEM images were obtained on a FEI Technai TF20 transmission electron microscope operated at 200 keV. With the image analysis software Image-J, circles were drawn around the nanoparticles to determine their diameters, as well as the packing distance between two nanoparticles [7].

In order to inject charges into a QD film, the band structure, comprising the conduction and valence bands, have to be determined. The optical band gap was determined from the fluorescence spectrum and from UV-VIS absorption following a protocol by Kucur *et al.* [8]. A Riken Keiki Photo-Electron Spectrometer in Air model AC-2 was used to measure the energy of the valence band of the QDs: monochromatic UV photons are generated by a deuterium lamp and focussed on the QDs. Thereby, photoelectrons are emitted from the sample and excited by a weak electric field. During flight time, an oxygen molecule is picked up from the atmosphere and creates a singlet oxygen radical anion that is accelerated and counted at the anode of the measuring system. In order to determine the ionisation energy (IP), the photon energy is plotted against the emission yield. When the sample is exposed to energy below its IP threshold, the photon energy does not change. Once the IP is overcome, the emission yield rises, marks the IP and gives the position of the valence band [9].

2.4 Quantum Dot Device Fabrication

For the reliable deposition of thin films of nanometer thickness, both the spin conditions and the particle concentration are important. The latter was measured in units of mg/ml. A volume of nanoparticles dissolved in a volatile solvent was added to a pre-weighed vial with a septum lid. Dry nitrogen was flowed through a syringe into

the vial to evaporate the solvent. Residual solvents were removed as the particles were vacuum dried for 30 min. The vial was re-weighed and the mass of the particles including the ligands was determined. The particles were then re-suspended in the desired solvent to a desired concentration, usually 20 mg/ml in toluene.

The QLEDs in this study were prepared in a clean room environment and designed with a sandwich architecture based on a patterned Sanyo Corp, 5 mm central indium tin oxide (ITO) striped 150 nm thick, covered glass substrate. The substrates were cleaned in an ultrasonicator with ethanol and water. Before the substrates were used, they were exposed to a UV-ozone treatment for 15 min. For the regular QLEDs, a 70 nm thick PEDOT:PSS (Al 4083) layer was deposited under ambient conditions by spin coating. After annealing at 200°C for 10 minutes a 50 nm thick poly(9-vinylcarbazole) (PVK) film was cast under air from a 10 mg/ml chlorobenzene solution and annealed for 30 minutes at 180°C. For the QLEDs with a memory effect, a 40 nm thick layer of NPB was thermally deposited followed by a 5nm thick aluminium layer.

In both cases, the samples were then transferred into a nitrogen filled glove box. A 25nm QD film of CdS/ZnS core/shell particles was deposited from toluene by spin coating and dried at 120°C for 20 minutes. A 25 nm thick layer of 3,3',5,5'-tetra[(m-pyridyl)-phen-3-yl]biphenyl (BP4mPy) was thermally deposited as the electron transport layer followed by a LiF/Al (1 nm/100 nm) electrode. The electrodes were deposited through a patterned mask with six strips of 2 mm width. Thereby, each substrate had six pixels with each having an area of 2 x 5 mm². Evaporated film thicknesses were confirmed with a Dektak profilometer. A typical device architecture is shown in figure 2.1

2.5 Device testing

Voltage-current-luminescence (VIL) measurements are a standard electrical testing method for optoelectronic devices and characterise the main parameters of an LED. A Keithley 2400 source-measure unit applies a voltage to a pixel and measures the current. Simultaneously, the light output of the pixel is measured through a luminescence colour meter (Topcon MB-7A). An ASEQ LR1 mini-spectrometer was used to measure the electroluminescence spectrum. Memory measurements were performed on an Agilent Semiconductor Analyser B1500A.

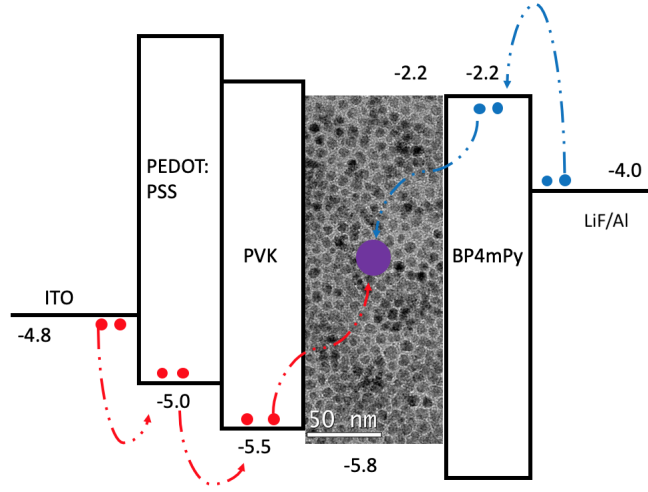


Figure 2.1: Typical QLED architecture used within this thesis.

2.5.1 cAFM resistive measurements

cAFM measurements were performed on a Dimension Icon operating in conductive AFM mode with a TUNA module attached, figure 2.2. Samples were stored in a glove box until measurement. To bias the ITO, silver epoxy was used to contact both the sample and the stage - this was confirmed with a multimeter. A conductive platinum-silicide coated silicon AFM probe was used to initially image the sample with no applied bias, followed by the collection of IV curves at random locations across the sample with the same small normal load applied to avoid short circuits.

2.5.2 Impedance Spectroscopy

Impedance Spectroscopy (IS) is a powerful, more advanced and non-destructive tool for the characterisation of optoelectronic devices. Whereas classic VIL measurements use a direct current (DC), IS applies an alternative current (AC) to the device. With the introduction of a frequency component, time-dependent phenomena can be resolved. Hence, with the ability to separately analyse transport [10, 11], accumulation [12, 13] and transfer [14, 15] phenomena in interfaces of solid state devices and in liquids, IS has become a valuable analytical tool to understand the behaviour of charges [16].

In IS, a DC voltage (V_{DC}) is typically superimposed with an AC voltage of much smaller amplitude ($V_{AC}(\omega)$) to generate a combined voltage signal $\hat{V}(\omega) = V_{DC} + V_{AC}(\omega)$ with ω being the angular frequency. A small angular perturbation of $\hat{V}(\omega)$ guarantees a linear dependence between the voltage $\hat{V}(\omega)$ and the current $\hat{I}(\omega)$ over

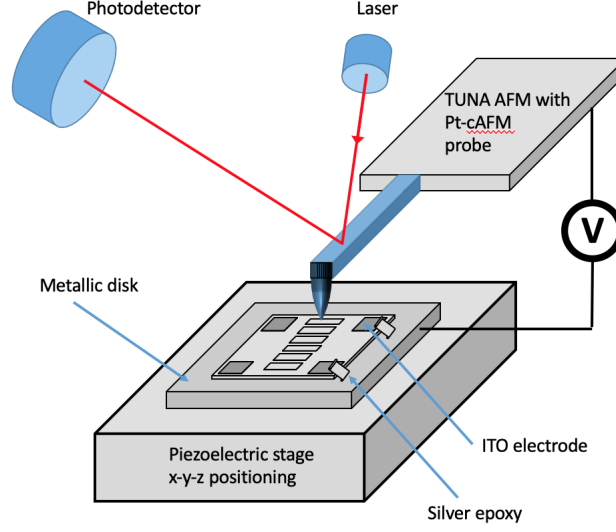


Figure 2.2: Schematic setup of the cAFM measurement system.

a wide range of frequencies. Thereby, stationary conditions are achieved. Unless otherwise mentioned, the AC amplitude was $0.05V$. The impedance $Z(\omega)$ is defined as the quotient of $\hat{V}(\omega)$ over $\hat{I}(\omega)$.

Driving a device with an AC signal reveals information on the electronic insights beyond purely ohmic measurements. With an AC input signal, the magnitude and phase of the resistivity Z , the capacitance C , as well as permittivity ϵ_r , can be measured. Therefore, the aforementioned electrical parameters have an in-phase part (real part) and an out-of phase part (imaginary part). In the case of a resistance measurement, the real part $Re(Z)$ corresponds to the DC resistance whereas the imaginary part $Im(Z)$ is the phase compound. The plot of $Im(Z)$ versus $Re(Z)$ is known as a Nyquist plot.

Capacitance C is defined as the ratio of change of charge ∂Q to the corresponding change in the applied electric potential ∂V and for a simple plate device, this is given by:

$$C = \frac{\partial Q}{\partial V} = \epsilon_0 \epsilon_r \frac{A}{d} \quad (2.1)$$

where ϵ_0 is the vacuum permittivity and ϵ_r is the relative permittivity of the material under investigation, d is the thickness of the layer and A is the area of the device. The time dependent dielectric response of the material, ϵ_r , to an external field is generally complex.

$$\hat{\varepsilon}_r = Re(\varepsilon_r) + jIm(\varepsilon_r) \quad (2.2)$$

Here $Re(\varepsilon_r)$ represents the real part of the dielectric function of the material and $Im(\varepsilon_r)$ represents its imaginary counterpart, while j is the square root of -1. Therefore, capacitance C has a real part $Re(C)$ and an imaginary part $Im(C)$. The dielectric loss $\tan(\delta)$ is defined as the quotient of the imaginary part of the relative permittivity over its real counterpart.

$$\tan(\delta) = \frac{Im(\varepsilon_r)}{Re(\varepsilon_r)} \quad (2.3)$$

This ratio can be understood as the quality factor of the capacitor since it relates the losses over the ability to store charge carriers [17]. Through $\sigma_{ac} = 2\pi f \varepsilon_0 Re(\varepsilon_r) \tan(\delta)$ the loss factor is directly proportional to the frequency (f) dependent *ac*-conductivity of the cavity.

In addition to capacitance, impedance spectroscopy measures the electrical impedance $\hat{Z} = Re(Z) + jIm(Z)$ of a device, with $Re(Z)$ being the real part of the impedance and $Im(Z)$ its imaginary counterpart. The electrical impedance is linked to the real part of the capacitance through equation 2.4

$$Re(C) = \frac{1}{2\pi f} \frac{-Im(Z)}{Re^2(Z) + Im^2(Z)} \quad (2.4)$$

With this equation it becomes clear that a positive capacitance requires a negative value of $Im(Z)$ while a negative capacitance implies $Im(Z) > 0$.

A Solartron SI-1255 and a frequency response analyser system were used for the IS and capacitance measurements within this thesis.

In order to relate the measured properties to a model, IS data is typically fitted to an equivalent circuit. The challenge is to connect the impedance response to physical processes relevant to the experiment. Like mathematical modelling, this involves fitting simulated circuits (equations) to the measured data to get an accurate fit between the simulated results and the experimental data. For optoelectronic devices, an accurate fit with passive compounds is particularly difficult as the software assumes a constant amount of charge carriers within the circuit and, for example, does not take the conversion of electrical charges into photons into consideration. The impedance data was fitted to a model using a least-squares fit by ZVIEW 2.0 software developed by Scribner Associates, Inc.

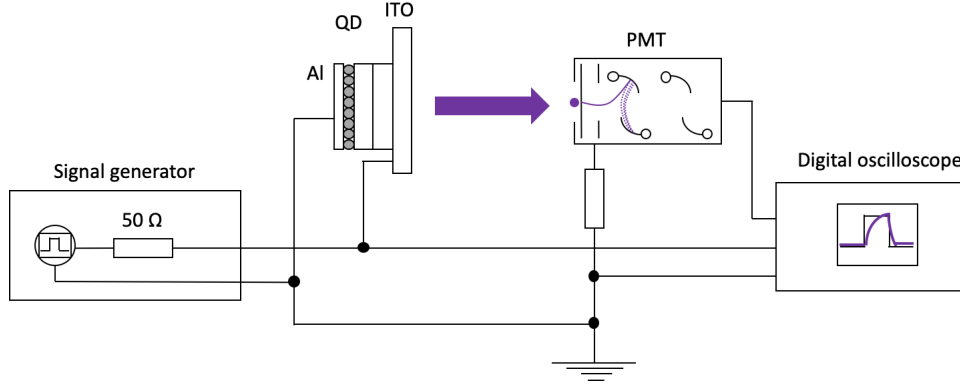


Figure 2.3: Schematic diagram of the test setup of the transient electroluminescence experiments.

2.5.3 Time resolved pulsed electroluminescence

With time-resolved pulsed electroluminescence the early stages of light emission can be studied [18–22]. This includes parameters such as the onset time for light emission [23], its characteristic rise time [24, 25] and various other, fundamental features of a light emitting device such as charge carrier mobility [19, 20, 26, 27] or accumulation and storage phenomena [13, 28]. The test setup used within this thesis is schematically shown in figure 2.3 . Rectangular pulse shapes of various amplitudes were generated by a RIGOL DG4162 Function/ArbitraryWaveform Generator to drive the device. The characteristics of the transient EL were collected with a Hamamatsu Photonics H10721-110 photomultiplier tube operated at its highest sensitivity setting. The electrical input signal and the current response of the PMT were recorded with a RIGOL DG1202 CA digital oscilloscope. All input impedances were set to $50\ \Omega$ and to $1M\ \Omega$ for the PMT.

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Chapter 3

Baseline for QDs and QLEDs

To establish a baseline for further experiments, this chapter summarises the standard device characteristics and points at ligand-dependent differences. Throughout this thesis, the effect of five ligands of various chain length and electrical conductivity was studied. Most of the data provided in this chapter is rather supplementary and presented as additional information in the publications.

3.1 Optical characteristics of QDs

Probably the most intuitive way to study ligand-dependent effects in QDs is to employ optical measurements. Figure 3.1 shows the absorbance and fluorescence spectra for the QDs after the ligand exchange. The excitation wavelength for the fluorescence spectra was 370 nm and the emission spectrum started at 390 nm. Interestingly, the ligand length or its conductivity has no impact on the absorbance or photoluminescence spectrum of the QDs.

Looking at the QDs under the TEM, figure 3.2 reveals some differences: as neither shape nor size are influenced by the ligand exchange, their packing density in a film is ligand-dependent. Purified QDs were diluted to a 10 mg/mL ink and the minimum volume of the nanoparticles was dropped onto a formvar-coated copper TEM grid (Proscitech) and dried under ambient conditions. Compared to the QD concentration used for device manufacturing, the QD concentration for microscopy imaging was further diluted. Thereby, the formation of a single layer of QDs on the grid could be used to determine the packing distance between two QDs.

For each ligand, 100 particles and interparticle distances were measured and averaged. Figure 3.2 and table 3.1 sum the impact of the ligand on the packing within the QD film up. QD films with short ligands, such as butylamine, result in densely packed QDs with small distances between QDs. Amines with a longer chain length, such

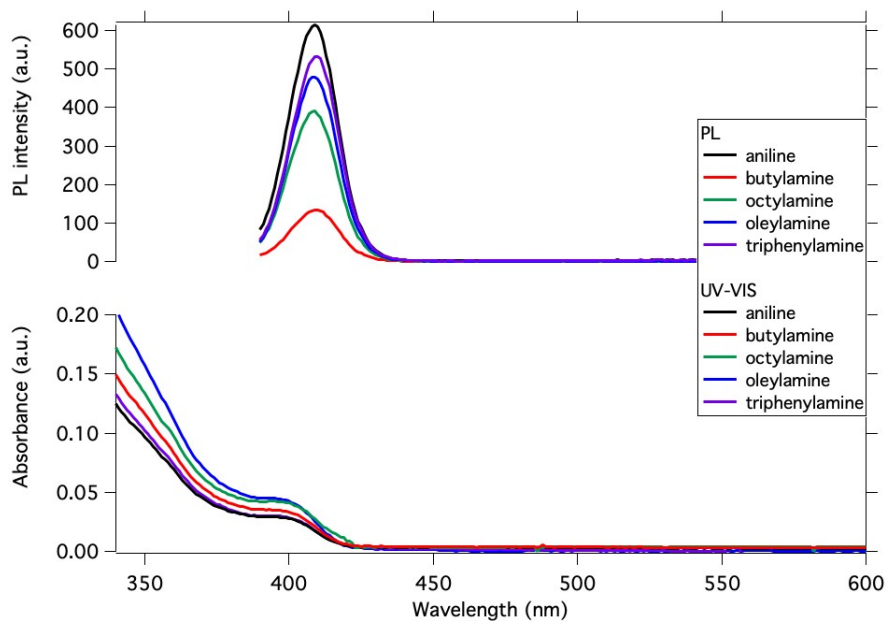


Figure 3.1: Absorbance and fluorescence spectra of the QDs after ligand exchange.

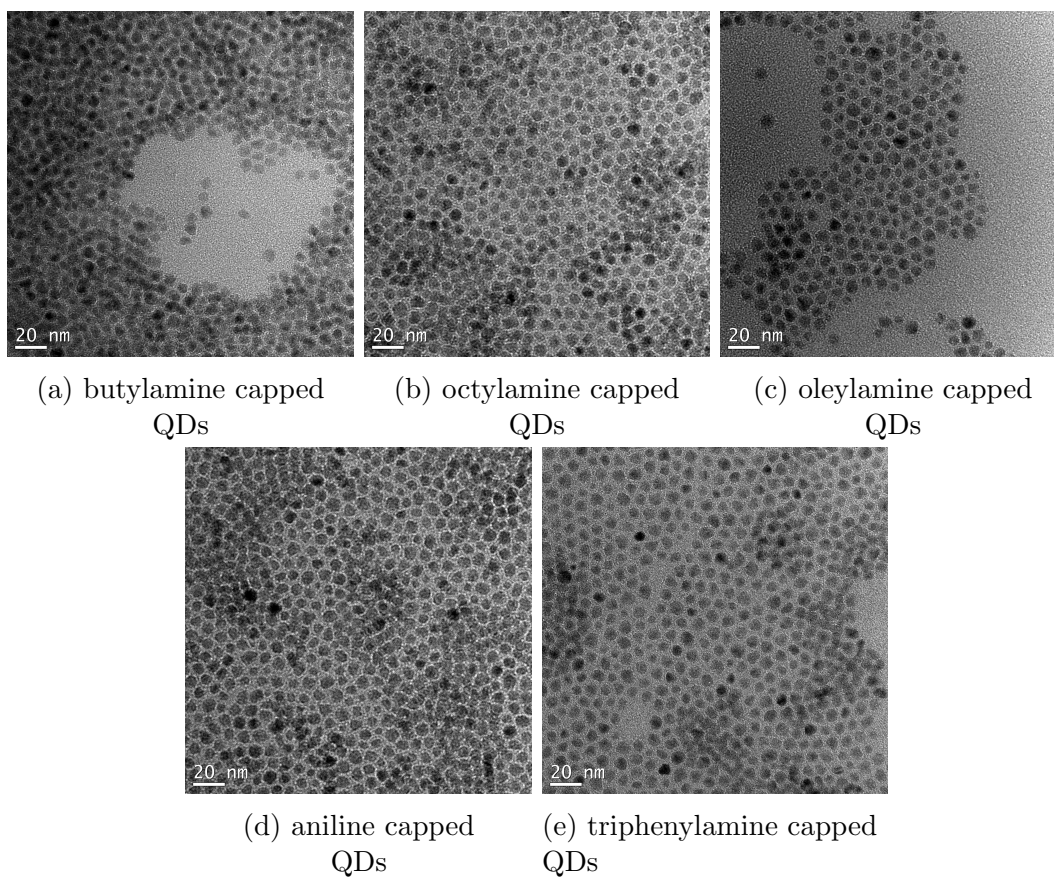


Figure 3.2: Overview of TEM images of QDs with various ligands.

amine	packing distance between QDs (nm)
butylamine	2.1 ± 0.5
octylamine	3.9 ± 0.9
oleylamine	4.8 ± 1.1
aniline	3.8 ± 1.0
triphenylamine	4.0 ± 1.2

Table 3.1: Overview of the packing distance with respect to the ligands surrounding the QDs.

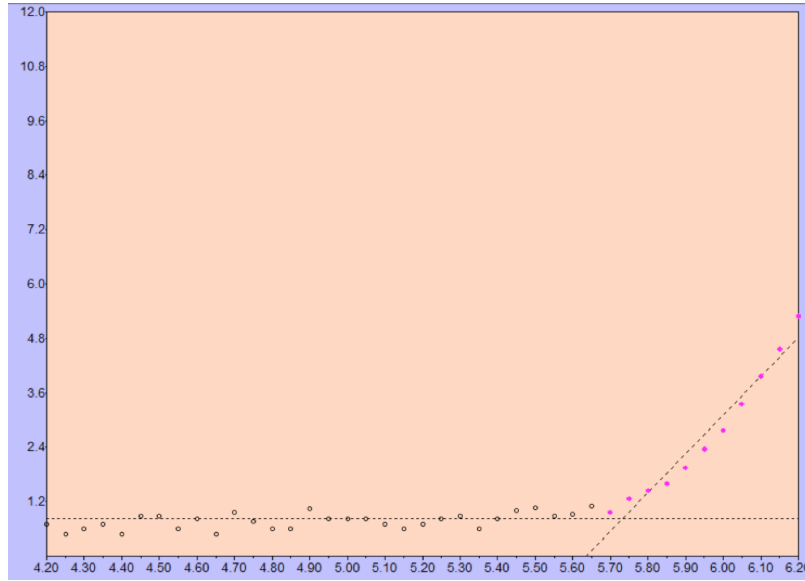


Figure 3.3: Photoelectron spectroscopy in air (PESA) analysis of a QD emitting at 410 nm.

as oleylamine or triphenylamine, increase the inter-particle distance, hence reducing the packing density of the QDs within the film. An increase in amine chain length increases the distance between particles in a film.

3.1.1 PESA measurements

To determine whether the ligand influences the ionisation potential of QDs, photoelectron spectroscopy in air (PESA) were performed. Figure 3.3 shows a PESA analysis of QDs emitting at 410 nm. Their emission wavelength was determined by photoluminescence measurements. QDs of the same emissive wavelength showed almost identical PESA responses. This confirms that the ligands do not influence the ionisation potential of the QDs, hence the same device architecture was applied when studying the impact of ligands in an electromagnetic field.

Flourescence wavelength (nm)	Ionisation potential (eV)	Valance band (eV)	Band gap (eV)
390	2.52	5.70	3.18
411	2.73	5.75	3.02
413	2.75	5.74	2.99
424	2.81	5.73	2.92
438	2.85	5.70	2.85

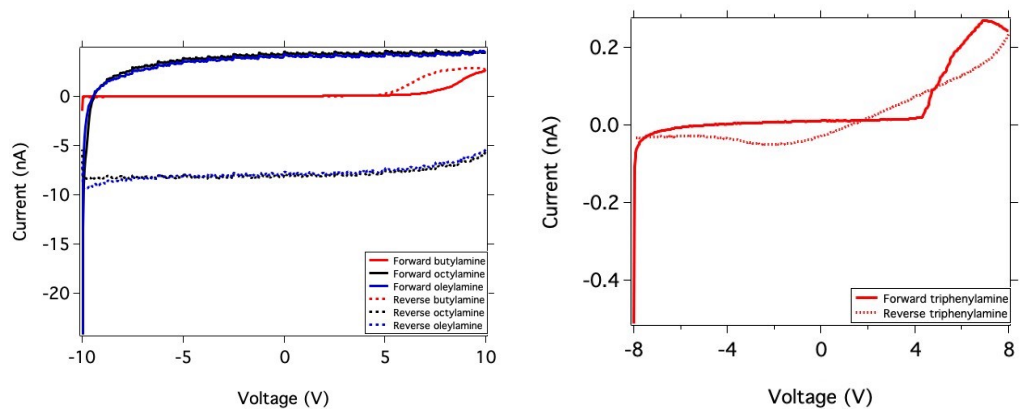
Table 3.2: Overview of the ionisation potential of blue QDs of different size.

Table 3.2 summarises the ionisation potentials for blue QDs of various sizes. Despite changing the size of the QDs, the energetic position of the valence band remains almost unchanged while the ionisation potential decreased with the particle size.

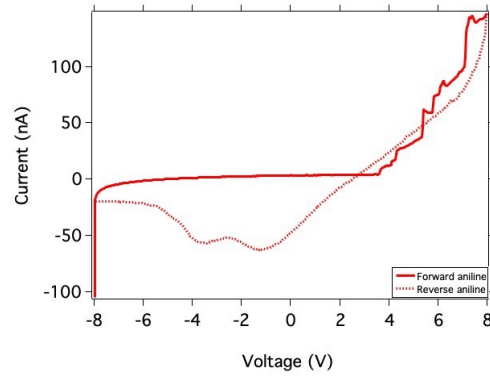
3.2 Electrical characteristics of QDs

Possibly the most obvious electrical characterisation of a QD films is a conductivity measurement. With the aim to study the ligand impact of QDs in an optoelectronic device, such as an LED, the electrical conductivity of the film was measured in a device architecture and through conductive AFM (cAFM). The devices were prepared like a standard device consisting of ITO/PEDOT:PSS/PVK and QDs, all deposited as described in chapter 2.4. The tip of the cAFM was used as the counter electrode for I-V measurements. With the additional charge injection and transport layers a more realistic understanding of the ligand impact in a device is achieved than by simply depositing QDs on a conductive surface.

Figure 3.4b shows the cAFM plots for the QDs capped with the five ligands. For the measurement, performed under ambient conditions, the bias was increased from a low to a high voltage in a forward sweep and decreased from high to low for a reversed voltage sweep. The current through the device was measured in both cases. For all measurements, 15 randomly chosen positions were measured and the I-V data were averaged to establish a general understanding of the film as a whole. For the QDs capped with insulating ligands, figure 3.4a, shows that there is very little electrical conductivity. Of all QDs, the butylamine capped QDs show the smallest hysteresis between forward and backward sweep. For the ligands with longer chain lengths, octylamine and oleylamine, no classical hysteresis was observed but an offset between the forward and backward sweep is seen. This suggests a capacitive behaviour of long-chained ligands. Interestingly, no change in electrical conductivity was seen between octylamine (C8) and oleylamine (C18) despite the carbon length being doubled for



(a) QDs capped with insulating ligands (b) QDs capped with triphenylamine



(c) QDs capped with aniline

Figure 3.4: Overview of cAFM plots of QDs with various ligands.

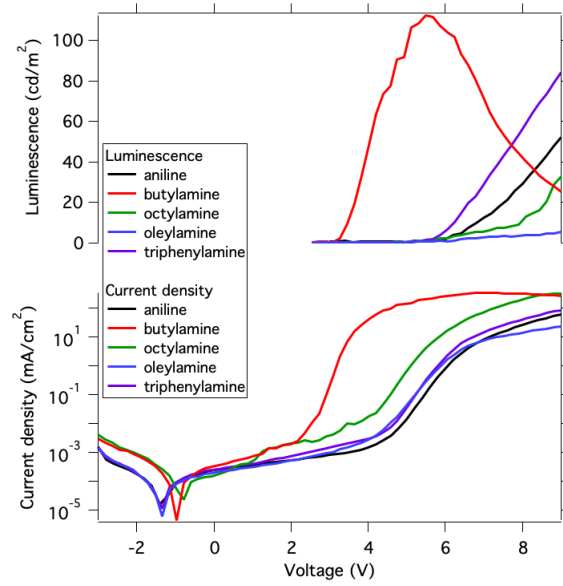


Figure 3.5: Voltage-current density-luminescence diagram for the QLEDs with the ligands under test.

the longest ligand.

When the electrical ligands are exchanged for conductive ligands, figures 3.4b and 3.4c a classical diode behaviour is seen. The triphenylamine case shows a small hysteresis and similar current to the previous currents. When the ligand is changed to aniline, the measured current is almost increased by a factor of 100 and a big hysteresis, in particular for negative bias on the reverse sweep, is measured. Possible reasons for the increased current flow and the strong hysteresis are not clear yet. Oxidation of aniline could create free charges that enhance the flow of current through the device.

Changes in the electrical conductivity of the QD layer suggest a ligand-dependent device performance of the QLED. Table 3.3 and figure 3.5 show a summary of the V-I-L performance of the QLEDs with various ligands. V_{th} is the threshold voltage indicating the injection of holes into the device and V_{on} is the turn-on voltage ($V > 1\text{cd/m}^2$), with before efficiencies reported at V_{on} .

With electrically insulating amines, both voltages shift to higher values with increasing ligand lengths. A longer amine chain length leads to lower electrical conductivity and a reduced QD packing density. Charge transport from the electrodes to the QDs is therefore reduced. Consequently, both the device efficiency and the brightness decrease.

Despite a change in ligand length and conductivity, V_{th} and V_{on} are similar for both

amine			V_{th} (V)	$V_{on}(V)$	efficiency (cd/A)	max. brightness (cd/m ²)
butylamine		insulating	2.8	2.8	0.14	112
octylamine			3.5	5.1	0.09	31
oleylamine			5.0	7.1	<0.03	5
aniline		conductive	4.0	5.9	0.15	52
triphenylamine			5.0	6.2	0.25	83

Table 3.3: Overview of the I-V performance of the QLEDs with various ligands.

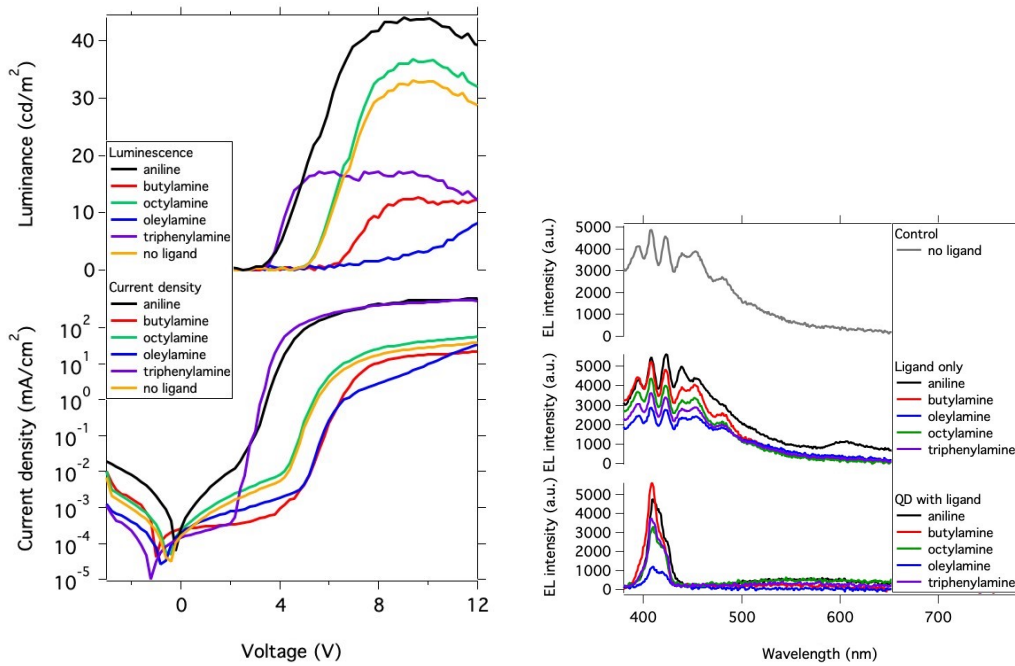
conductive amines. With its $\pi - \pi$ stacking, triphenylamine is the most conductive amine in this study and shows the highest efficiency.

3.2.1 Control devices

In order to study the effect of the capping ligands on QDs in QLEDs, two control experiments were performed: First, an OLED was manufactured where the QD-ligand layer was completely omitted, and no ligand was added. In a second set of control devices, the QD/ligand layer was replaced with a ligand-only layer of the same thickness as in the original device. The V-I-L performance is shown in figure 3.6a. As expected, the conductive ligands, aniline and triphenylamine, show the highest current density in a control device and enhance the flow of charges through the device. When the active layer is replaced with electrically insulating ligands the flow of current is reduced. These results correlate with the conductive AFM measurements from chapter 3.2 and underline the impact of ligands on the device performance.

Even when QDs are incorporated into a standard device architecture, figure 2.1, the electroluminescence spectrum, figure 3.6b, does not show any ligand-dependent changes. The main peak in the EL spectrum can be attributed to QD emission, however, a secondary smaller peak at a slightly larger wavelength is attributed to trap emission from the charge transport layer.

Due to the recombination between the charge transport layers, some electroluminescence is measured for the control devices, as shown in figure 3.6b. For all control devices, independent of the ligand, the EL spectrum shows a triple peak around 415



(a) Voltage-current density-luminescence diagram for the control (Q)LEDs. (b) Electroluminescence diagram for the QLEDs and their control (Q)LEDs

Figure 3.6: Overview of optoelectronic properties of control (Q)LEDs.

nm, followed by a long tail reaching into the green and red. Because the spectrum is very broad it shows strong similarities to an organic emitter. The EL spectrum of a QD in a device, figure 3.6b, shows a single peak around its photoluminescence peak. It can, therefore, be confirmed that electrically conductive or insulating ligands do not impact the EL spectrum of a true QLED.

3.3 Summary

While a change in ligands surrounding the QDs might not impact their absorption or fluorescence characteristics, ligands do change the packing distance between QDs in a film. Long chained ligands increase the space between QDs and show a capacitative behaviour under I-V measurements. Ligands influence the conductivity of the active layer and can thereby control the current density, turn-on voltage and the light output of a QLED. Interestingly, the electroluminescence spectrum is not influenced by the ligand.

In the following chapters the role of ligands in a device is studied, to understand the different device performance that can not be explained by simple changes in electrical conductivity. Therefore, charge injection and their transport to the QD are studied - both from an optical and electrical point of view.

Chapter 4

Negative Capacitance as a Diagnostic Tool For Recombination in Purple Quantum Dot LEDs

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Individual contribution of involved authors

I performed all experiments and analysed the data. Together with Dr Tadahiko Hirai and Prof. Paul Mulvaney I wrote the manuscript.

4.1 Abstract

Impedance spectroscopy (IS) is a powerful and non-destructive tool for studying charge carrier dynamics in quantum dot light emitting diodes (QLEDs). We report here that QLEDs exhibit unique capacitance behaviour that strongly depends on the ligand chemistry of the quantum dots (QDs). At low frequencies and under bipolar injection the capacitance of the QLEDs becomes negative before it returns to positive values at even lower frequencies. This behaviour is fundamentally different to that observed in OLEDs and is attributed to the accumulation of charge carriers within the ligand shells during operation. The capacitive response depends on both the conductivity and the length of the QD ligands, and can be used as a diagnostic tool for understanding the luminescent recombination efficiency of a QLED. We find that short and conductive ligands result in positive device capacitances only and this correlates with enhanced device efficiency.

4.2 Introduction

Over the last decades tremendous improvements in lifetime and brightness have enabled the integration of red and green as well as white organic light emitting diodes (OLEDs) into smartphone displays and TV screens [1–6]. With a 50% brightness drop after 200 000h of operation at 1000 cd/m^2 , and an efficiency of over 30 cd/A for red and 70 cd/A for green emitting devices, these solution processed OLEDs exhibit astounding long term stability. Conversely, blue/purple OLEDs, exhibit lifetimes of several thousand hours only, and typically display decreased efficiencies of around 10 cd/A [2, 7]. Furthermore, their emission is spectrally broad, typically reaching into the green and red [2].

Light-emitting semiconductor quantum dots (QDs) have recently garnered attention because of their potential application in next generation, high-performance displays and solid-state lighting [8–10]. QDs in principle show greater photostability than organic fluorophores and possess size-tunable narrow-band emission spectra reaching from the UV to NIR spectral regions [8, 11–13]. Since the first report of a QLED in 1994, [14] their performance has increased due to improved synthetic routes, as well as development of more sophisticated device architectures, [10] with recent devices displaying brightnesses of over $50\,000\text{ cd/m}^2$ for green light, over $45\,000\text{ cd/m}^2$ for red light and over $10\,000\text{ cd/m}^2$ for blue wavelengths [15]. The reduced performance of blue QLEDs mainly originates from the larger optical band gap, the presence of more

trap states, higher loss factors and the increased difficulties in efficiently injecting charge carriers into the QDs. For blue emission at 452 nm, high operating voltages of over 5V are required to reach a brightness of over 100 cd/m^2 , which decreases the luminous power efficiency and the overall lifetime of the device [10, 16]. These problems are further exacerbated for shorter emissive wavelengths, making purple QLEDs more challenging to fabricate.

Impedance spectroscopy (IS) is a powerful and non-destructive tool for the characterisation of optoelectronic devices; it is particularly suited to study the effect of trap states in large band gap QD devices and their impact on recombination and device performance as a whole. IS has been widely used in OLEDs to determine the injection of charge carriers [17, 18], their transport and mobility through localised states, [19, 20] and finally to determine degradation of electrically-aged OLEDs [21].

Changes in capacitance reflect the changes in density of charge carriers within the active layer and can be used to capture complex and unusual electrical responses with the phenomenon of negative capacitance (NC) being perhaps the most prominent example [22]. The NC effect has been reported in various electronic devices, such as crystalline and amorphous semiconductors, as well as in organic and nanoparticle devices spanning GaAs IR detectors, superconductors and OLEDs [23–32]. As fundamentally different as these devices are, so are the origins of NC, ranging from contact problems which cause parasitic resistances in series, [22, 33] to interface [24] and minority injection [34] problems.

Many systems exhibiting NC consist of a conductor or a semiconductor sandwiched between two electrical contacts, with charge carriers stored and released from trap states when a sufficient bias and ac-voltage are applied. This phenomenon is enhanced in thin interface layers [31, 35] and is theoretically described by a positive-valued time derivative of the transient current response to a voltage step [22].

IS has been applied to QDs integrated into solar cells, with their superior performance electrically modelled through equivalent circuits [36, 37]. The recombination pathways of QD sensitized [37] and core/shell QD solar cells [38] have also been reported. Uddin and Teo [39] have studied the differential capacitance of a hybrid QD/organic LED where the total capacitance of the device can drop below 0 based on the formation of a time-dependent transient current originating from the organic/QD interfacial states. However, this study does not consider the role of recombination pathways in the formation of NC.

In this report, IS is used to study the capacitive and recombinative behaviour of charge carriers in purple QLEDs emitting at 410nm , figure 3.5. We show that varying the

length and conductivity of the capping ligand determines the accumulation of injected charge carriers in the active QD layer. A simple numerical model qualitatively describes the impact of electron and hole accumulation on capacitance. Luminescent recombination leads to a slight drop in capacitance whereas, non-luminescent recombination and the formation of a recombination current are both ligand dependent and lead to negative device capacitances. The dependence of the capacitance on frequency can be used as an indicator for device performance.

4.3 Experimental Procedures

The QDs were synthesised following a protocol developed by Bae *et al.* [40] whereby 0.5 mmol of cadmium oxide CdO (99.95%) , 5 mmol of zinc acetate dihydrate $Zn(acet)_2$ (>98%, reagent grade), 7 ml of 1-octadecene (ODE) (tech grade, 90%), and 3.5 mL of oleic acid (OA) (tech grade, 90%) were firstly placed in a 50 mL round bottom flask. The mixture was heated to 100°C and degassed under vacuum for 1h before it was heated to 310°C under N_2 to form a transparent solution of the metal oleates, $Cd(OA)_2$ and $Zn(OA)_2$. At this temperature, 3 mmol of sulfur powder (99.98%) dissolved in 3 mL of 1-ODE, which was heated to 150°C, was swiftly injected into the reaction flask to trigger the growth of $Cd_{1-x}Zn_xS$ cores. After 6 min, 4 mmol of sulfur powder dissolved in tributylphosphine (TBP) (97%) was introduced into the reactor to overcoat the existing $Cd_{1-x}Zn_xS$ cores with a ZnS shell. The reaction was stopped after 70 min and the flask cooled down to room temperature. The QDs were purified through 3 centrifuge steps: The crude solution was washed by adding acetone until the solution became turbid, usually by doubling the volume. The addition of small amounts of ethanol helped to quantitatively precipitate the particles. The precipitate was collected after centrifugation at 4000 rpm and redispersed in a minimal volume of toluene [41]. The batch was then split into 5 parts and a ligand exchange was performed: For the insulating ligands, (butylamine (99%), octylamine (99%) and oleylamine (70%, technical grade)) an excess of the appropriate amine was added to the QD solution while for the electrically conducting ligands (aniline (>99.5%) and triphenylamine (98%)) a 1 wt% to 10 wt% was added based on the ligand to QD mass ratio, and determined by UV-VIS absorption spectroscopy. All QDs were precipitated another 3 times to ensure that non-binding ligands were washed away. UV-VIS absorption and fluorescence spectra of the ligand exchanged quantum dots are shown in figure 3.1.

The QLEDs in this study were prepared in a clean room environment and designed

in a sandwich architecture based on patterned 150 nm thick indium tin oxide (ITO) covered glass substrate. The substrates were cleaned in a ultrasonicator with ethanol and water. A 70nm thick PEDOT:PSS (Al 4083) layer was deposited by spin coating. After annealing at 200°C for 10 minutes a 50nm thick poly(9-vinylcarbazole) (PVK) film was cast from a 10mg/ml chlorobenzene solution and annealed for 30 minutes at 180°C. The samples were then transferred into a nitrogen filled glove box. A 25nm QD film was deposited from toluene by spin coating and dried at 120°C for 20 minutes. A 25nm thick layer of 3,3',5,5'-tetra[(m-pyridyl)-phen-3-yl]biphenyl (BP4mPy) was thermally deposited as the electron transport layer followed by a LiF/Al (1nm/100nm) electrode.

All chemicals were purchased from Sigma Aldrich and were used without further purification. Acetone and ethanol were purchased as analytical grade from Univar, Toluene and chlorobenzene from ChemSupply TBP from Capot Chemical Co. Ltd., PEDOT:PSS was purchased from Heraeus Clevis, PVK (> 99% (HPLC)) and BP4mPy (> 99% (HPLC)) from Luminescence Technology Corp. UV-visible absorbance measurements were performed on an HP Agilent 8453 spectrophotometer. Fluorescence emission and excitation spectra were recorded on a Horiba Jobin Yvon Fluorolog-3 spectrometer. Luminescence and $I-V$ characteristics were obtained with a luminescence colour meter (Topcon MB-7A) and a Keithley 2400 source-measure unit. A Solartron SI-1255 and a frequency response analyser system were used for the IS and capacitance measurements.

4.4 Simple numerical model

Negative capacitance NC has the same small-signal voltage and current relationship as positive inductance $L = j\omega L = -\frac{1}{j\omega C}$ [22]. However, the treatment of NC as an inductance is not meaningful, because a QLED does not produce a significant magnetic field nor does it display an inductance that increases with frequency. A more suitable interpretation of a NC is based on an analysis of the transient current $\delta j(t)$ response to a voltage step. The total capacitance can then be described through equation 5.1, as the sum of $C_0 = C(\infty)$ as the geometric, frequency independent capacitance and a frequency trap state dependent capacitance. A decrease in capacitance occurs if the function $-d\delta j(t)/dt$ is negative and monotonically increasing to 0, making $C(\omega)$ negative [22, 27]. In the case of a small negative value of $-d\delta j(t)/dt$ the total

capacitance can decrease but remain positive, which we refer to here as decreasing capacitance. If the slope of dj/dt is increased sufficiently we observe two situations: if capacitance drops below 0 and remains negative we refer to this as the OLED NC case [27]. Conversely, if C drops below 0 but then returns to positive values we call this the QLED NC case [39].

$$C(\omega) = C_0 + \frac{1}{\Delta V} \int_0^\infty \delta j(t) \cos(\omega t) dt \quad (4.1)$$

The physical origin of the transient current response to a voltage step, and its effect on the frequency dependent capacitance, can be broad. In this study we propose that the ligand-dependent accumulation of charge carriers as additional cause contributing to the formation of NC. For an optoelectronic device we assume that capacitance depends on the accumulation and recombination of charge carriers. When electrons and holes are injected into the active layer and recombine at a finite rate, a finite volume exists where electrons and holes overlap, leading to a recombination current [27]. Therefore, let us consider the transient current response of positive and negative exponential components, using equation 4.2 [22].

$$\Delta j(t) = \Delta V \{a_1 \exp(-t/\tau_1) - (a_2 \exp(-t/\tau_2))\} \quad (4.2)$$

where a_1 is an arbitrary constant and τ_1 are the accumulation constant and the related time constant, respectively, whereas a_2 and τ_2 are the equivalent recombination constants. The capacitance corresponding to this transient is shown in equation 4.3.

$$\begin{aligned} C(\omega) &= C_0 + C_{acu} - C_{rec} \\ &= C_0 + \frac{a_1 \tau_1}{1 + (\omega \tau_1)^2} - \frac{a_2 \tau_2}{1 + (\omega \tau_2)^2} \end{aligned} \quad (4.3)$$

4.4.1 Relation to numerical model

Assuming that a ligand variation mainly affects the accumulation and transport of charge carriers and has only a small effect on their recombination properties, the impact of the accumulation parameter a_1 can be modelled. The details of the numerical model are listed in Table 4.1. An accumulation of charge carriers leads to an increase in the capacitance as more charge carriers are stored [42, 43]. During recombination, electrons and holes recombine and the population of charge carriers is reduced, hence the capacitance decreases [44].

Figure 4.1 summarises the impact of a_1 on the behaviour of the capacitance, both in a linear and a logarithmic plot [39]. In the OLED NC, fig.4.1c case the capacitance

	C0	a1	τ_1	a2	τ_2
OLED NC	10^{-9}	10^{-6}	2	$2 \cdot 10^{-5}$	1.4
decreasing C	10^{-9}	$1.5 \cdot 10^{-5}$	2	$2 \cdot 10^{-5}$	1.4
QLED NC	10^{-9}	$2.84 \cdot 10^{-5}$	2	$2 \cdot 10^{-5}$	1.4

Table 4.1: Overview of the simulation parameters for the three different cases of negative capacitance in QLEDs

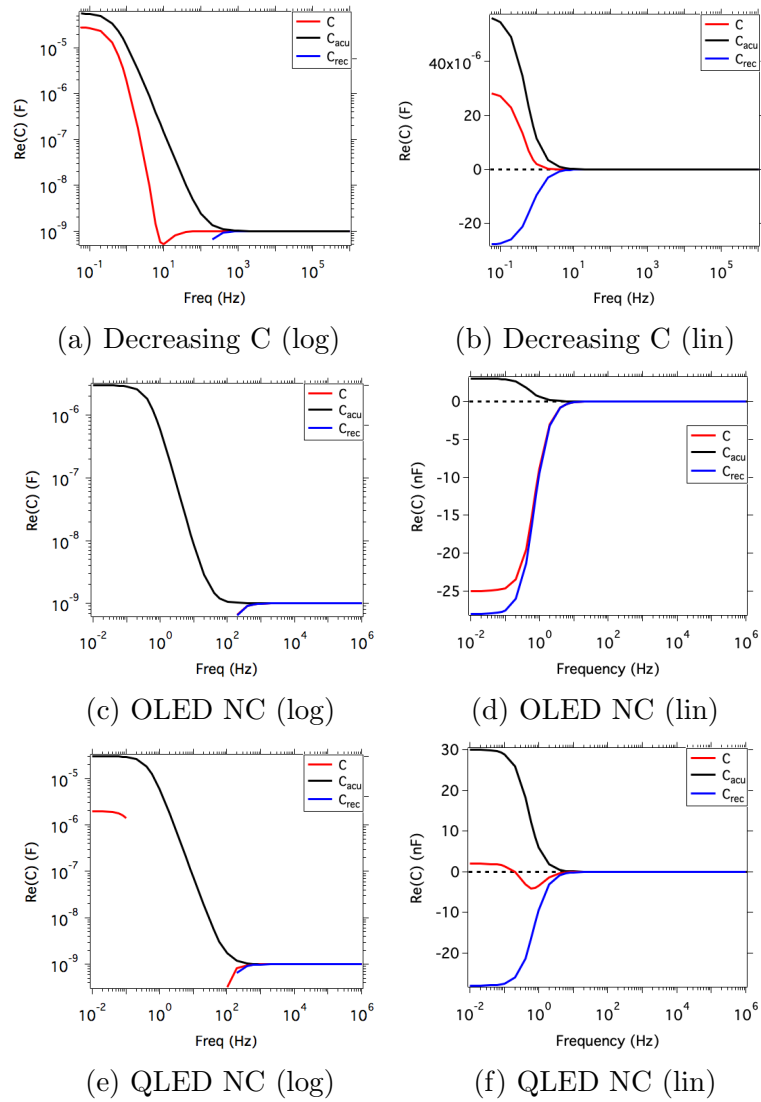


Figure 4.1: Overview of the simulation of the three cases NC dependent on various accumulation constants. Figures 4.1a and 4.1b (decreasing capacitance), figures 4.1c and 4.1d (OLED NC), figures 4.1e and 4.1f (QLED NC) show the different cases of NC in a logarithmic and linear plot, respectively.

drops below 0 at a defined threshold frequency and stays negative for decreasing frequencies [27, 39, 45, 46]. Under fixed recombination conditions the accumulation is lowest in this case and we therefore assume that luminescent recombination is dominant. If the accumulation constant is increased, the decreasing C , fig. 4.1a, case is achieved. In this case the total capacitance remains positive for all frequencies and only decreases slightly for low frequencies before it increases for even lower frequencies. In this case the accumulation is strong enough to maintain a positive capacitance, which is only slightly reduced in case of weak recombination. As the accumulation increases the capacitance increases the QD NC case, fig. 4.1e, is achieved. In this case the capacitance drops below 0 before it returns to positive values for decreasing frequencies. If more charge carriers are injected, this internal capacitance is discharged by generation of a recombination current. In this case non-luminescent recombination is dominant. In impedance spectroscopy this current causes the capacitance to drop below 0.

Experimental data support our model: Figure 4.5 shows the luminescence efficiency of a butylamine capped QLED. At low bias of 4V the efficiency of the device is highest suggesting that most charges recombine under the formation of light and an OLED NC is seen. If the bias is increased, more charges are injected but the device efficiency decreases suggesting that non-luminescent recombination pathways become more dominant and the capacitance follows the QLED NC case.

4.5 Results and discussion

4.5.1 Results of IS measurements

Figure 4.2 compares the real part of the capacitance $Re(C)$ with imaginary part $Im(Z)$ of the impedance, as well as the capacitance loss factor $\tan(\delta)$ of QLEDs, with different insulating ligands (section 2.5.2). The areas of negative capacitance are outlined in the $C - f$ plots. Section 2.5.2 outlines the principles of an in-phase and out-of-phase component of an electrical capacitance as well as for a quality factor for a capacitance.

At low bias the capacitance of QLEDs with oleylamine-capped QDs remains almost constant over a frequency range from 0.4 Hz to 200kHz, as shown in fig. 4.2a. With an increased bias, charge carriers are trapped and, at a bias-dependent threshold frequency the real part of the capacitance increases with decreased frequency. If

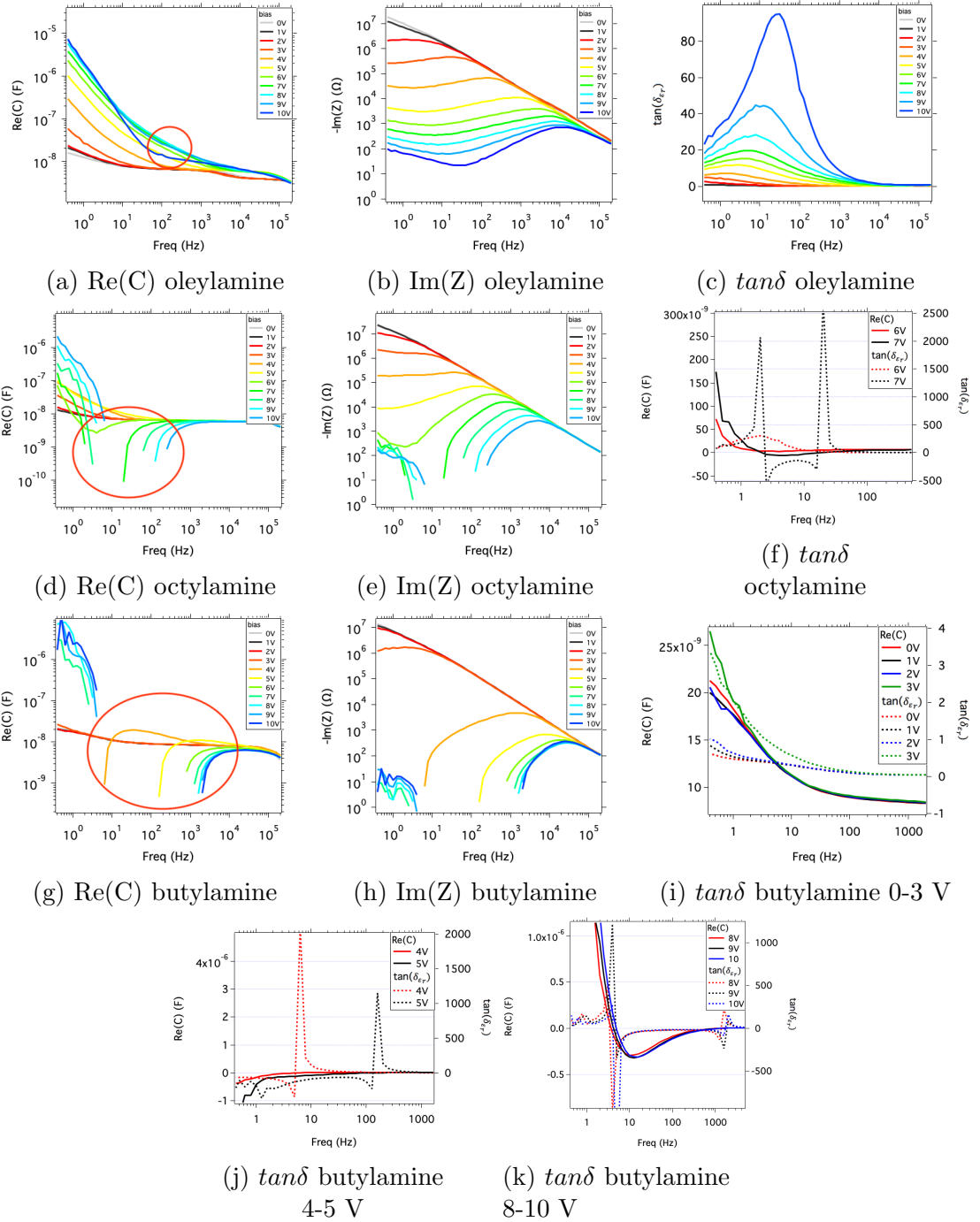


Figure 4.2: Summary of the of the real part of the capacitance, the imaginary part of the impedance and the capacitance loss factor of a QLED with insulating ligands of different length. Figures 4.2a to 4.2c summarise the oleylamine case. Figures 4.2d to 4.2f sum up the octylamine case. Figures 4.2g to 4.2k conclude the butylamine case.

the applied bias is increased charge carriers are trapped at higher frequencies and the capacitance increases with the bias. However, in the 10V case, between 10Hz and 10kHz, the capacitance decreases slightly but stays positive, before it reaches its threshold frequency at 40Hz and increases again. This behaviour is the first indicator of a NC and is referred to here as decreasing capacitance. The QLED with oleylamine capped ligands shows the highest capacitance in this study. Due to the strong insulating properties of the ligand, injection and transport of charge carriers to the QD and recombination are both reduced and instead a large capacitance is observed, fig. 4.2a.

As is evident from figure 4.2b, $\text{Im}(Z)$ increases with increasing bias. The threshold frequency for an almost constant $\text{Im}(Z)$ moves to higher frequencies with an increased bias, resulting in an increase in the density of charge carriers in the active layer. The value of $\tan\delta$ also increases, which implies the active layer is becoming more electrically conductive, as seen in figure 4.2c. The dielectric-loss maximum shifts to higher frequencies with an increased bias.

For the QLEDs fabricated with the shorter octylamine ligand, $\text{Re}(C)$ increases with an applied bias, fig. 4.2d. For a bias of up to 5V, the capacitive behaviour is comparable to the oleylamine analogue with the threshold frequency increasing with the bias. At 6V the capacitance decreases but stays positive (decreasing capacitance case). With a further increase in bias, the real part of the capacitance drops below 0 before it reaches positive values for lower frequencies again. This is referred to here as the QLED-NC case. For a negative capacitance the imaginary part of the impedance becomes positive (equation 2.4). As figure 4.2f indicates, the loss factor increase in the NC case is over fivefold and maximises where $\text{Re}(C)$ reaches 0. The loss factor changes sign and then decreases further. Once a critical loss threshold is reached, $\text{Im}(Z)$ becomes negative and finally $\text{Re}(C)$ becomes positive. With an increased bias the threshold frequency for NC shifts to higher frequencies and the frequency range over which NC is observed is enlarged.

As is the case for longer alkylamine cases, $\text{Re}(C)$ for butylamine-capped QDs increases with bias from $0 < V < 3$, fig. 4.2g, and more charge carriers are injected as $\text{Im}(Z)$ increases. With this bias, the losses increase with an increased real part of the capacitance, fig. 4.2i. Once the bias is further increased to 5V the capacitance drops below 0 and $\text{Im}(Z)$ becomes negative. The dielectric losses maximise when the capacitance reaches 0 and again it changes sign to negative as the frequency decreases further, fig. 4.2j. The losses decrease further and stay negative throughout the decreasing frequency range. Other than in the octylamine case the capacitance does

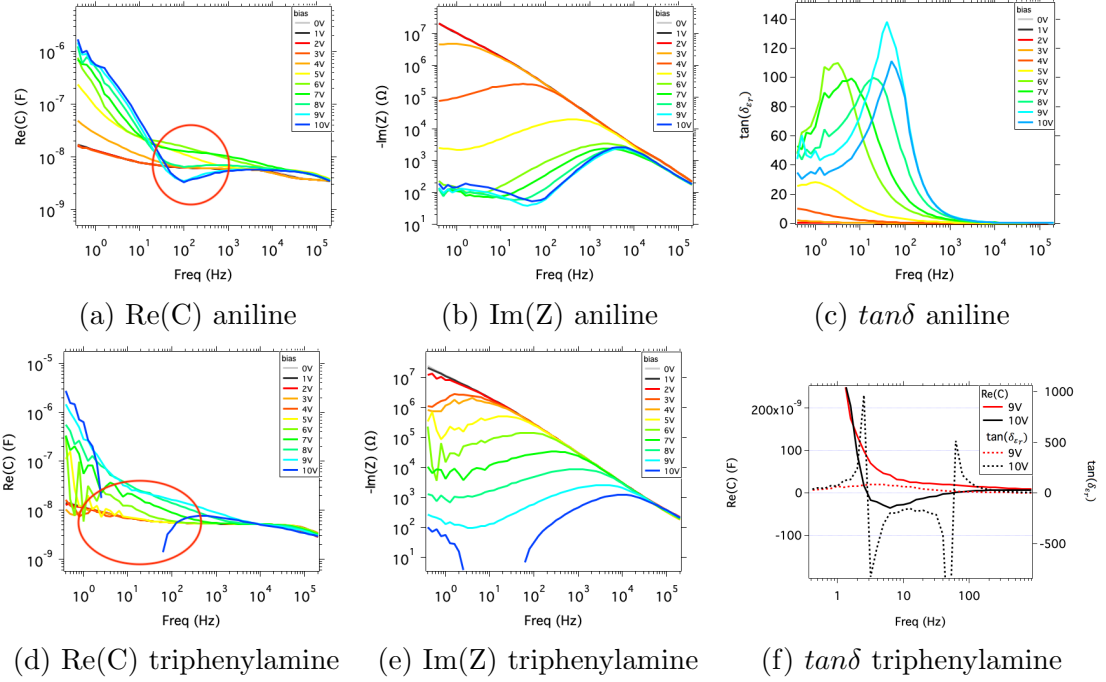


Figure 4.3: Summary of the real part of the capacitance, the imaginary part of the impedance and the capacitance loss factor of a QLED with conductive ligands. Figures 4.3a to 4.3c summarise the aniline case. Figures 4.3d to 4.3f sum up the triphenylamine case.

not return to positive values. This case is very similar to the typical OLED NC case, as reported by Ehrenfreund *et al.* [27]. If the bias is further increased, the "QLED NC" case is established, with the capacitance value dropping below 0 and returning to positive values as the frequency further decreases.

With an increased bias, the dielectric-loss threshold $\tan(\delta)$ for NC decreases, figure 4.2k, indicating that NC leads to a reduced capability to store charge carriers within the device and an increase in dielectric loss, as well as a first indicator of degradation. Whereas the luminescence recombination efficiency of a butylamine capped QLED decreases with bias the QLED NC case becomes more dominant, fig 4.5.

When the insulating ligands are replaced with conductive ones, as shown in figure 4.3, the capacitance behaviour changes significantly. For the aniline case, fig. 4.3a, the capacitance increases with bias and the threshold frequency moves to higher frequencies. The capacitance stays positive for all applied biases and only drops slightly. Along with a more pronounced drop in capacitance, the imaginary part of the impedance decreases but does not change sign (fig 4.3b). As in the oleylamine case, the dielectric-loss factor increases with applied bias and its maximum shifts to higher frequencies, fig. 4.3c. The similarity between electrically insulating and electrically conducting

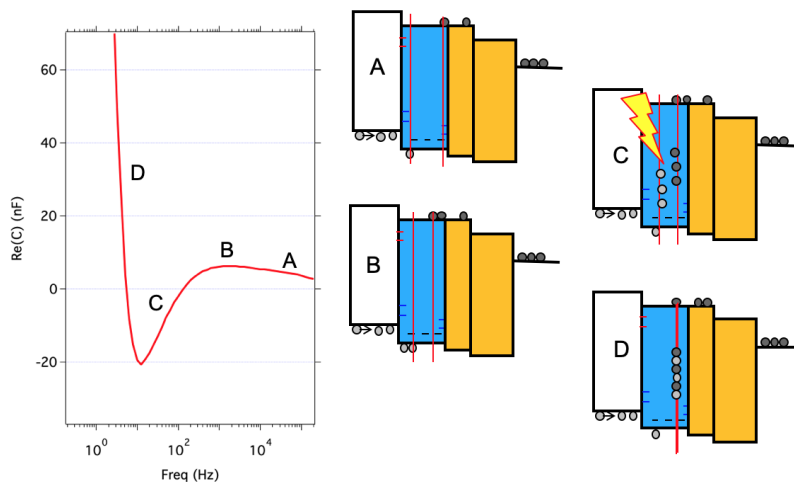


Figure 4.4: Illustration for the interpretation of a negative capacitance in a QLED.

ligands in regards to their capacitance and impedance response are based on a similar amount of charge carriers in the active layer. However, the light output differs quite significantly, suggesting that the recombination efficiency differs greatly between the two ligands, fig 3.5.

The triphenylamine is a larger and more conductive ligand than the alkylamines. In QLEDs with triphenylamine-capped QDs the capacitive response is similar to aniline devices, however under strong recombination the QLED NC case is still observed and the capacitance drops below 0 and returns to positive values with decreased frequencies, figure 4.3d. For the NC, the dielectric-loss factor increases almost five-fold compared to the drop NC in the aniline analogue, fig. 4.3f.

4.5.2 Discussion

Our explanation for the formation of a negative capacitance is shown in figure 4.4. In the simplest case a capacitor consists of two electrodes with a dielectric sandwiched in between. Its capacitance depends on the distance between the plates; the smaller the distance of the plates the larger the capacitance value. In a QLED the frequency determines the amount of charge carriers located in the active layer. At a very high frequency, as shown in region A of figure 4.4, the active area is wide, and the capacitance is low. At this frequency charges get trapped and released at a small time constant making a stationary accumulation of charges difficult. In this case the capacitance value equals its geometric capacitance. When the frequency decreases, shown in region B, charges become trapped and fewer are released from their

trap states leading to charge accumulation and an increase in capacitance. When electrons and holes recombine, the total amount of charges within the active layer is reduced and therefore the capacitance decreases. A decrease in capacitance due to a population change, as shown in region C, is expected within a light out-coupling device. Up to this point OLEDs and QLEDs behave very similarly as in both cases the capacitance can drop below 0. Whereas the organic devices show an only decreasing capacitance their quantum dot counterparts typically show a negative and positive capacitance as illustrated in region D. In organic LEDs a strong luminescent recombination along with little charge accumulation results in a decreasing capacitance. Trap states on the ligands surrounding the QD can store charges, preventing efficient transport to the recombination centre and instead an internal capacitance builds up. When the threshold frequency is reached this capacitance can no longer store charges and it releases charges under recombination current which appears as a negative capacitance. Therefore, a strong negative capacitance in QLEDs can be understood as an over-injection of charge carriers into the active layer, leading to an enhanced non-luminescent recombination. With the frequency further decreasing, charges become more stationary and fill the now vacant trap states and can not be released. Consequently the total capacitance of the device builds up, as shown in region D.

The formation of a recombination current and the increased charge carrier movement can limit the long term stability of the device.

Short and conductive amines show superior behaviour as they enable a high device brightness and efficiency by transporting charges efficiently through the active layer. These ligands enable dense quantum dot packing, resulting in less chance of charge carriers being trapped. By further preventing an accumulation of charge carriers, the dielectric stress and the release of a recombination current are reduced. The capacitance drops only slightly but remains positive over the whole frequency range. However, efficiently transporting charge carriers through the device, while enhancing luminescent and reducing non-luminescent recombination, remains a challenge. We propose that a strong negative capacitance is linked to an over-injection of charge carriers which leads to an increased charge carrier-accumulation time on the ligand. Assuming that only a defined number of electrons and holes can recombine at a given time, more charges are injected into the active layer than can recombine. This leads to an accumulation of charges and an increase in accumulation/storage time, as well as to non-luminescent recombination pathways becoming more dominant. Finally, the

overinjection leads to the discharge of the internal capacitance under the formation of a recombination current, which looks like a NC in Impedance spectroscopy.

In the OLED NC case the applied bias is rather low and the luminescence efficiency is highest. The drop of capacitance is therefore related to the reduced accumulation of charge carriers and is dominated by a strong emissive recombination. The balance between accumulation and recombination shifts towards the latter, leading to a decrease of the overall capacitance. We believe that the overall time constant in this case should be reduced compared to the QLED case.

4.6 Summary

Impedance spectroscopy and the study of capacitance have been used for the first time to determine the effects of ligand length on the recombination of charge carriers in QLEDs. When the conductivity of the active layer is lowered, charge carriers accumulate and create an internal capacitor within the QD layer. At high frequencies, the trap states play only a minor role. However, below a critical frequency the capacitance discharges due to the formation of a recombination current and a negative capacitance is observed. If the frequency is further decreased the capacitance returns to positive values again. A strong negative capacitance is linked to an over-injection of charge carriers, which leads to an enhanced non-luminescent recombination. A simple numerical model relates the impact of the accumulation and recombination of charge carriers to the total measured capacitance. QLEDs comprising QDs with short and conductive ligands exhibit superior performance, because charge carrier transport to QDs is facilitated.

4.7 Acknowledgments

The authors thank the ARC for support through grant No. CE170100026.

4.8 Supplementary Information

Figure 4.5 shows the luminescence efficiency of a butylamine capped QLED.

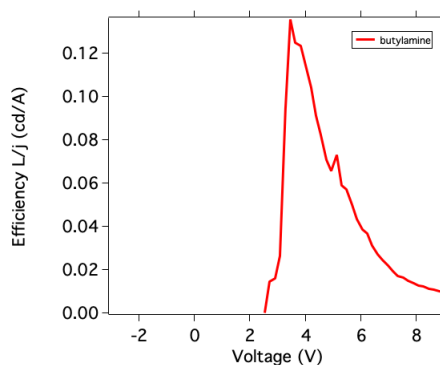


Figure 4.5: Typical luminescence efficiency of a butylamine capped QLED.

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Chapter 5

Inductive Loop: Recombination and Accumulation of Charge Carriers in Purple Quantum Dot LEDs

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The results presented in this chapter are prepared as a manuscript, ready for submission.

Individual contribution of involved authors

I performed all experiments and analysed the data. Together with Dr Tadahiko Hirai and Prof. Paul Mulvaney I wrote the manuscript.

5.1 Abstract

The analysis of purple quantum dot light emitting diodes (QLEDs) by impedance spectroscopy (IS) provides great insight into charge accumulation and recombination mechanisms. At low frequencies, and depending on the ligand, the capacitance can drop below 0 and return to positive values for even lower frequencies. In the impedance plane, a negative capacitance can look like an inductive loop or like an inductive arc. For the first time, we clarify key factors for a negative capacitance and relate the impedance response to the ratio of luminescent and non-luminescent recombination in a QLED.

For the formation of an inductive behaviour, charge carriers accumulate and are trapped on the ligands surrounding the quantum dots. To quantify the trapping of charge carriers, measured IS data is fitted to an equivalent circuit model to determine typical accumulation times of charge carriers. With charges building up, non-luminescent recombination pathways are enhanced and finally the capacitance can become negative. We are thereby able to relate the reduced luminescence efficiency under increased bias to its impedance response and explain an exotic feature of a QLED. By exclusively looking at the impedance response of a QLED we can qualitatively describe the dominant recombination pathway in the device. Additionally, we propose short and conductive ligands for a better device efficiency, reduced non-luminescent recombination and longer device lifetime.

5.2 Introduction

The unique properties of light-emitting semiconductor quantum dots (QDs) in particular their solution processability and tunable narrow-band emissions reaching beyond the visible spectrum [1–4] has garnered attention for their potential application to new generation high-performance displays and solid-state lighting [2, 5, 6]. Understanding the physical properties of QLEDs is critical to controlling the device quality and improving stability of purple/blue QLEDs. Impedance Spectroscopy (IS) is a powerful tool to probe the physical processes inside a QLED, with a focus on charge carrier movement and recombination.

IS measurements have resulted in the identification of many interesting phenomena, most notably negative capacitance (NC) and an inductive loop in the complex impedance response [7–10]. The NC effect has been reported in various electronic devices, such as crystalline and amorphous semiconductors, as well as in organic

and nanoparticle devices spanning GaAs IR detectors, superconductors and OLEDs [7, 11–19]. The origins of NC can fundamentally differ across these devices, ranging from contact problems causing parasitic resistances in series, [8, 20] to interface [12] and minority injection [21], as well as surface polarisation and ionic accumulation [22, 23] problems. Many systems with NC consist of a conductor or a semiconductor sandwiched between two electrical contacts, with charge carriers stored and released from trap states when a sufficient bias and ac-voltage are applied. This relaxation phenomena leading to NC is enhanced in thin interface layers [18, 24] and is theoretically described by a positive-valued time derivative of the transient current response to a voltage step [8]. In the impedance response, this behaviour typically leads to a positive imaginary part and can look like an inductive loop in the cole-cole plot. This phenomena has been reported in polycrystalline [25] and perovskite [10] solar cells based on a surface polarisation model explaining the accumulation of charge carriers at the electron contact electrode.

IS has been applied to QDs integrated into solar cells, with their superior performance electrically modelled through equivalent circuits [26, 27]. The recombination pathways of QD-sensitised [27] and core/shell QD solar cells [28] have also been reported. Negative capacitance in QLEDs has been reported in organic/QD LEDs where the decrease in capacitance is linked to a time-dependent transient current originating from the organic/QD interfacial states [29] but also to a change in population of charge carriers in the active layer [30]. An accumulation of charge carriers at the ligand/quantum dot interface enhances non-luminescent recombination pathways and the formation of a recombination current [7, 8, 30].

In this paper, we relate the impedance response of a negative capacitance of a QLED to the accumulation of charge carriers, and distinguish luminescent from non-luminescent recombination for the first time. Based on a set of five different ligands of different lengths and electrical conductivity, we provide a novel understanding of the accumulation of charge carriers in purple Quantum Dot LEDs. Within the active layer, charge carriers accumulate and cause a build up in an internal capacitance. If a critical frequency is reached the capacitance discharges under the formation of a recombination current and a negative capacitance is observed. If the frequency is further decreased the capacitance returns to positive values. This behaviour can appear as an inductive loop or an inductive arc in the complex impedance diagram.

By fitting measured data to an equivalent circuit model we are further able to link the

accumulation times of charge carriers to both the decrease in capacitance as well as to a reduced luminescent recombination. We are thereby able to explain an inductive loop in a QLED and examine the limitations of the equivalent circuit fitting.

With an interpretation of the impedance response we provide a qualitative method to estimate the ratio between luminescent and non-luminescent recombination in a QLED without having to explicitly measure the light output of the device.

5.3 Experimental Procedures

The QDs were synthesised following a protocol developed by Bae *et al.* [31] whereby 0.5 mmol of cadmium oxide CdO (99.95%) , 5 mmol of zinc acetate dihydrate $Zn(acet)_2$ (>98%, reagent grade), 7 ml of 1-octadecene (ODE) (tech grade, 90%), and 3.5 mL of oleic acid (OA) (tech grade, 90%) were firstly placed in a 50 mL round bottom flask. The mixture was heated to 100°C and degassed under vacuum for 1h before it was heated to 310°C under N_2 to form a transparent solution of the metal oleates, $Cd(OA)_2$ and $Zn(OA)_2$. At this temperature, 3 mmol of sulfur powder (99.98%) dissolved in 3 mL of 1-ODE, which was heated to 150°C, was swiftly injected into the reaction flask to trigger the growth of $Cd_{1-x}Zn_xS$ cores. After 6 min, 4 mmol of sulfur powder dissolved in tributylphosphine (TBP) (97%) was introduced into the reactor to overcoat the existing $Cd_{1-x}Zn_xS$ cores with a ZnS shell. The reaction was stopped after 70 min and the flask cooled down to room temperature. The QDs were purified through 3 centrifuge steps: The crude solution was washed by adding acetone until the solution became turbid, usually by doubling the volume. The addition of small amounts of ethanol helped to quantitatively precipitate the particles. The precipitate was collected after centrifugation at 4g and redispersed in a minimal volume of toluene [32]. The batch was then split into 5 parts and a ligand exchange was performed: For the insulating ligands, (butylamine (99%), octylamine (99%) and oleylamine (70%, technical grade)) an excess of the appropriate amine was added to the QD solution while for the electrically conducting ligands (aniline (>99.5%) and triphenylamine (98%)) a 1 wt% to 10 wt% was added based on the ligand to QD mass ratio, and determined by UV-VIS absorption spectroscopy. All QDs were precipitated another 3 times to ensure that non-binding ligands were washed away. UV-VIS absorption and fluorescence spectra of the ligand exchanged quantum dots are shown in figure 3.1.

The QLEDs in this study were prepared in a clean room environment and designed in a sandwich architecture based on patterned 150 nm thick indium tin oxide (ITO)

covered glass substrate. The substrates were cleaned in a ultrasonicator with ethanol and water. A 70nm thick PEDOT:PSS (Al 4083) layer was deposited by spin coating. After annealing at 200°C for 10 minutes a 50nm thick poly(9-vinylcarbazole) (PVK) film was cast from a 10mg/ml chlorobenzene solution and annealed for 30 minutes at 180°C. The samples were then transferred into a nitrogen filled glove box. A 25nm QD film was deposited from toluene by spin coating and dried at 120°C for 20 minutes. A 25nm thick layer of 3,3',5,5'-tetra[(m-pyridyl)-phen-3-yl]biphenyl (BP4mPy) was thermally deposited as the electron transport layer followed by a LiF/Al (1nm/100nm) electrode.

All chemicals were purchased from Sigma Aldrich and were used without further purification. Acetone and ethanol were purchased as analytical grade from Univar, Toluene and chlorobenzene from ChemSupply TBP from Capot Chemical Co. Ltd., PEDOT:PSS was purchased from Heraeus Clevis, PVK (> 99% (HPLC)) and BP4mPy (> 99% (HPLC)) from Luminescence Technology Corp.

UV-visible absorbance measurements were performed on an HP Agilent 8453 spectrophotometer. Fluorescence emission and excitation spectra were recorded on a Horiba Jobin Yvon Fluorolog-3 spectrometer. Luminescence and $I - V$ characteristics were obtained with a luminescence colour meter (Topcon MB-7A) and a Keithley 2400 source-measure unit. A Solartron SI-1255 and a frequency response analyser system were used for the IS and capacitance measurements.

5.4 Background and Equivalent circuit

A suitable theoretical interpretation of a NC is based on an analysis of the transient current $\delta j(t)$ response to a voltage step [7, 8]. The capacitance can then be described by equation 5.1, as the sum of $C_0 = C(\infty)$ as the geometric, frequency independent capacitance and a frequency dependent capacitance. A decrease in capacitance occurs if the function $-d\delta j(t)/dt$ is negative and monotonically increasing to 0, making $C(\omega)$ negative [7, 8]. In case of a small negative $-d\delta j(t)/dt$ the total capacitance can decrease but remain positive, which is referred to here as decreasing capacitance. If the negativity is increased two phenomena are observed: the capacitance can drop below 0 and remain negative for even lower frequencies or C can drop below 0 and return to positive values for decreasing frequencies.

$$C(\omega) = C_0 + \frac{1}{\Delta V} \int_0^\infty \delta j(t) \cos(\omega t) dt \quad (5.1)$$

In Impedance Spectroscopy (IS) both the resistivity and the capacitance of a device are measured as a function of a small angular perturbation. Equation 5.2 relates the real part of the capacitance to the complex impedance of a device. With this equation, it becomes clear that the imaginary part of impedance, $Im(Z)$, has to change sign for the capacitance to drop below 0. Further, the real part of the impedance $Re(Z)$ does not affect the formation of a negative capacitance.

$$Re(C) = \frac{1}{2\pi f} \frac{-Im(Z)}{Re^2(Z) + Im^2(Z)} \quad (5.2)$$

Capacitance C is defined as the ratio of change of charge ∂Q to the corresponding change in its electric potential ∂V and is defined as

$$C = \frac{\partial Q}{\partial V} = \varepsilon_0 \hat{\varepsilon}_r \frac{A}{d} \quad (5.3)$$

where ε_0 is the vacuum permittivity and ε_r is the relative permittivity depending on the dielectric, d is the thickness of the cavity and A is the area of the electrodes. The dielectric response of a material to an external field can depend on the frequency of the field and reflects the material's polarisation. Since this response does not have to be instantaneous, the dielectric is generally understood as a complex number. $Re(\varepsilon_r)$ represents the real part of the dielectric constant of the material, $Im(\varepsilon_r)$ its imaginary counterpart and j is the complex imaginary number.

$$\hat{\varepsilon}_r = Re(\varepsilon_r) + jIm(\varepsilon_r) \quad (5.4)$$

Therefore, capacitance C has a real part $Re(C)$ and an imaginary part $Im(C)$. The dielectric loss $\tan(\delta)$ is defined as the quotient of the imaginary part of the relative permittivity over its real counterpart.

$$\tan(\delta) = \frac{Im(\varepsilon_r)}{Re(\varepsilon_r)} \quad (5.5)$$

This ratio can be understood as a quality factor of the capacitor relating the losses over the ability to store charge carriers. If this ratio becomes negative we understand this as a big change of charge carriers within the active layer and a discharging of the built-up capacitance [18].

Here we sum up our experimental model of accumulated charge carriers resulting in a NC and an inductive arc or a loop. Based on our experimental data we conclude that the QD ligand has a major impact on the accumulation of charge carriers and

therefore on the formation of a NC and the inductive response.

Recently Ghahremanirad *et al.* [10] introduced an equivalent circuit model based on the accumulation of electric and ionic charge carriers at the electron electrode to describe an inductive loop in the impedance response in pervoskite solar cells. Here we briefly summarise the assumptions leading to this model. Since we see the strongest NC with the shortest organic ligand we believe that the electric accumulation is dominant in our QLEDs.

The accumulation $Q = \rho q$ linearly depends on the elementary electrical charge q and the charge carrier density function ρ . We further understand this accumulation of charge carriers as the formation of an accumulation capacitance $C_{acc} = \frac{\delta Q}{\delta V}$. Assuming a pure accumulation capacitance, the voltage at the accumulation point is $V_{acc} = V - V_{bi}$ where the bias voltage is reduced by a build-in voltage V_{bi} . As the trapping of charges and their accumulation requires a time τ_{acc} , the relative voltage over time at the accumulation point can be described by a relaxation equation (equation 5.6) [22].

$$\frac{\delta V_{acc}}{\delta t} = -\frac{V_{acc} - (V - V_{bi})}{\tau_{acc}} \quad (5.6)$$

In a solar cell, and in the case of a discharging capacitance a recombination current j_{rec} is generated. It is described in equation 5.7

$$j_{rec} = k_{acc} n Q \quad (5.7)$$

which depends on the accumulation rate k_{acc} , the electron concentration n and the accumulated charge Q . The bulk electron concentration is defined as $n = n_0 \exp(qV/k_B T \beta)$ with V being the bias voltage, k_B the Boltzmann constant, T the temperature and β being an ideality parameter. The total current in a transient setting is then given through equation 5.8

$$j = -j_{rec0} + C \frac{\delta V_s}{\delta t} \quad (5.8)$$

with $-j_{rec0}$ being the recombination parameter at steady state.

In IS a constant dc bias is superimposed by a small ac signal with an angular frequency ω and the device's capacitive and resistive responses are measured. By applying the Fourier transform the small signal amplitude current is given through equation 5.10 where steady state characteristics are indicated through overbars and small amplitude

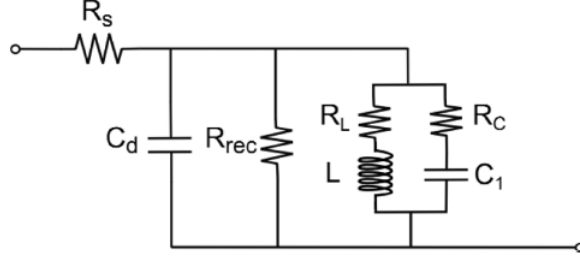


Figure 5.1: Equivalent circuit modelling the accumulation of charge carriers in the devices. R_s represents the serial charge injection resistance, C_d is the dielectric capacitance and R_{rec} the recombination resistance. R_c and C_1 represent the internal charging of the active layer through a resistor and an accumulation capacitance whereas the discharging/recombination of charge carriers is modelled through a resistor R_L and an inductance L [10].

changes through tildes, j represents the complex imaginary number. The factor 2 results from a purely electronic accumulation capacitance [33].

$$\tilde{j} = j_{rec0}^- \left[\frac{q\tilde{V}_s}{2k_B T} + \frac{q\tilde{V}_s}{\beta k_B T} \right] + j\omega C\tilde{V}_s \quad (5.9)$$

The small perturbation voltage is derived from the Laplace transform of equation 5.6 and is given through

$$\tilde{V}_s = \frac{\tilde{V}}{1 + j\omega\tau_{acc}} \quad (5.10)$$

The impedance response Z is then given through equation 5.11.

$$Z = \frac{\tilde{V}}{\tilde{j}} = \left[j\omega C_d + \frac{1}{R_L + j\omega L} + \frac{1}{R_{rec}} + \frac{1}{R_C - \frac{1}{j\omega C_1}} \right]^{-1} \quad (5.11)$$

In an equivalent circuit the electronic components represent the following model parameters:

$$\begin{aligned} R_{rec} &= \frac{\beta k_B T}{q\tilde{j}_{rec}} \\ R_L &= \frac{2k_B T}{q\tilde{j}_{rec}} \\ L &= \tau_{acc} R_L \\ R_C &= \frac{b\tau_{acc}}{C_1} \end{aligned} \quad (5.12)$$

Figure 5.1 shows the equivalent circuit based on the previous assumptions.

In the proposed equivalent circuit, the parallel $R_{rec} - C_d$ represents the standard

ac circuit for an optoelectronic device based on recombination. Further, there are two parallel branches that correspond to the trapping and accumulation. First, the $R_C - C$ represents the charging and discharging of charge carriers determined by the accumulation time τ_{acc} . The second branch with the $R_L - L$ circuit represents the time delay in the charging due to delay of τ_{acc} , described by equation 5.6.

As Ghahremanirad *et al.* [10] reported, this equivalent circuit shows two positive arcs with R_{rec} and R_L determining the diameter of the arcs. When τ_{acc} and C_1 are increased the inductance becomes more dominant and leads to a positive inductive loop. If τ_{acc} is further increased the loop gets enlarged, crosses the x -axis and becomes negative. In this case the capacitance drops below 0. The inductance in this circuit is required to model the accumulation and the release of an oppositely directed recombination current due to the recombination behaviour of some charge carriers. Despite a negative capacitance might look like an inductance, this interpretation is unphysical as the inductance increases with decreasing frequencies.

5.5 Results and discussion

Three different types of negative capacitance have been described for quantum dot light emitting diodes [30]: the capacitance can decrease but remain positive, it can drop below 0 and stay negative for decreasing frequencies but it can also return to positive values for decreasing frequencies (fig. 5.2a, 5.7a, 5.8a). In order to confirm that the described impedance response is directly linked to a ligand/quantum dot phenomenon two control experiments were performed: first, an LED without the ligand/quantum dot layer was manufactured and IS performed. In this case, the device performs like an OLED with capacitance dropping below 0 at a threshold frequency and remaining negative for even lower frequencies. In a second control experiment the QD film was replaced by a film of the relevant ligand at the same thickness as the initial quantum dot layer and IS performed. Despite the ligand film changing the conductivity of the active layer, the capacitive response remains unchanged: as before, at a threshold frequency, capacitance drops below 0 and remains negative for even lower frequencies. The results of the control experiments are shown in the supplementary information with figure 5.10 showing the capacitance-frequency response and figure 5.11 showing a typical cole cole plot. All devices were operated at 7V. We therefore conclude, that the effect of capacitance dropping below 0 and returning

amine	applied bias (V)	positive capacitance	negative capacitance		
			positive arc		inductive loop
			Re(C) remains negative	Re(C) returns to positive	Re(C) returns to positive
butylamine $V_{on} = 3V$	4 – 6		x		
	7 – 8			x	
	9 – 10				x
octylamine $V_{on} = 3.5V$	4 – 6	x			
	7 – 10				x
oleylamine $V_{on} = 5V$	4 – 10	x			
aniline $V_{on} = 4V$	4 – 10	x			
triphenylamine $V_{on} = 5V$	4 – 8	x			
	9 – 10			x	

Table 5.1: Summary of the ligand based negative capacitance and the corresponding impedance answer. A bipolar injection of charge carriers leads to a negative capacitance, resulting in the impedance answer in an inductive arc or in an inductive loop.

to positive values for even lower frequencies is a quantum dot/ligand phenomenon. Further, the impedance response with an inductive loop i.e. an inductive arc is not related to the QLED design but only to the quantum dot/ligand interface.

Table 6.1 summaries the capacitative and impedance response with respect to 5 different ligands. It becomes clear that in the impedance response, a negative capacitance can look like either an inductive loop or like an inductive arc.

A decreasing but overall positive capacitance is the initial step of a negative capacitance which is summarised in figure 5.2 with figure 5.2a showing the typical capacitance-frequency and figure 5.7b the impedance response. At low frequencies the capacitance decreases but remains positive before it finally increases at even lower frequencies. We assume that at low frequencies trapped charge carriers can be released and recombine. Therefore, within a small frequency range, the population of charge carriers is significantly reduced leading to a decreased capacitance value. The cole-cole plot represents a typical R-C circuit where luminescent recombination is dominant. $-Im(Z)$ decreases with frequency and reaches its minimum with the lowest capacitance value but does not change sign. With further decreasing frequencies the capacitance increases again. In the impedance plane, this behaviour leads to a positive arc shaped increase of $-Im(Z)$ towards higher resistive values since the

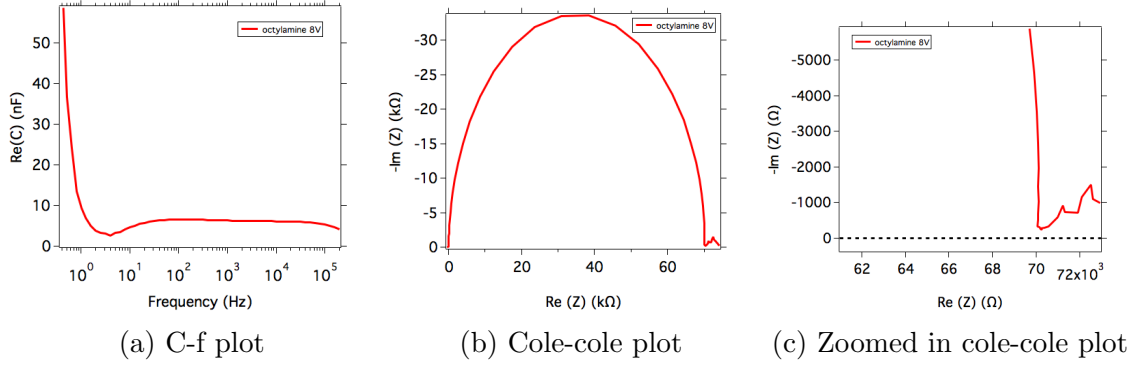


Figure 5.2: Typical measured $C - f$ plot and complex plane impedance plots for a purple QLED showing a decreasing capacitance.

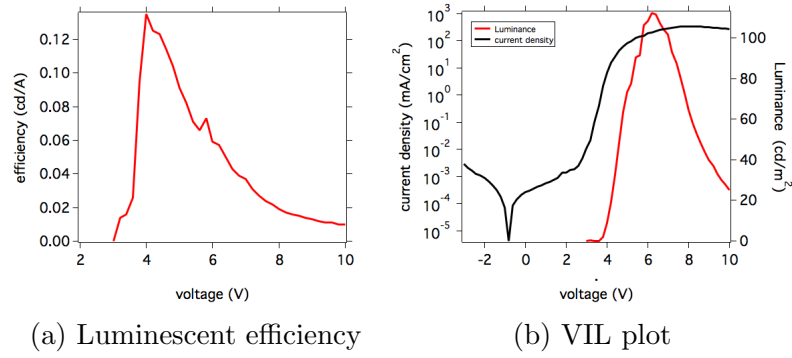


Figure 5.3: Typical luminescent efficiency and VIL diagram of a butylamine capped QLED.

disappearance of charge carriers increases the resistivity of the device.

A full negative capacitance is only seen under bipolar injection [7] indicating that the recombination of charge carriers is closely linked to the decrease of capacitance below 0. Once the capacitance changes sign, the imaginary part of the impedance becomes positive, equation 5.2, and the total impedance can either open towards higher resistive values and form an inductive, positive arc or towards a lower resistivity values and create an inductive loop.

Since butylamine, the shortest ligand in the study, shows a negative capacitance with all three impedance responses we want to use this example to explain the different accumulation and recombination properties within the QLED. Figure 5.3a relates the luminescent efficiency of a butylamine capped QLED to the applied bias.

At low bias, and once a critical frequency is reached, $\text{Re}(C)$ drops below 0 and remains negative for decreasing frequencies.

In this case, figure 5.4c indicates a strong accumulation of charge carriers making the

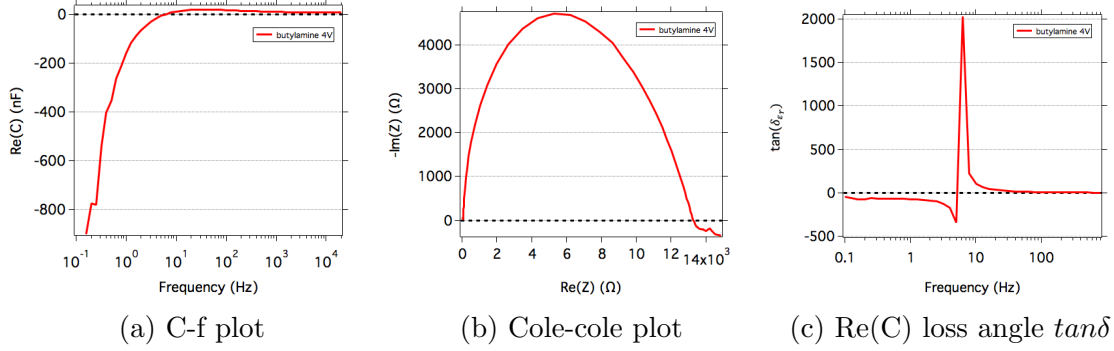


Figure 5.4: Typical $C - f$ plot and complex plane impedance plots, and a $\tan\delta$ -frequency plot for a purple QLED showing a negative capacitance which remains negative for decreasing frequencies.

active layer very conductive before the capacitance decreases below 0. At a bias of 4V and at a low frequency of 20Hz, charges get trapped on the ligand and the loss factor $\tan\delta$ increases strongly within a small frequency range and finally peaks at 8Hz. When the capacitance finally becomes negative, this internal capacitance gets discharged and $\tan\delta$ changes sign. Physically, the internal capacitance can no longer store charges and releases charge carriers under the formation of a current. The ratio between the positive overshoot and the negative undershoot is roughly 20 : 3. With decreasing frequencies $\tan\delta$ remains at a constant negative value indicating a steady and almost constant recombination rate of charge carriers. With more charges disappearing, the active layers gets less conductive and the impedance response forms an arc opening towards more resistive values. In this case, the device shows the highest luminescent efficiency indicating that luminescent recombination is dominant.

With increased bias, figure 5.5 the active layer becomes less resistive, fig. 5.5b, and the trap states are filled quicker. Compared to the previous case, figure 5.4, the amount of accumulation in figure 5.5c is reduced.

When the capacitance changes sign $\tan\delta$ becomes negative. The positive accumulation $\tan\delta$ is roughly 50% larger than its negative counterpart indicating a slower recombination. Therefore, a great amount of charge carriers recombine and push $\text{Re}(C)$ below 0. With a negative slope, $\tan\delta$ is further decreasing indicating that the active layer becomes more deprived of charge carriers and hence more resistive. With more charges recombining than being injected or released from trap states, $\tan\delta$ decreases further. Therefore, the impedance response opens towards more resistive values. When the capacitance returns to positive values the dielectric loss angle drops

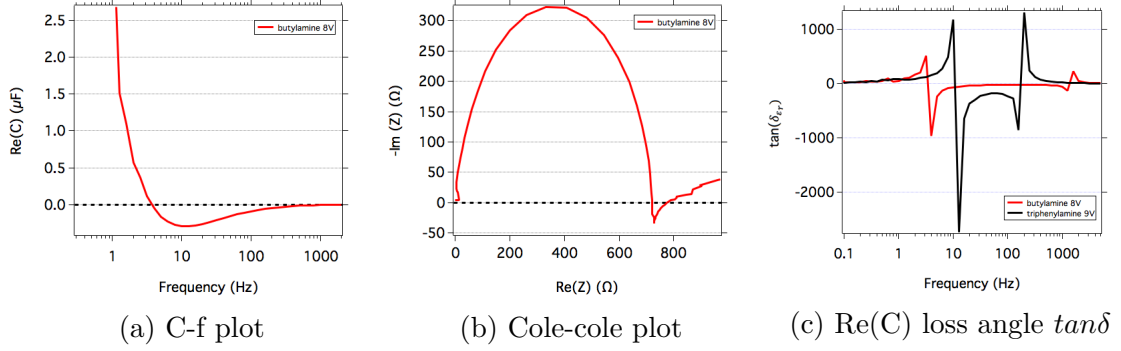


Figure 5.5: Typical $C - f$ plot and complex plane impedance plots, and a $\tan\delta$ -frequency plot for a QLED showing a NC which returns to positive values for decreasing frequencies.

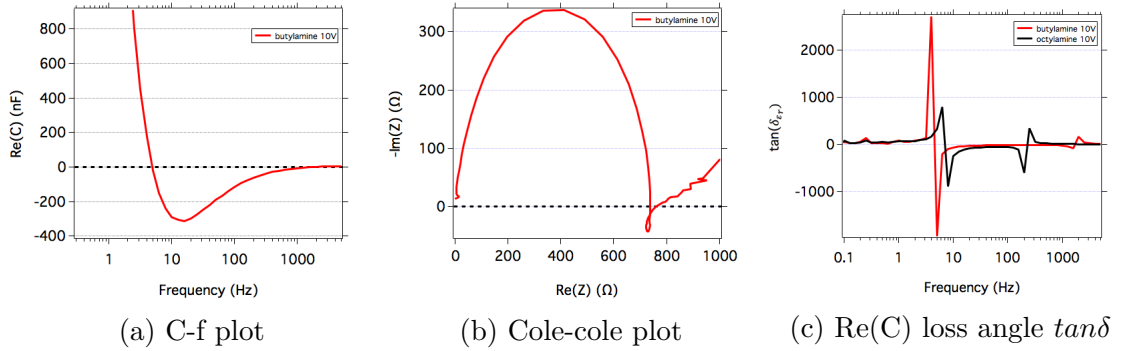


Figure 5.6: Typical $C - f$ plot and complex plane impedance plots, and a $\tan\delta$ -frequency plot for a QLED showing a NC which returns to positive values for decreasing frequencies.

strongly before it changes sign and reaches almost its maximum value again. After a strong recombination the internal capacitance can store charges again. With decreasing frequencies the accumulation is slowly reduced. Since the total luminescence efficiency is reduced, despite an increased injection of charge carriers we assume that the luminescent recombination becomes less pronounced and non-luminescent recombination becomes stronger.

If the bias is further increased to 9V and 10V, fig. 5.6, the capacitive response as well as the total resistivity of the device remain similar to the previous case. The impedance response however opens towards lower resistive values and forms a loop. The amount of accumulated charges is further reduced suggesting an already fairly conductive active layer. Once the internal capacitance can no longer store charges the capacitance drops below 0. The undershoot of $\tan\delta$, fig. 5.6c is still larger but closer to its overshoot counterpart indicating a larger recombination than accumula-

tion. With $\tan\delta$ having a positive slope, the resistivity of the active layer is reduced leading to an inductive loop in the impedance plane. Despite a recombination and a change in population of charge carriers in the active layer, the amount of injected carriers remains high keeping the device fairly conductive. At the turnover back to positive capacitance values, $\tan\delta$ increases again suggesting that the internal capacitance regained its charge storage capability. With a large amount of charge carriers injected and the formation of an inductive loop opening towards lower resistive values and lowest luminescent efficiency, non-luminescent recombination is dominant.

Octylamine is a longer and therefore more insulating amine. In case of negative capacitance, the impedance response shows an inductive loop. We assume that due to the longer ligand charges are more likely to get trapped but are still sufficiently transported to the QD to recombine. The active layer remains relatively conductive and the amount of recombined charges is comparably small leading to a less resistive active layer and an inductive loop in the impedance response.

Triphenylamine, however, is a longer, but due to its π - π stacking, conductive amine which transports charges efficiently to the QD. With the enhanced transport a large internal capacitance builds up and discharges under the formation of a negative capacitance. With a large amount of charge carriers in the active layer non-luminescent recombination pathways become more likely. With the strong recombination, the impedance response increases towards the more resistive side and forms an inductive, positive arc.

By changing the ligands, the formation of a negative capacitance can be prevented. With oleylamine, a very long and electrically insulating ligand, the turn on voltage is increased. Charges get trapped on the ligand and their transport to the QD is reduced. Therefore, fewer charge carriers are injected into the QD and only a small change in population due to recombination is seen. All in all this leads to a completely positive capacitance answer. Both the high turn on voltage and the limited light output are not ideal for an efficient device.

Aniline however, also shows a positive only capacitance as well. We assume that a short and conductive ligand is less likely to trap charges but instead transports charges efficiently to the QDs. With reduced trapping, charge carriers are less likely to accumulate and build up an internal capacitance which leads to a more efficient device and preventing the capacitance from dropping below 0.

With the a negative capacitance leading to the formation of a recombination current and the formation of an inductive arc or loop which can be linked to the ratio of

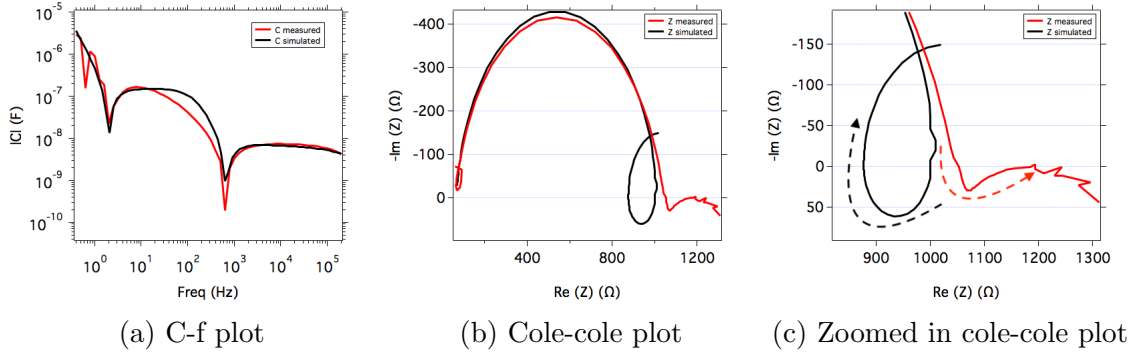


Figure 5.7: Typical measured and calculated $|C| - f$ plots and complex plane impedance plots, and a $\tan\delta$ -frequency plot for a purple QLED where a negative capacitance acts as an inductive arc in the cole-cole plot.

luminescent and non-luminescent recombination, a positive capacitance leads to a stable and efficient device.

5.5.1 Relation towards equivalent circuit

The proposed equivalent circuit shows two arcs in the impedance plane. With an enlarged time constant and thereby an increased value for the inductance both arcs overlap and $\text{Im}(Z)$ drops below 0 showing a negative capacitance and an inductive loop. With this model, a positive capacitance as well a negative capacitance with an inductive loop in the impedance plane can be fitted. The inductance in the equivalent circuit is an essential component to achieve a positive imaginary part of the impedance $+\text{Im}(Z)$ and to model the recombination of charge carriers. With this model the electrical transit of holes and electrons from injection into the active layer to the point of recombination can be described. A separation between luminescent and non-luminescent recombination is not possible. We can therefore describe an inductive loop with two arcs overlapping. For the case of an over-injection of charge carriers combined with a reduced luminescent recombination, the inductive behaviour looks like an arc. An exact fit for this inductive arc, figure 5.7 remains a challenge.

Figure 5.8 shows an overview of the measured and simulated impedance spectroscopy response of a purple QLED with a strong negative capacitance returning via and inductive loop to positive values for decreasing frequencies. In figure 5.8a the absolute values of the real part of the measured capacitance $|\text{Re}(C)|$ following equation 5.2. The measured and simulated curves fit well, in particular the simulated curve corresponds to the undershoots corresponding to a decrease and finally a negative capacitance. In the impedance plane, fig. 5.8b, the first arc overlaps with the measured

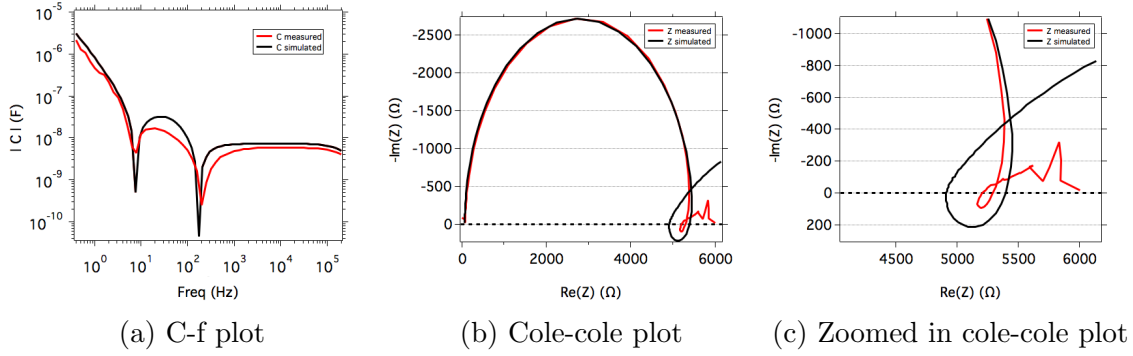


Figure 5.8: Typical measured and calculated $|C| - f$ plots and complex plane impedance plots for a purple QLED.

data. Through zooming into the highly resistive part, the simulated inductive loop in fig. 5.8c gets close to the measured values both in shape and absolute values.

With equation 5.12, typical accumulation times of charges within the device can be determined. For the case of an inductive arc the circuit model shows a limited fit only, however the capacitance response can be simulated well. Being able to fit the capacitance suggests that the total amount of injected charges can be modelled, however their recombination pathway can not exactly be described by an equivalent circuit model.

Figure 5.8 shows an overview of the measured and simulated impedance spectroscopy response of a purple QLED with a strong negative capacitance returning via an inductive loop to positive values for decreasing frequencies. In figure 5.8a the absolute values of the real part of the measured capacitance $|Re(C)|$ following equation 5.2. The measured and simulated curves fit well, in particular the simulated curve corresponds to the undershoots corresponding to a decrease and finally a negative capacitance. In the impedance plane, fig. 5.8b, the first arc overlaps with the measured data. Through zooming into the highly resistive part, the simulated inductive loop in fig. 5.8c gets close to the measured values both in shape and absolute values.

With the given model and its limitations with regards to the inductive arc, the capacitance- frequency response of the QLEDs in this study, as well as the inductive loop in the impedance plane, can be modelled. The general shape of the measured data can be modelled very well, however, a perfect fit remains a challenge. With a good $C - f$ fit and equation 5.12 the characteristic, ligand dependent, accumulation times of charge carriers (fig 5.9) are determined. At low bias all ligands show a similar and fairly high accumulation time, which we attribute to the initial filling of trap

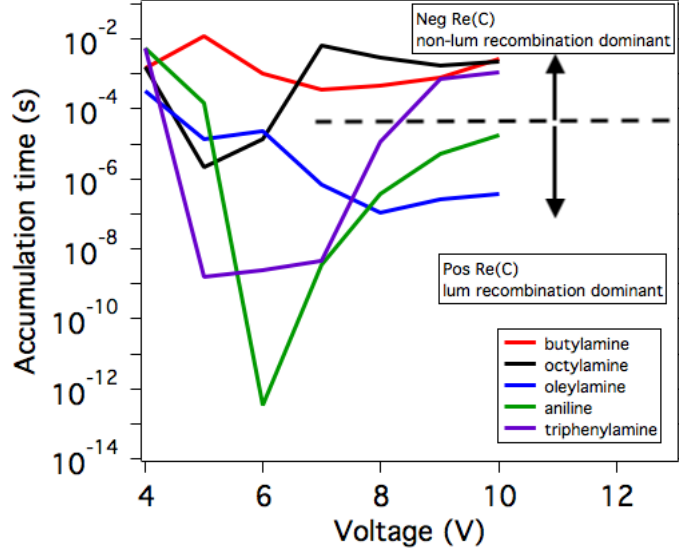


Figure 5.9: Typical charge accumulation times for five different ligands of various length and conductivity.

states. Butylamine-capped QLEDs show an almost bias independent accumulation time in the millisecond-range. Based on its short length and the dense packing of QDs, charges are injected easily and trap states are filled quickly. Once the QLED reaches the turn on voltage, the accumulation times decrease strongly. In this case the luminescent recombination is dominant where the electron-hole ratio is most balanced. With increased bias the amount of injected charges and their accumulation time increase. With more charges in the active layer, the ratio of luminescent to non-luminescent recombination shifts towards the latter. Based on our experimental data, a negative capacitance occurs in a switched on device if the accumulation time is larger than 10ms. At long accumulation times, an overinjection of charge carriers builds up an internal capacitance. The release charges under the formation of a recombination current and push the total capacitance to negative values.

5.6 Summary

In conclusion, we show for the first time ligand-based inductive behaviour in the impedance response of a QLED. Through trapping, charges accumulate on the ligand and build up a capacitance. When the capacitance drops below 0, the impedance shows either an inductive arc or an inductive loop. Based on an equivalent circuit model, the slope of the capacitance quality factor $\tan\delta$, and light output measurements we are able to link the dominant luminescent recombination mechanism

to short accumulation times. Whereas trap states in all five ligands are filled at similar time constants, short and conductive ligands prevent a strong accumulation of charges and instead enable efficient transport and luminescent recombination. With increased bias, accumulation times increase and the capacitance becomes negative. Non-luminescent recombination pathways dominate and thereby reduce the light output efficiency of the QLED. Longer and electrically insulating ligands reduce charge transport, increase charge trapping and facilitate the accumulation of charges. Thereby non-luminescent recombination pathways become more dominant and decrease the overall efficiency of the QLED.

For an efficient device, short accumulation times and a positive capacitance is beneficial. A short ligand can further increase the device lifetime as the accumulation of charges and the formation of a recombination current can potentially damage the device. We therefore suggest a short and conductive ligand for an efficient charge transport and a stable device performance with a dominant luminescent recombination.

In such manner, an inductive pattern in the impedance plane can be used to estimate whether luminescent or non-luminescent recombination pathways are dominant in a QLED.

5.7 Acknowledgement

The authors thank Sonia Ruiz Raga from Udo Bach's group for valuable discussion and Anthony Chesman for draft editing.

5.8 Supplementary Information

Figure 5.10 shows a capacitance-frequency plot of the control devices with ligands only in the active layer. For all control devices, capacitance drops below 0 and remains negative for decreasing frequencies. In this case, the devices perform similarly to OLEDs. The addition of a ligand layer has very little impact on the capacitive response of the device and does not change the behaviour of the capacitance.

The cole-cole plots of the control devices operated at 7V is shown in figure 5.11. By varying the ligands in the active layer, the conductivity of the diode changes. Just like a quantum dot film with the respective ligand, the ligand alone changes the conductivity of the active layer i.e. the width of the semicircle in the cole-cole plot. With its $\pi - \pi$ stacking, triphenylamine makes the most conductive and the

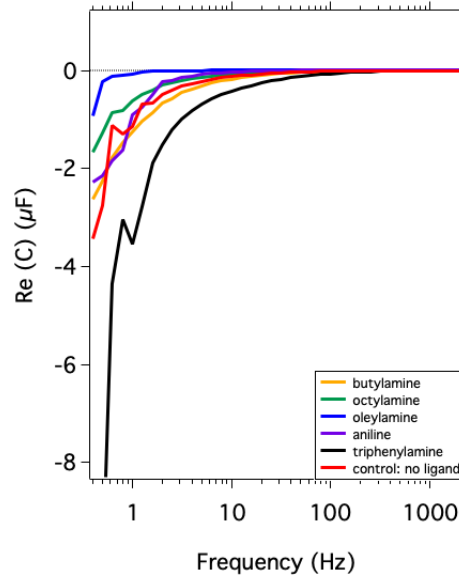


Figure 5.10: Capacitance-frequency plot of the control devices with ligands only in the active layer and a control device operated at 7V.

long chained amine oleylamine the most electrically insulating layer. In all cases, when capacitance drops below 0, $Im(Z)$ changes sign and an inductive behaviour is revealed. Once below 0, the imaginary part of the impedance $Im(Z)$ remains almost constant whereas the real part $Re(Z)$ increases. Thereby a constant dielectric loss factor is achieved for frequencies below the threshold frequency supporting the OLED character of the device where accumulation and storage of charges plays a minor role only and luminescent recombination pathways dominate.

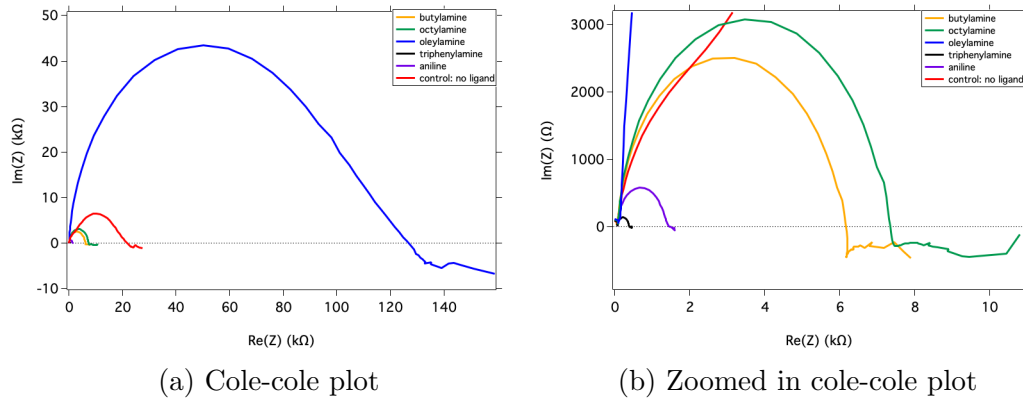


Figure 5.11: Cole-Cole plot of the control devices with the respective ligands in the active layer as well as the impedance response of a LED without ligands.

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Chapter 6

Transient Overshoot and Storage of Charge Carriers on Ligands in Quantum Dot LEDs

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Individual contribution of involved authors

I performed all experiments and analysed the data. Together with Dr Tadahiko Hirai and Prof. Paul Mulvaney I wrote the manuscript.

6.1 Abstract

Quantum dot light emitting diodes (QLEDs) emitting at 410 nm were studied by time-resolved electroluminescence measurements. A transient overshoot after voltage turn-off was seen, which is attributed to the accumulation and storage of charge carriers at the ligand-quantum dot interface. Shorter ligands showed a faster rise time and prevented the formation of an overshoot, whereas longer ligands caused a storage of charges, responded slower and showed an overshoot. When the external voltage was switched off the electric field between the injected and stored electrons and holes led to the occurrence of the overshoot. Applying a dual voltage pulse avoided this overshoot and instead a delayed luminescence was observed. As the accumulated charges were immobile and trapped in shallow states, a reverse pulse was applied to fully deplete the emissive layer. Because the transient overshoot disappeared after the device had been turned on, this can be used as a measure of the degradation of QLEDs. The ligands constitute a major obstacle for an efficient and long lasting blue/purple quantum dot emitter.

6.2 Introduction

Over the last decades, tremendous improvements in lifetime and brightness have enabled the integration of red and green organic light emitting diodes (OLEDs) into smartphone displays and TV screens [1–4]. Despite extensive research, the lifetime of blue/purple organic emitters is still significantly reduced compared to their red and green counterparts, with the mechanism of their degradation pathways also remaining unclear. Furthermore, their emission is spectrally broad, typically reaching into the green and red [2].

In a light emitting diode (LED) charge carriers need to be injected into the device and transported to the emissive layer before they can recombine radiatively or non-radiatively. On their way to recombination charges can accumulate [5] and thereby reduce the efficiency of the diode. In OLEDs, high charge carrier densities in the emissive layer lead to field induced exciton quenching where the electric field dissociates electron-hole pairs [6–8] and to triplet-polaron annihilation [9]. Time-resolved electroluminescence measurements have proved to be an efficient diagnostic tool for describing both charge transport [10–12] and annihilation phenomena in organic LEDs [13, 14]. A slower response time to a rectangular bias after current stress has been attributed to an increase in interface trap states, and this effect can be used as an

indicator of degradation in OLEDs [15]. Under high current densities the decrease in external quantum efficiency follows a singlet-singlet annihilation model, suggesting that possible heating effects in high current OLEDs are negligible [16].

Weichsel *et al.* [7] have shown that the accumulation of charge carriers in the active layer of an OLED can be studied with time resolved electroluminescence (EL) measurements following a rectangular bias. Transient overshoots after a bias turn-off have been widely reported in various OLEDs. Delayed fluorescence caused by triplet-triplet annihilation [17–19], the release and recombination of trapped charge carriers [20] and field induced exciton quenching [21], as well as changes in the drift and diffusion currents [22], can lead to a characteristic overshoot in the transient EL spectrum. Poor hole injection and the accumulation of electrons have been found to cause delayed luminescence [23]. Weichsel *et al.* [7] have localised the storage of charge carriers on the emitter molecules in OLEDs. Finally Zhang *et al.* [24] reported the storage of charges in a thin PMMA passivation layer under the emitter layer and linked the storage to the electroluminescence, and suggested that an AC driven OLED could be used to improve stability issues [8].

In this report, we apply transient EL measurements for the first time to a quantum dot LED (QLED) to study the ligand-dependent accumulation of charge carriers. In a QLED, quantum dots are typically being surrounded by organic, electrically insulating ligands that are likely to trap charges prior to recombination. By looking at a set of five different ligands of various lengths and electrical conductivity we relate the transient overshoot after a rectangular voltage pulse to the accumulation of charges on the ligands. Driving a QLED with a double rectangular pulse removes the overshoot and instead leads to a delayed luminescence from the stored charge carriers. These stored and immobile charges are finally released from their trap states with a reversed pulse and lead to a delayed luminescence response. We further investigate the luminescence rise time as well, as the formation of a transient overshoot before and after turn-on, to elucidate the degradation pathway in QLEDs. With the disappearance of the overshoot after device operation, we present for the first time an indicator for the degradation of QLEDs. Our findings suggest that the ligands surrounding the nanoparticle are a major obstacle for the realisation of a stable and efficient blue/purple quantum dot light emitting diode.

6.3 Experimental procedures

6.3.1 QD synthesis and device fabrication

The QDs were synthesised following a protocol developed by Bae *et al.* [25] whereby 0.5 mmol of cadmium oxide CdO (99.95%), 5 mmol of zinc acetate dihydrate $Zn(acet)_2$ (>98%, reagent grade), 7 ml of 1-octadecene (ODE) (tech grade, 90%), and 3.5 mL of oleic acid (OA) (tech grade, 90%) were firstly placed in a 50 mL round bottom flask. The mixture was heated to 100°C and degassed under vacuum for 1h before it was heated to 310°C under N_2 to form a transparent solution of the metal oleates, $Cd(OA)_2$ and $Zn(OA)_2$. At this temperature, 3 mmol of sulfur powder (99.98%) dissolved in 3 mL of 1-ODE, which was heated to 150°C, was swiftly injected into the reaction flask to trigger the growth of $Cd_{1-x}Zn_xS$ cores. After 6 min, 4 mmol of sulfur powder dissolved in tributylphosphine (TBP) (97%) was introduced into the reactor to overcoat the existing $Cd_{1-x}Zn_xS$ cores with a ZnS shell. The reaction was stopped after 70 min and the flask cooled down to room temperature. The QDs were purified through 3 centrifuge steps: The crude solution was washed by adding acetone until the solution became turbid, usually by doubling the volume. The addition of small amounts of ethanol helped to quantitatively precipitate the particles. The precipitate was collected after centrifugation at 4000 rpm and redispersed in a minimal volume of toluene [26]. The batch was then split into 5 parts and a ligand exchange was performed: For the insulating ligands, (butylamine (99%), octylamine (99%) and oleylamine (70%, technical grade)) an excess of the appropriate amine was added to the QD solution while for the electrically conducting ligands (aniline (>99.5%) and triphenylamine (98%)) a 1 wt% to 10 wt% was added based on the ligand to QD mass ratio, as determined by UV-VIS absorption spectroscopy. All QDs were precipitated another 3 times to ensure that non-binding ligands were washed away. UV-VIS absorption and fluorescence spectra of the ligand exchanged quantum dots are shown in figure S1.

The QLEDs in this study were prepared in a clean room environment and using a sandwich architecture based on patterned 150 nm thick indium tin oxide (ITO) covered glass substrate. The substrates were cleaned in an ultrasonicator with ethanol and water. A 70nm thick PEDOT:PSS (Al 4083) layer was deposited by spin coating. After annealing at 200°C for 10 minutes a 50nm thick poly(9-vinylcarbazole) (PVK) film was cast from a 10mg/ml chlorobenzene solution and annealed for 30 minutes at 180°C. The samples were then transferred into a nitrogen filled glove box. A 25nm QD film was deposited from toluene by spin coating and dried at 120°C

for 20 minutes. A 25nm thick layer of 3,3',5,5'-tetra[(m-pyridyl)-phen-3-yl]biphenyl (BP4mPy) was thermally deposited as the electron transport layer followed by a LiF/Al (1nm/100nm) electrode.

All chemicals were purchased from Sigma Aldrich and were used without further purification. Acetone and ethanol were purchased as analytical grade from Univar, Toluene and chlorobenzene from ChemSupply, TBP from Capot Chemical Co. Ltd., PEDOT:PSS was purchased from Heraeus Clevis, PVK (> 99% (HPLC)) and BP4mPy (> 99% (HPLC)) from Luminescence Technology Corp.

UV-visible absorbance measurements were performed on an HP Agilent 8453 spectrophotometer. Fluorescence emission and excitation spectra were recorded on a Horiba Jobin Yvon Fluorolog-3 spectrometer.

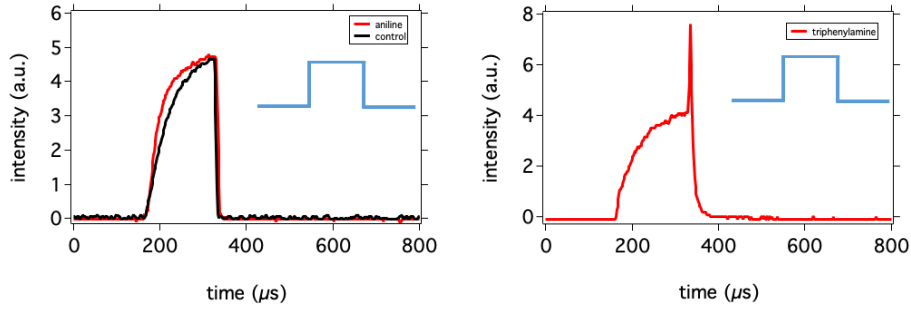
6.3.2 Device testing

Luminescence and $I-V$ characteristics were obtained with a luminescence colour meter (Topcon MB-7A) and a Keithley 2400 source-measure unit. The pulse shapes were generated by RIGOL DG4162 Function/ArbitraryWaveform Generator. The characteristics of transient EL were collected with a Hamamatsu Photonics H10721-110 photomultiplier tube and recorded with a RIGOL DG1202 CA digital oscilloscope. All measurements were carried out at room temperature under an ambient atmosphere.

6.4 Results and discussion

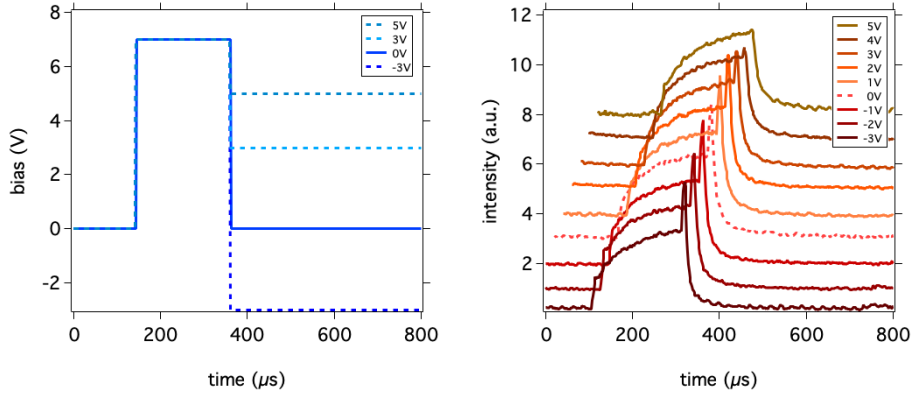
Time-resolved EL measurements reveal a ligand dependent transient overshoot after the applied rectangular voltage pulse is turned off (Fig 6.1). Figure 6.1a shows the transient EL measurements for aniline-capped QDs and for a control device. The control device has the same architecture as the other devices with the QDs being omitted. We expect electroluminescence from the control device due to recombination between the hole and electron transport layer, fig 3.6b.

The transient EL rises once the voltage pulse is applied and stops when it is turned off. In figure 6.1b however, where the ligand has been changed to triphenylamine, the transient exhibits an overshoot i.e. there is an electroluminescence spike immediately after the bias is turned off. Given the difference in the response behaviour and the fact that the electroluminescence spectrum, fig. S1, does not change during the pulsed operation we can confirm that the QDs with their ligands surrounding them are the active component leading to the transient overshoot. We have therefore performed experiments to explain the mechanism leading to this overshoot and relate it to the



(a) Transient EL response of an aniline capped QLED and a control device. (b) Transient EL response of a triphenylamine capped QLED.

Figure 6.1: The effect of a QD capping ligand on the occurrence of transient overshoot with figure 6.1a not showing an overshoot whereas figure 6.1b does.



(a) Change in pulse shape with variation in off voltage. (b) Transient EL response due to different off voltages.

Figure 6.2: An increased off-voltage, fig 6.2a reduces the transient overshoot and broadens its transient EL response in figure 6.2b.

degradation of QLEDs.

Table 6.1 summarises the transient overshoot behaviour with respect to the ligand-capping the quantum dots. In total, 12 pixels for each of the 5 ligands were manufactured and tested. Interestingly, we can see the transient overshoot even below the actual turn on voltage of the device that is required for the emission of 1 cd/m^2 , fig. 6.8. By measuring the smallest recombination we conclude that charges accumulate and the trap states are filled before the device lights up completely.

amine	Voltage (V)	transient overshoot		
		fresh device	device after stress	
			stress below V_{on}	stress above V_{on}
butylamine				
	3-10	x	x	x
$V_{on}=3V$				
octylamine	3.2-6.8	✓	✓	x
$V_{on}=3.5V$	7.0-10	x	x	x
oleylamine	4.6-8.2	✓	✓	x
$V_{on}=5V$	8.4-10	x	x	x
aniline				
$V_{on}=4V$	4-10	x	x	x
triphenylamine	4.6-8.6	✓	✓	x
$V_{on}=5V$	8.8-10	x	x	x

Table 6.1: Summary of the different ligand-capped QDs with regards to their transient overshoot behaviour.

6.4.1 Influence of the off-bias

We have investigated the origin of the transient overshoot in the EL to prove that it is an electrical phenomena, and due to an accumulation of charge carriers. The device is therefore subjected to a rectangular pulse that consists of three steps: first, a bias of $0V$ is applied, followed by a pulse above the turn-on voltage V_{on} , typically $1V$ above V_{on} , and a variable off-bias ranging from $-3V$ to $+5V$ (fig. 6.2a). Figure 6.2b summarises the transient EL pulses based on a change in the off-bias. It becomes clear that the height of the overshoot decreases and the overshoot becomes wider when the off-bias is increased to a positive bias. A larger difference between driving and off-bias leads to a stronger electric field difference and a sharper, narrower transient response after the driving bias is turned off. When the off-bias is close to the main bias, typically $1V$ below, the overshoot disappears completely. When the off-bias is decreased the overshoot occurs earlier and exhibits a sharper profile. Following Weichsel *et al.* [7] the transient overshoot in QLEDs is clearly an electrical, charge accumulating effect. Because the off-bias changes both the duration and the height of the overshoot, comparisons to a field induced quenching while the device is turned on are not meaningful [7, 21]. After the bias is turned off the accumulated charges can diffuse and drift to the QD core and recombine, resulting in the overshoot. Because the overshoot appears faster with decreasing off-bias and slower with increasing off-bias, we assume there is an accumulation of charges at the QD-ligand interface.

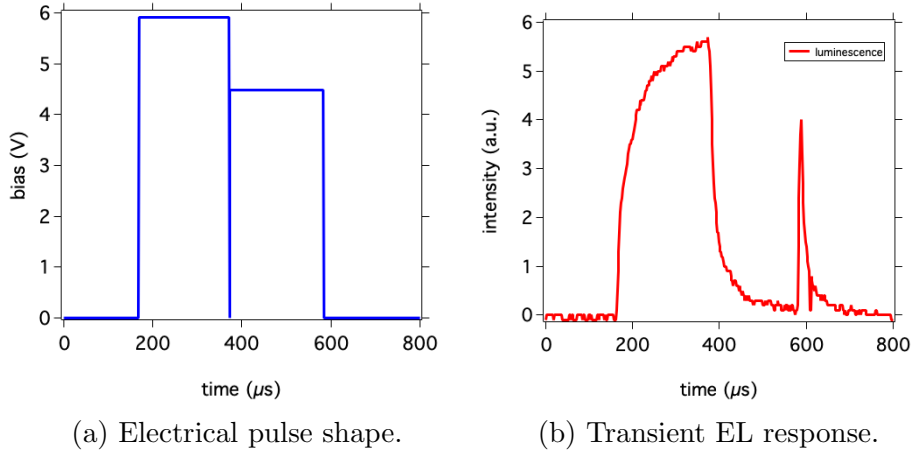


Figure 6.3: (a) The shape of a double rectangular pulse and (b) the resulting transient EL response. Note the application of the double rectangular pulse avoids the storage of charges after the first pulse, instead leading to a delayed luminescence after the second pulse.

The impact of the off-bias indicates that a transient overshoot can be avoided by applying a second positive pulse, slightly smaller than the first pulse but larger than the turn-on voltage of the device. This should be a logical approach as an applied electric field leads to the storage of charge carriers in an accumulation reservoir. Thus, we apply a set of two rectangular pulses above V_{on} as described before.

Figure 6.3 shows the electrical pulse and the transient electroluminescence response of a triphenylamine capped QLED. The first pulse drives the devices regularly without showing a transient overshoot in the EL spectrum. After the bias drops to 0V, a second, smaller bias pulse is applied and the EL decreases. At the end of the second pulse, an overshoot in the EL spectrum is seen. By applying a second pulse an additional electric field prevents the accumulation of charges after the first pulse and instead, the accumulation is shifted after the second pulse is turned off, charges diffuse and recombine under the formation of a spiky emission. The duration of the second bias (up to 500ms) has no impact on the formation of the overshoot indicating that charges are stored, rather than just accumulated. The delayed luminescence after the second voltage pulse further indicates that a difference between the two voltage pulses larger than 1V is needed for the charges to diffuse and recombine. A large voltage difference between the first and the second pulse corresponds to a strong electric field change that finally pushes the stored charge to the QD core where they recombine. Equally, a downwards-stepping voltage pulse, with small electric field changes between each voltage step removes the overshoot completely. Despite

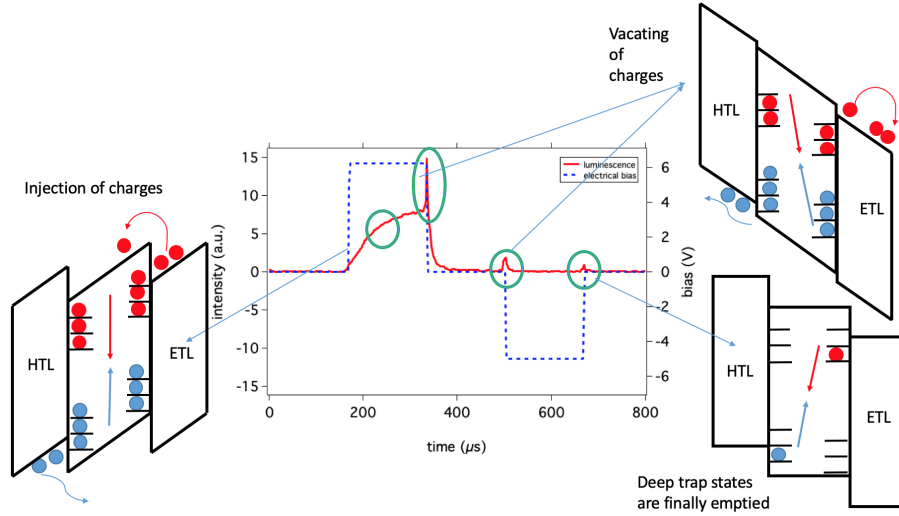


Figure 6.4: A schematic diagram illustrates the stored charges resulting in a transient overshoot and a delayed luminescence: Region 1, 2 and 3 represent the injection and accumulation of charge carriers on the ligands, their trapping in shallow states and finally in deep trap states, respectively.

different device architectures and emissive materials, the QLEDs in this study and the OLEDs from Weichsel *et al.* [7] show strong similarities.

6.4.2 Charge trapping mechanism

In order to fully study the trapping of charges we drive the device with a rectangular forward pulse followed by a rectangular reversed pulse (Fig 6.4). We are thereby able to fill the trap states and consequently release the stored charges. During the first positive rectangular pulse charges are injected from the electrodes into the active layer. The ligands surrounding the QDs limit the transport of charges, causing charges to accumulate and finally become trapped. Most of these charges may accumulate near the interface between the quantum dot and the ligand (region 1), with some located in shallow trap states on the ligand (region 2), while the few remaining charges are stored in deep trap states (region 3).

When the first pulse ends, the bias returns to 0V and the electric field disappears. Charges close to the charge transport layers diffuse back to the electrode. Accumulated charges trapped in shallow states (located at the QD/ligand interface) are released and suddenly recombine, resulting in the spikey emission (region 2). Other than purely accumulated charges, trapped charges cannot be released in one step and instead their detrapping is facilitated by a reversed pulse.

Once the bias is reversed, the release of the trapped charges results in a delayed lu-

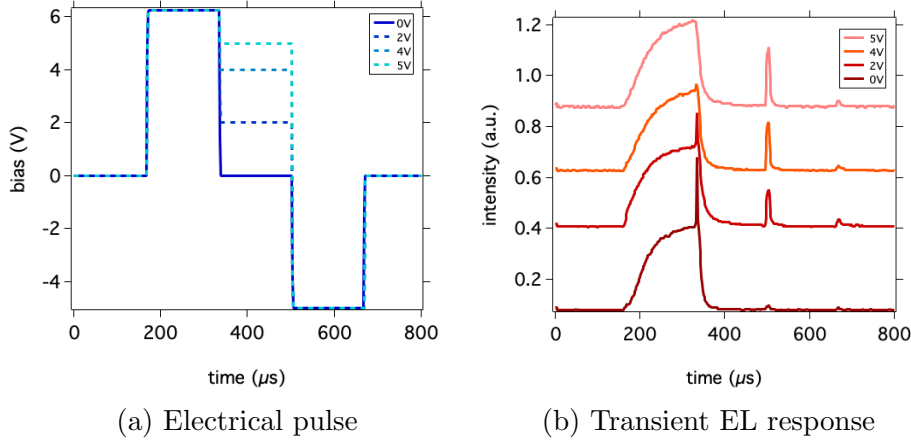


Figure 6.5: Effect of variation of the off-bias, fig. 6.5a on the release time of accumulated charge carriers. This variation has no impact on the EL response of stored charges carriers in deep trap states, fig 6.5b.

minescence (region 2). This luminescence depends on the applied bias before it is reversed: Figure 6.5 shows that an increased off-bias leads to a decrease in the overshoot and instead the delayed luminescence is enhanced.

In a similar manner to the dual pulse operation, the application of a second, smaller than the initial pulse, delays the accumulation of charges until the end of the second pulse. Interestingly, the amount of charge released from deep trap states when the reversed bias returns to 0V does not change. We assume therefore, that the amount of stored charges in deep trap states is independent of possible accumulated charge. When the negative bias returns to 0V a third delayed, and much smaller luminescence signal from deep, trapped charges is seen (region 3). As the resulting luminescence is significantly smaller, independent of the ligand and previous bias, we conclude that deeply trapped charges are less common than their accumulated counterparts.

The accumulation and trapping of charge carriers on the ligands surrounding the QDs may increase non-radiative recombination, quench excitons and clearly limit the performance of the QLED in terms of efficiency and lifetime. We can therefore use the transient electroluminescence measurements to elucidate the degradation pathway of purple QLEDs.

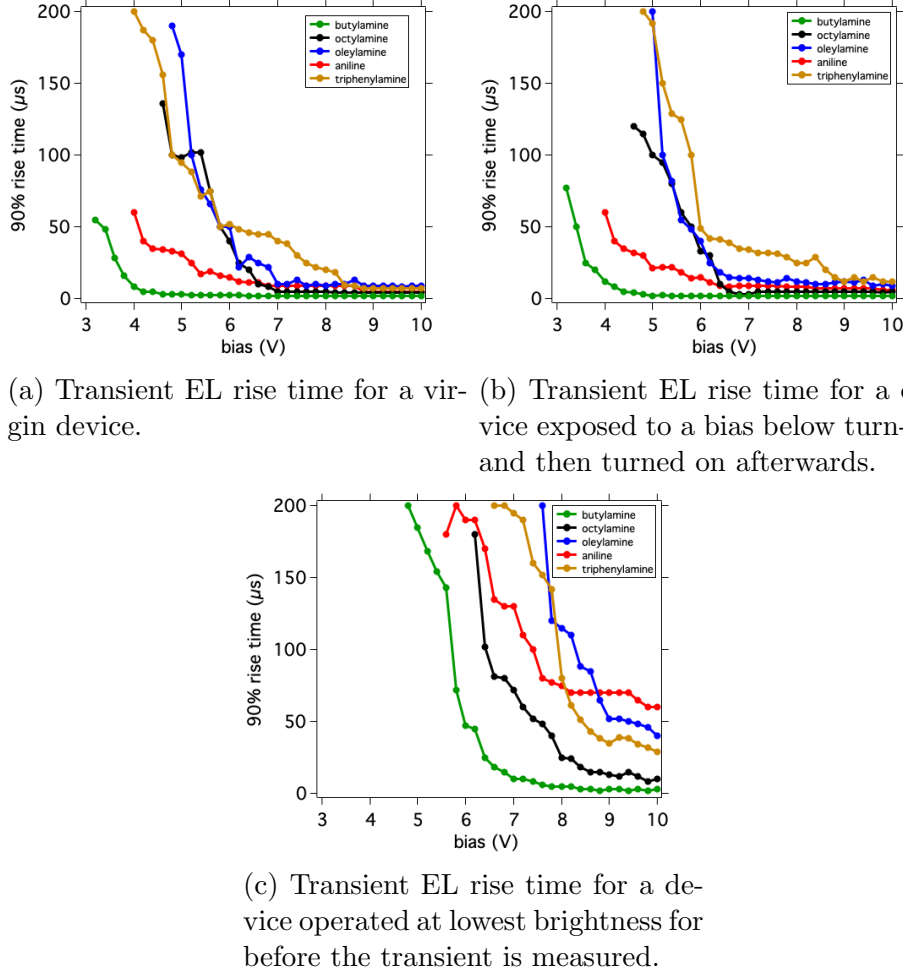


Figure 6.6: 90% rise time of the transient EL for a virgin device, fig. 6.6a, a device exposed to bias stress below, fig 6.6b, and above turn-on voltage, fig. 6.6c.

6.5 Approach to degradation mechanism

In order to study degradation we measure the 90% rise time of the ligand-dependent transient electroluminescence signal of a virgin device and compare it to a device which has been exposed to a bias 1V below its turn-on voltage. In a second step the devices are turned-on at lowest brightness (usually 3cd/m^2) corresponding to a current of $100\mu\text{A}$. The initial current is maintained by increasing the applied bias. In both cases, the devices are exposed to bias for one hour. We believe that a flow of current causes greater damage than a high voltage, which is why a rather small current is applied to drive the QLED.

Figure 6.6 shows the 90% rise time of the QLEDs capped with the five ligands of this study. For all ligands the 90% rise time decreases with increased bias, indicating that

50 μs as 90% rise time			
amine	bias virgin device (V)	bias below turn on (V)	bias above turn on (V)
butylamine	3.4	3.4	7.8
octylamine	5.8	5.8	7.6
oleylamine	5.8	5.8	9.4
aniline	4.2	4.1	9.4
triphenylamine	5.8	6	8.4

Table 6.2: Summary of the increased bias needed for a rise time of 50 μs .

with a higher bias more charges are injected and recombine. The shorter ligands, butylamine and aniline, show a short rise time after turn-on, indicating that charges don't accumulate and instead recombine quickly. Together with the ligand length the 90% rise time of the QLED increases before it decreases with increased bias. Compared to the short ligands, octylamine, oleylamine and triphenylamine exhibit a rise time that is three to four times higher. A slower rise time is attributed to the increased ligand size and the reduced electrical conductivity in the case of octylamine and oleylamine. However, for a sufficient bias, all devices attain a 90% rise time within less than 10 μs .

If the devices are exposed to a bias below their turn-on voltage for 1h and are turned on afterwards to measure the transient EL, the 90% rise time does not change significantly (fig. 6.6b). The shortest ligand (butylamine) shows the quickest rise time, whereas the a longer ligands are characterised by a slower rise time. With an almost identical rise time for the remaining four ligands, we assume that a bias below turn on has no impact on the stability of the device and does not lead to degradation of the QLED.

Once the devices are turned on and driven for 1 hour at a low brightness the transient rise time increases strongly (fig. 6.6c). Besides an increase in the turn-on voltage for all devices the rise time increases significantly (table 6.2). Whereas the QLEDs with the short ligands initially have had a quick rise time of less than 100 μs at turn-on, the rise time after device has been operated for an hour doubles. The very short ligand length of butylamine does not sufficiently protect the QD and enhances the degradation of the QLED. The QLEDs with long ligands maintain their initial rise time; however, the applied bias required to turn on the device has increased by almost 3V indicating that the device become more resistive. With increasing bias the amount of injected charges increases and the rise time therefore decreases.

Table 6.2 summarises the typical $50\mu s$ as a 90% rise time for the QLEDs capped with different ligands. With a rise time of $50\mu s$ we assume that all trap states are filled and the device operates efficiently. It confirms that a bias below its turn on voltage has hardly any impact on the bias for a typical rise time of $50\mu s$. Instead, after the device has been turned on, the bias needed for a $50\mu s$ response increases strongly, typically between 2.5 and 5V. Whereas the bias after turn on increases for QDs capped with a long ligand (octylamine, oleylamine and triphenylamine) by roughly half, it more than doubles for the QDs with a short ligand (butylamine and aniline). The presence of the longer ligands induces trap states that prevent the accumulation of charges in shallow trap states, which can easily be released with the return of the bias. As the shorter ligands show less accumulation in a virgin device, such devices requires a much stronger increase in bias after turn on. We assume that deeper trap states cause a built-in potential, an increased resistivity and potentially enhance non-luminescent recombination pathways.

Interestingly, the formation of a transient overshoot for the longer ligands (octylamine, oleylamine and triphenylamine) is not affected by a bias stress below turn on; however if the device is operated the transient overshoot disappears completely. With its disappearance we have found a method to qualitatively measure the degradation of QLEDs.

It appears that the ligands surrounding the QDs limit the efficient and long lasting operation of a purple/blue QLED. Short and conductive ligands show the best performance in terms of a quick rise time, improved device stability after turn-on and an efficient injection of charges into the QD without storing them. This leads to no overshoot once the bias is turned off. Possibly, accelerated electrons cause damage when injected into the active layer.

Because three ligands exhibit a transient overshoot after the bias is turned off we have identified the storage of charges on the ligands, as the primary origin of device instability. Our findings suggest that the charges are not stored equally over the ligands but instead accumulate and are stored at the quantum dot-ligand interface. The height and the width of the transient overshoot is not ligand dependent, but can be decreased by a second bias that enables the stored charges to be released in the form of delayed luminescence. In case of a forward and reversed pulse shape (figure 6.5) the delayed luminescence from deep trap states, region 3 where a negative bias is increased to 0V, does not change. This finding indicates that a bias above turn on affects the accumulation and the shallow trap states and has little impact on the deep trap states. A longer and less conductive ligand requires an increased

bias to drive the QLED, and also results in a slower response time to a rectangular pulse. When charges accumulate, a higher bias is required to operate the device and non-luminescent recombination pathways become more likely, reducing the device efficiency.

We anticipate that further research on novel, more stable inorganic ligands with mediocre electrical conductivity or the advent of ligand-free device architectures could potentially reduce the accumulation of charges and thereby enhance both the stability and life time of purple QLEDs.

6.6 Summary

Purple quantum dot light emitting diodes with five different ligands of various length and electrical conductivity were studied for the first time with transient electroluminescence measurements. For QDs capped with short ligands (butylamine and aniline) a short response time to a rectangular pulse was measured. For their long counterparts (octylamine, oleylamine and triphenylamine) an overshoot was detected when the bias was turned off. In addition, their response time to a rectangular pulse was increased, almost by a factor of 4. The transient overshoot can be avoided by applying a second, smaller pulse which avoids the accumulation of charges and instead leads to a delayed luminescence. In order to fill trap states a rectangular, forwards pulse is applied. In order to release the trapped charges, a reverse-bias rectangular pulse is applied. We find that the accumulated charges lead to a delayed luminescence, while deeply trapped charges generate a third, smaller luminescence signal when released from their trap states. Since overshoot and delayed luminescence behaviour have no impact on the ligand length, we assume that charges are stored at the QD-ligand interface before they recombine when the bias is turned off.

Once the devices are turned on for an hour, the applied bias required to drive the device increases by $2 - 3V$ indicating that the active layer becomes more resistive. With an increased response time and the disappearance of the transient overshoot we believe that the organic ligands surrounding the QDs are a major obstacle for the realisation of a stable and efficient purple quantum dot LED.

6.7 Acknowledgements

The authors thank the ARC for support through grant No. CE170100026 and Anthony Chesman for valuable discussions.

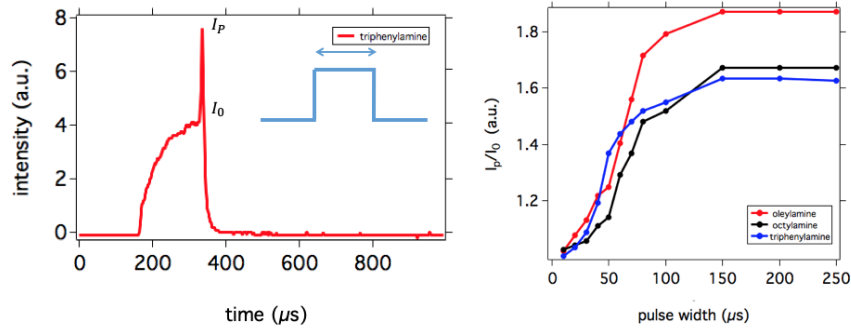


Figure 6.7: Change of pulse width for longer amines.

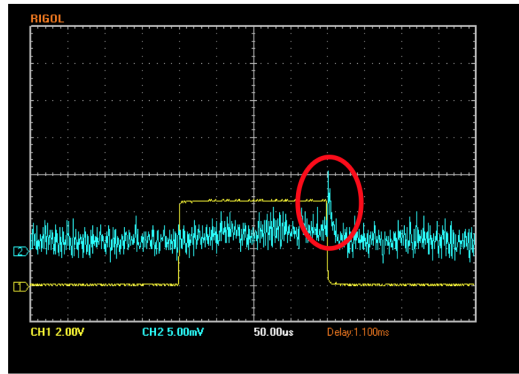


Figure 6.8: Overshoot visible before device turned on.

6.8 Supplementary Information

See supplementary information for spectroscopic characterisation of the QDs after ligand exchange and voltage-current-luminescence as well as spectral emission data of the QLEDs.

Figure 6.7 shows the ratio of the overshoot with a variation of the initial pulse width for octylamine, oleylamine and triphenylamine capped QDs. The ratio between I_p and I_0 increases from small pulse width and reaches a saturated value after a pulse width of around $100 \mu s$. Interestingly, even small pulse widths as $10 \mu s$ lead to an overshoot. The formation of an overshoot shows a similar trend for all three ligands with the longest ligand showing the greatest ratio.

Figure 6.8 shows a transient overshoot before the device turns on. We assume therefore, that trap states are filled prior the device is turned on.

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Chapter 7

Ligand Memory Effect in Purple Quantum Dot LEDs

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The results presented in this chapter were published as Editor's pick in *Applied Physics Letters*, **2019**, Vol 115, Issue 17, with the permission of AIP Publishing.

Individual contribution of involved authors

I performed all experiments and analysed the data. Together with Dr Tadahiko Hirai and Prof. Paul Mulvaney I wrote the manuscript.

7.1 Abstract

We report a ligand-dependent, trap state memory effect in a purple quantum dot LED (QLED). The measured, bistable current-voltage characteristics show a high conductance and a low conductance state. Thereby, a memory window with an ON and an OFF state is achieved that can be reversed by applying a negative bias. The height of the memory window depends strongly on the length of ligand passivating the quantum dot (QD). Together with a 5 nm thick aluminium film under the hole transport layer, charges accumulate at the charge transport/quantum dot ligand interface, leading to an increase in conductance during the forward voltage sweep. During a reverse voltage sweep, previously injected charge carriers recombine until the active layer is free of charge carriers. Voltage-capacitance measurements confirm the changes in charge carrier population within the active layer and demonstrate that they depend on both the direction of the bias sweep, as well as on ligands surrounding the QD.

7.2 Introduction

Due to their highly tunable bandgap and their size-dependent electronic and optical characteristics, colloidal quantum dots (QDs) have garnered a lot of attention as potential light emissive layers in next-generation optoelectronic devices, with applications ranging from light emitting diodes (LEDs) in displays, photovoltaic devices and transistor applications through to light emitting transistors that combine switching with light emission [1–5]. However, relatively little research has been performed on the memory functionality of nanomaterials [6–8]. In general, organic/metal/organic device architectures have been used to achieve memory effects in optoelectronic devices, with holes typically being the dominant charge type for the memory effect. [9–11]. In 2004, Kang *et al.* [11] reported a memory effect in a layered organic light emitting diode where either a thin silver layer or an organic heterojunction controllably traps and releases electrical charges. A light emitting diode with gold nanoparticles incorporated into the polymer bistable electron transport layer was introduced, which enabled the authors to demonstrate that electrons can be the dominant charge type leading to the memory effect [12]. Depending on the device architecture, electrons or holes can be trapped and thereby create either a low or a high conductivity state. An adjustable memory effect based on the position of particles within the charge transport layer has also been demonstrated through the introduction of silver nanoparticles

into a pentacene layer [13]. A layer-by-layer architecture with a polyelectrolyte (PE) ligand /gold nanoparticle was shown to have a flash memory functionality. The memory window itself was controlled by the thickness of the tunnelling oxide layer, as well as by the charge trapping mechanism of the ligand/gold nanoparticle interface [14]. Li *et al.* [7] have presented a nonvolatile, bistable memory device where CdSe/ZnS quantum dots were sandwiched between two C_{60} layers. Furthermore, QDs have been embedded into the hole transport layer of an organic bistable LED and this device exhibited bistability under negative bias and light emission under positive bias [15]. In this report, we incorporate purple quantum dots (QDs), figure 3.1, capped with various ligands of different lengths and electrical conductivities into a standard QLED architecture where the hole transport layer consists of an organic/metal/organic layer. We report the trapping of charges on the ligands and a ligand-dependent memory effect. We find that the devices fabricated from QDs capped with either longer ligands or less conductive ligands exhibit a large memory window, whereas QDs capped with shorter ligands show limited memory functionality. A full read-write-erase cycle is also demonstrated using capacitance measurements. A simple model explains the formation of the memory window.

7.3 Experimental Procedures

The QDs were synthesised following a protocol developed by Bae *et al.* [16]. A detailed synthetic route as well as the ligand exchange procedure have been reported before [17] and are described in the supplementary information.

The QLEDs in this study were prepared in a clean room environment and designed in a sandwich architecture based on patterned 150 nm thick indium tin oxide (ITO) coated glass substrates as the anode. The substrates were cleaned in an ultrasonicator with ethanol and water. 40 nm of N,N'-bis(naphthalen-1-yl)-N,N' -bis(phenyl)-2,2'-dimethylbenzidine (NPD) and a 5nm thick Al layer were deposited by thermal evaporation. A 50nm thick poly(9-vinylcarbazole) (PVK) film was cast from a 10mg/ml chlorobenzene solution and annealed for 30 minutes at 180°C. The samples were then transferred into a nitrogen filled glove box. A 25 nm QD film was deposited from a 20 mg/ml toluene solution by spin coating and dried at 120°C for 20 minutes. A 25 nm thick layer of 3,3',5,5'-tetra[(m-pyridyl)-phen-3-yl]biphenyl (BP4mPy) was thermally deposited as the electron transport layer followed by a LiF/Al (1 nm/100

nm) electrode as the cathode.

7.4 Results and discussion

Figure 7.1 shows the I-V characteristics of the QLEDs capped with the various amines. The starting voltage for the sweep was always 0 V. A variation in the starting voltage or the pre-sweep charging time had very little impact on the memory functionality of the devices, suggesting that trap states are filled both quickly and spontaneously. To underline the importance of the Al interlayer, and to prove that the effects are truly ligand-based, two control experiments were performed with the same device architecture: first, the Al interlayer was omitted and a device with triphenylamine capped QD was measured. In a second experiment a device without QDs was tested. By omitting the Al interlayer the device operates like a standard QLED and does not show a memory window. A change in sweep direction has little impact on the I-V characteristics. We conclude therefore that the Al interlayer is fundamental for the memory effect.

For all amines, including the control device, we found that a current spike was achieved at 2.5 V during the forward sweep, which creates a high current ON state. At around 4 V, the current overshoot decreased, thereby closing the memory functionality. With increasing bias, a higher current turned the device on. As the memory functionality occurs at a voltage below the device turn-on voltage, no luminescence was observed despite the current density being high enough for luminescent recombination. A low conductance, OFF state, is achieved when the voltage was swept from high to low bias. The difference between the ON and OFF states, as well as the height of the memory window, depend on the ligand surrounding the QDs; short ligands like butylamine show a narrow memory window ($0.1 \mu\text{A}$), comparable to the control device, whereas their longer counterparts, such as oleylamine or triphenylamine, show an up to 50-fold increase in the memory window with $3.7 \mu\text{A}$ and $5.6 \mu\text{A}$ respectively. Despite the fact that the ligands surrounding the QDs change the conductivity of the active layer considerably, the memory window appears at a similar bias for all five ligands.

Figure 7.2 describes the operating mechanism of the memory effect in a QLED. When the device is driven under forward bias holes are injected into the NPD/Al interface where they accumulate and build up a memory window - independent of the ligand

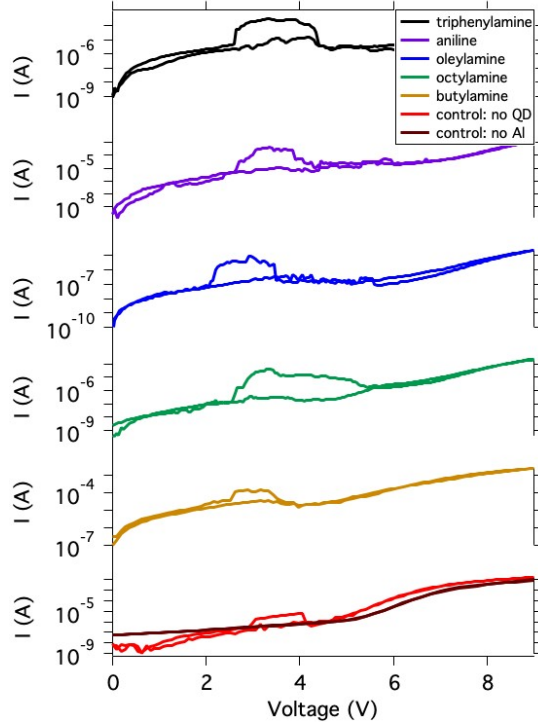


Figure 7.1: Current-Voltage characteristics of the five amines under test, as well as a control device with the voltage sweep starting at 0 V.

in the active layer. Bozano *et al.* [18] and Ma *et al.* [8] have shown that thin metal films ($< 10\text{nm}$) on an organic layer cause a discontinuous, cluster-like structure that is thin enough for charges to tunnel through. Electronically, these clusters can be described as an assembly of quantum wells close to each other. Due to the large band gap of the organic charge transport layers surrounding this Al cluster, electrons tunnel through the barrier, against the direction of the applied electric field, polarise the Al interlayer, with the charge stored [8]. When the bias is further increased, holes are injected into the PVK and transported to the quantum dot. At the interface, between the PVK and the ligand, charges are trapped again and finally open the ligand-dependent memory window [17]. Because we see a small memory effect with the Al interlayer without QDs, but not when the Al interlayer is left out, we conclude that the Al layer is a prerequisite for the memory effect. Since the type of ligand strongly impacts the height of the memory window, we conclude that the charge trapping at the PVK-ligand interface is dominant. The larger the ligand, the more likely it is for the charges to be trapped and accumulate at the ligand/QD interface, which, in turn leads to a larger memory window. More charges are injected into the device with an increased bias, overcoming the trapping and allowing holes

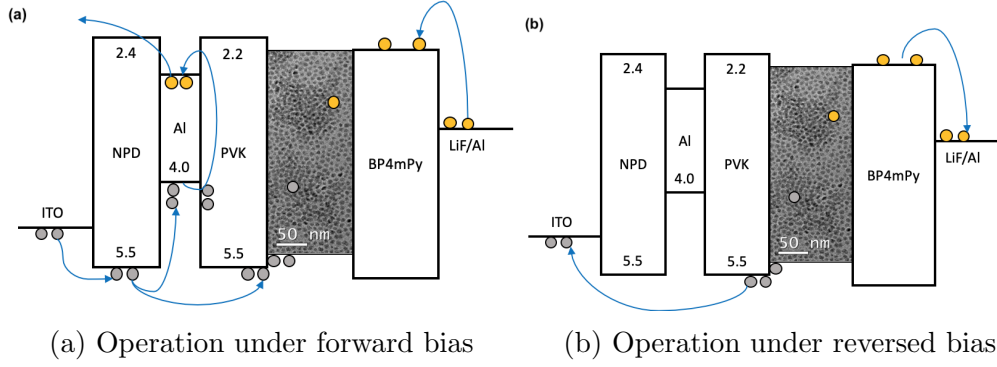


Figure 7.2: Operational principle of the memory effect under forward (a) and reversed bias (b).

and electrons to recombine and for the device to turn on.

Under reverse bias, the amount of injected charge decreases. Charges at the interface close to the electrodes return to their metal contacts and those in the active layer recombine, making the active layer resistive. While recombining, an electric field builds up that releases charges from shallow trap states and empties the active layer.

The change in the population of charge carriers was confirmed through voltage-capacitance measurements, figure 7.3. In order to approach the DC operating conditions of a QLED, the capacitance measurements were performed at 0.1 Hz. For the purpose of this study, the QLED was modelled as a plate capacitor with the ligand/quantum dot interface defining the active layer. When charges accumulate during increased bias, the active layer is large due to holes and electrons being physically separated, resulting in a rather small capacitance [19]. At 3V forward sweep the current increases and opens the memory window while the capacitance remains low. We can therefore conclude that charges accumulate at the NPd/Al interface and broaden the active layer. With more charges being injected, the capacitance increases and finally turns the device on. When the bias is decreased the capacitance decreases until approximately 4 V. At this bias the majority of charges have recombined and the active layer becomes more resistive. Between 4 V and 3 V the capacitance increases strongly, suggesting that deep trapped charge carriers are released, which makes the the active layer highly conductive. Again, at this voltage a memory window is observed. When the bias is further decreased, the freshly released charges are transported to their electrodes, resulting in the device turning off. Because the control device without QDs shows almost no change between forward and backward sweep we conclude the ligands trap charges and the Al interlayer does not

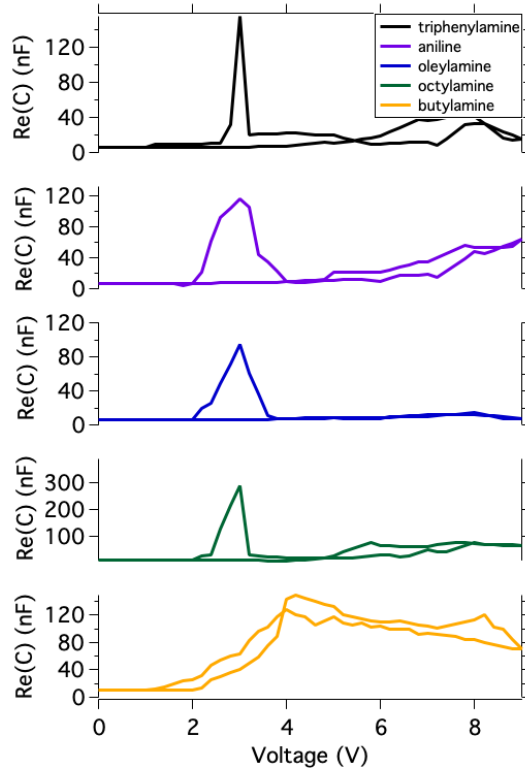


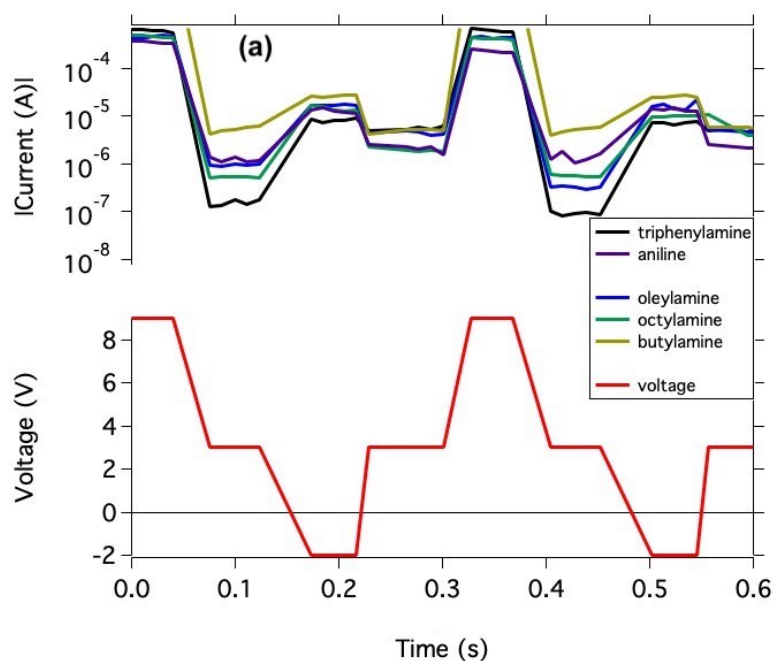
Figure 7.3: C-V measurements for the QLEDs with the memory functionality

impact charges during the reverse sweep.

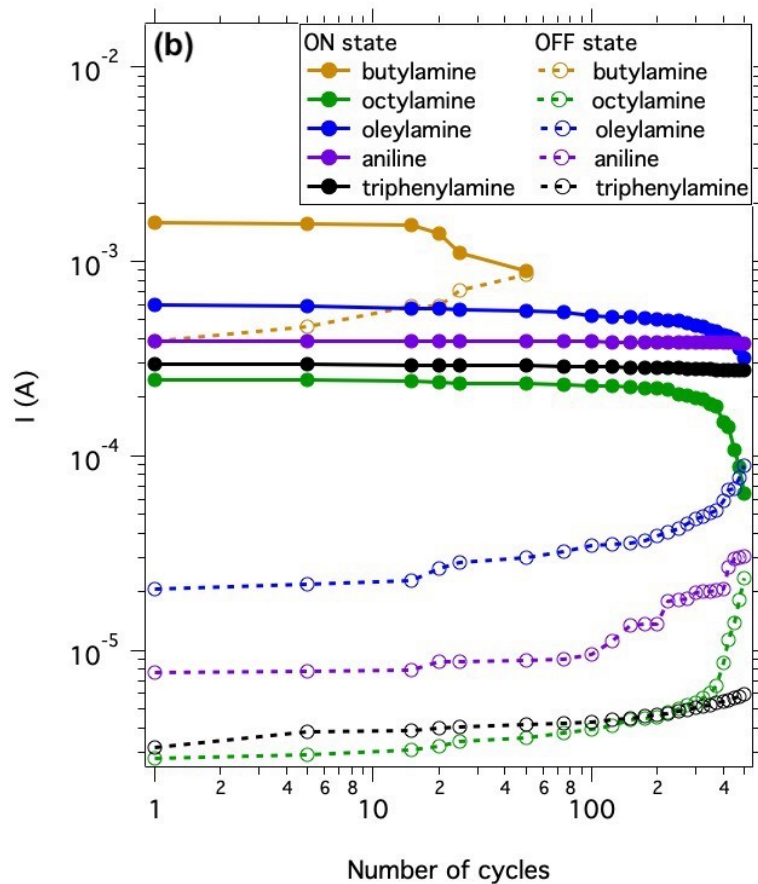
The ligands surrounding the QDs change the resistance of the active layer, which causes a build-up in capacitance. With the exception of butylamine, all ligands showed a strong increase in capacitance when the bias was decreased. The different behaviour of the butylamine capped QLEDs can be explained by the much shorter ligand length and its reduced capability to accumulate and trap charges on the ligand. As figure 7.1 shows, butylamine has the smallest memory window and proportionally the smallest change in capacitance. The larger the memory window in the I-V curves, the larger the accumulation and the storage of charge carriers and hence the bigger the capacitance change on the reverse voltage sweep.

Figure 7.4a shows the I-V characteristics of two memory cycles for devices with each of the five amines used in this study. The different read and re-read currents at a bias of 3 V are presented and figure 7.4b shows a stability test.

The memory window is stable for more than 20 cycles for all amines. After the operation of over 25 memory cycles, in particular for the butylamine case, additional trap states appear, and these require larger erase voltages to reset the memory functionality. The QLEDs with electrically conductive ligands, such as triphenylamine



(a) Memory functionality of all five ligands showing a write-read-erase-reread cycle. The voltages for writing, reading, erasing are 9 V, 3 V and -2 V, respectively.



(b) Stability test for the various QLEDs.

Figure 7.4: Memory effect: driving conditions (a) and stability test (b).

and particularly aniline, are stable over 500 cycles. QLEDs fabricated from QDs with the electrically insulating ligands, octylamine and oleylamine, retained their memory functionality for more than 400 cycles. The stability of the memory effect is further shown by measuring the retention time, figure 7.5. This is easily achieved by delaying the discharge time before applying a positive reading bias. A bias of +3 V was applied every 10 s. Butylamine-capped QDs showed a current spike for up to two hours, whereas the aniline- and triphenylamine-capped QLEDs showed a memory window even after 8 h. The electrically insulating amines retained their charge storage capability for up to 6 h. Currently, the QLEDs with a memory functionality are not stable enough for a commercial application, however, hybrid devices that combine light emission and the storage of charges could be a valuable asset for future electronics. More electrically stable ligands, potentially inorganic ones, could enhance the lifetime of the memory window.

7.5 Summary

In conclusion, ligands surrounding QDs can store and trap charges, creating a memory window in QLEDs. A metal film together with a charge transport/QD interface can trap and accumulates charges. All ligands show memory functionality. However, the ligand length and electrical conductivity alter the resistivity of the active layer, the charge injection properties and thereby the height of the memory window. QDs with short ligands show a narrow window ($0.1 \mu A$), whereas longer ligands and more electrically conductive ligands open a big memory window of up to $5 \mu A$. Different accumulation properties lead to a memory effect which have been proved through capacitance-voltage measurements. A memory cycle, with a write-read-erase-reread functionality is established for all QLEDs, with short ligands showing limited stability and their longer counterparts demonstrating more resilient and repetitive storage and release of charge carriers.

See supplementary information for a detailed description of the QD synthesis and spectroscopic characterisation of the QDs after ligand exchange as well as spectral emission data of the QLEDs.

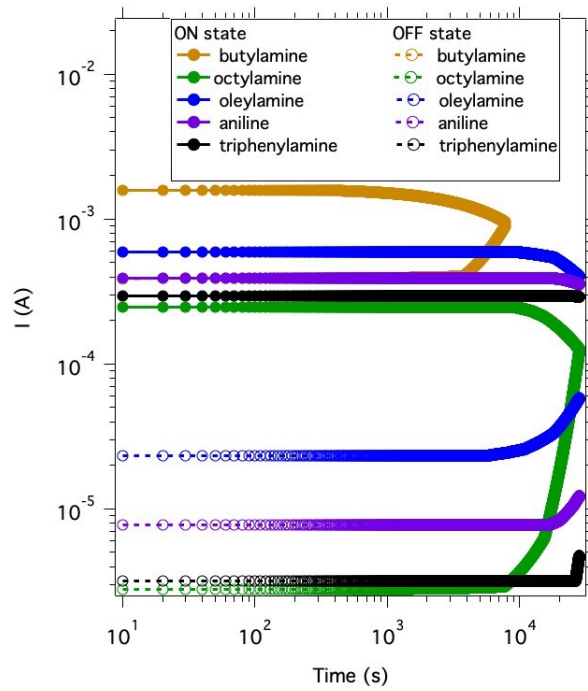


Figure 7.5: Retention time of the QLEDs with different ligands.

7.6 Acknowledgements

The authors thank the ARC for support through grant CE170100026 and Anthony Chesman for valuable discussions.

7.7 Supplementary Information

Figure 7.5 shows the retention time for the QLEDs with various ligands. For this experiment the devices were biased with +3V every 10s. Short and insulting ligands show a reduced memory stability whereas their conductive counterparts show an enhanced stability.

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Chapter 8

Towards Overcoming Charge Trapping on Ligands

The results from chapters 4, 5, 6 and 7 suggest that the ligands capping the QD trap and accumulate charges, and thereby prevent efficient transport and injection of charges into the QD. Hence the ligands pose a major obstacle for the realisation of a stable, blue QD emitter. This chapter describes several ideas to overcome the ligand problem.

8.1 Overcoating of ligands with metal chalcogenides

One way to overcome the ligand issues could be to reduce electronic traps and to enhance the passivation of the QD surface. Studies have shown that the photoluminescence quantum yield (PLQY) of QDs can be increased by adding a shell of 2-3 monolayers a metal chalcogenide [1–3]. Fu *et al.* [4] have shown that the PLQY of CdSe@ZnS/ZnS quantum dots can be doubled by growing a 1.9 nm thick shell around the QDs. They concluded that a thicker shell reduced surface trap states and thereby suppressed energy transfer between QDs. On top of that, a thicker shell was attributed to a reduction of non-radiative Auger recombination and thereby enhancing the device performance [5]. Because ZnS has a lower charge density on the surface than CdS, the shell structure can reduce photo-induced degradation of QDs in a device [6]. By adding that 1.9nm thick shell, Fu *et al.* [4] were able to triple the brightness and increase both the current and the external quantum efficiency by seven times, compared to the performance of shell-free QDs in a device,.

Chemical bath deposition (CBD) offers a simple, low temperature, inexpensive and potentially scalable controlled deposition method of metal chalcogenides by precipitation [7]. For a soft layer, the substrate is dipped into an alkaline solution that contains

three ingredients: the chalcogenide, the metal ion typically dissolved in water and a base [8]. At the deposition, the formation of homogeneous particles competes with a heterogeneous film reaction [9, 10]. During the hydrolysis of the metal ion, S^{2-} ions are released into the alkaline solution where the free metal ions are dissolved in a low concentration. Sulfide ions are released from an equilibrium hydrolysis reaction of an organic sulfur compound such as thiourea or thioacetamide. When free metal ions react with free sulfide ions, particles in bulk solution are formed. At the surface, metal complex ions react with thiourea to form the metal chalcogenide through a decomposition process of metastable complexes [10]. Thereby a film of metal chalcogenides is deposited on the substrate.

While an additional layer of metal chalcogenide may increase the luminescence efficiency of a QD on a glass substrate, its deposition in a device architecture is challenging and can potentially decrease the efficiency of an LED. The standard device architecture within this research project uses PEDOT: PSS, a water-soluble polymer mix, for an enhanced hole injection into the active layer. With most CBD methods using water as a solvent, a partial dissolving or a reduced film quality of the previously deposited hole injection layer are not uncommon. Further, Emin *et al.* [11] have shown that the photo-stability of water-soluble CdTe QDs decreases under light irradiation and in the presence of oxygen. Additionally, water can dissolve some amines such as butylamine and thereby reduce the passivation cover of QDs. On top of that water can further encourage oxidation reactions with arylamines such as aniline and hence change the surface chemistry of the QDs. To reduce the potential damage of a water-based deposition, the standard architecture was simplified by removing the hole transport layer PVK.

To study the conceptional idea of overcoating QDs with a thin layer of a metal chalcogenide, QDs capped with oleic acid were used as an emitter in a QLED. Note ligand exchange with other ligands of different length and electrical conductivity was not performed. Because the deposition of CdS through CBD is more standardised, blue-emitting CdS/ZnS QDs from chapters 4 to 7 were replaced with red, 625 nm emitting CdSe/CdS QDs. Ideally, the additional deposition of CdS does not lead to a lattice mismatch and instead increases the brightness of the QDs. By varying the deposition time, the added film thickness is changed: 1s after the nucleation started a film thickness of 1nm was deposited, after 30s 2.5 nm and finally after 60s 3 nm of CdS were deposited. With such thin film thicknesses, a homogeneous film is not deposited. Comparably to LiF, a very thin and possibly not consistent film can significantly improve the device.

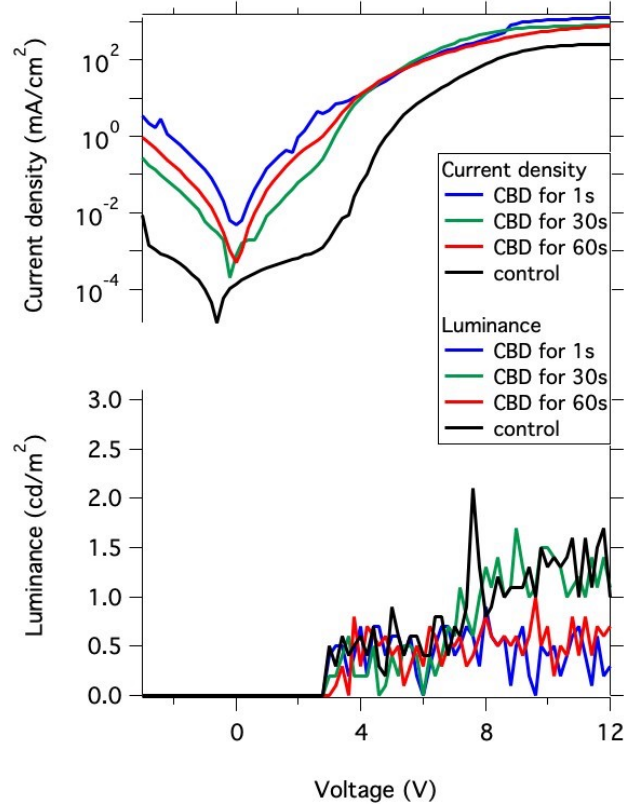


Figure 8.1: Voltage-current density-luminescence diagram for CdSe/CdS QLEDs with an additional CdS layer of various thicknesses.

The devices consisted of glass / ITO / PEDOT:PSS / CdSe/CdS + CdS / BP4mPY / LiF / Al. The QDs were deposited through spin coating and the final film thickness was 25nm plus the additional CDB layer. For a control device, the QDs were deposited and the additional CdS layer was omitted.

Figure 8.1 shows a voltage-current density-luminescence plot of the QLEDs of respect to an additional CdS layer. Through adding an additional layer of CdS the current density increases by 1 to 2 decades. The sub-threshold current density for negative bias is higher than the control device which points towards higher losses within the device, potentially due to less perfect film formation after the CBD. Interestingly, the CdS thickness has rather little impact on the current density in particular for larger bias, $V > 4V$. Unfortunately, the light output of all devices is low and unstable hence a clear trend is not visible. Because the devices with a thicker CdS layer, larger than 10 nm, produce a significant amount of thermal heat and due to the low luminescent recombination, we assume that CdS deposited through CBD enhances non-luminescent recombination pathways. The release of heat further points towards charge injection problems within the active layer: the injection of holes and electrons

becomes even more unbalanced, charge transport properties are changed and potentially a flow of current is created. All in all the stability of the devices is significantly decreased and the pixel burns in from around $\sim 10V$. Due to thermal heating issues, little device stability and the lack of increased luminescent recombination the idea of overcoating the ligands through CBD was not pursued further.

Alternatively, a metal chalcogenide layer can be deposited through a sputter coating. This physical vapour deposition process allows the deposition of thin and functional coatings. A sputter cathode is electrically charged and once turned on, forms a plasma that deposits material from the target surface. Because sputtering is a high energy process, the materials impact the substrate and is driven onto the surface of the target. Thereby, a strong coating is formed that remains on the substrate [12–14]. However, due to the plasma and a large amount of energy the layers underneath can be damaged during the deposition.

In a second attempt to overcoat the ligands ZnS was deposited on CdSe/CdS QDs, stabilised with oleic acid. The voltage-current density-luminescence results of the QLEDs with CdSe/CdS QDs covered with an additional layer of ZnS are shown in figure 8.2a. Three-layer thicknesses and a control device without an additional ZnS layer were tested.

While a good electrical performance with high current densities is measured the luminescent recombination is barely visible. Instead, the devices, in particular with the thickest ZnS layer produce a significant amount of heat and show burn-ins. We conclude, therefore, that non-luminescent recombination pathways become dominant when an additional semiconductor interlayer is added to the device architecture.

To gain insight into the impact of the ZnS interlayer on the behaviour of charges within the device, Impedance Spectroscopy, figure 8.2b was performed on the device with the thinnest ZnS layer. Assuming that charges have to tunnel through the additional layer, a thicker layer might pose an injection obstacle of charges into the QD.

Once charges are injected into the active layer, $V > 3V$, the resistivity plot shows steady impedance values for decreasing frequencies. At the same time the real part of the capacitance increase for small frequencies. So far, the device behaves as expected. With the bias further increasing, the $\text{Re}(Z)$ decreases further and approaches a steady value for higher frequencies. From a bias $V > 5V$ the real part of the capacitance become more and more unstable, drops below 0 and returns to positive values.

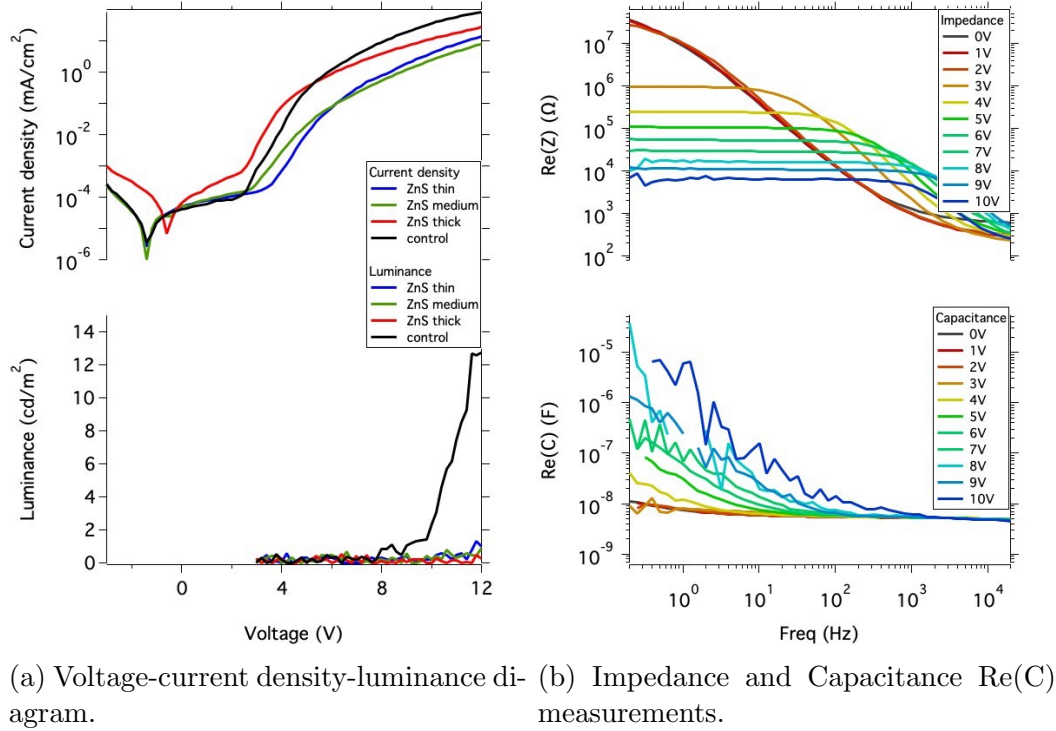


Figure 8.2: Electro-optical characterisation of the QLEDs with an additional ZnS layer.

Other than negative capacitance (NC) described in chapter 4 ZnS overcoated devices do not show a clear trend towards a steady NC. With bias further increasing, both impedance and capacitance become unstable and the latter become more negative. As hardly any luminescence is detected, the changes in capacitance can only be related to non-luminescent recombination. The unstable capacitance plot and in particular the resistivity plot, as well as burn-in effects, point towards the formation of a charge reservoir at the ZnS/QD interface. Charges are not injected and instead, a flow of current builds up that consequently heats the device and causes fatal damages. The plasma deposition itself might have damaged the QDs or the underlying charge transport polymers which might have further contributed to an unsteady charge behaviour within the device.

By connecting QDs through the soldering of Na₂Cd₂Se₃ metal chalcogenide ligands Jang *et al.* [15] have been able to achieve record charge mobilities up to 400 cm²/Vs in a Quantum Dot transistor. Their mobilities are comparable to those of polycrystalline silicon transistors and suggest that charges are efficiently transported and no trapped on the way [16]. Because on the one hand overcoating organic ligands with

CdS or ZnS increased the conductivity of the active layer and thereby encouraged non-luminescent recombination pathways and on the other hand long electrically insulating ligands not efficiently transporting charges to the QDs, a short ligand of mediocre conductivity might be the happy medium. Because $\text{Sn}_2\text{S}_6^{4-}$ ligands showed charge mobilities of around $5 \text{ cm}^2/\text{Vs}$ [17] in a transistor architecture and due to their inorganic nature they might be more stable in an electromagnetic field than their organic counterparts. Beyond transistor architectures, $\text{Sn}_2\text{S}_6^{4-}$ ligands have mainly been used in thin-film solar cell applications [18, 19] to stabilise non-toxic nanocrystal inks; their incorporation as stabilising ligands has, to the best of our knowledge, not been reported yet.

For the synthesis of $\text{Sn}_2\text{S}_6^{4-}$ ligands, a procedure developed by Liu *et al.* [20] was modified as follows: For the $\text{Na}_4\text{Sn}_2\text{S}_6 \cdot 14\text{H}_2\text{O}$ complex, 60 mmol of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ were dissolved in 50 ml of Milli-Q water. In a second vile, 15 mmol of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ were dissolved in 5ml of Mili-Q water. Through mixing the two solutions and under vigorous stirring, yellow flakes form that finally dissolved and form a transparent-yellowish solution. The clear solution is then added to 500 ml of acetone which then changes colour to a light green where a yellow oil is formed on the bottom of the flask. To increase the yield, the solution is frozen at -20°C for 72h. The top layer is decanted, the precipitate collected, washed with acetone and dried under a mild vacuum. $\text{Na}_4\text{Sn}_2\text{S}_6 \cdot 14\text{H}_2\text{O}$ is stored as a dry powder and only redissolved before its incorporation into a device architecture.

Because the QDs described in chapters 4 to 7 are made of CdS/ZnS core-shell particles, the addition of a second $\text{Sn}_2\text{S}_6^{4-}$ ligand might act as charge injection obstacle. Therefore, stoichiometry of the inorganic ligand has to be changed to a material composition with a closer lattice match towards the original QD. In doing so, zinc nitrate $\text{Zn}(\text{NO}_3)_2$ is added to change the ratio of Sn to Zn in the ligand. By dissolving both compounds in water and by adding a 1:1 molar ratio of $\text{Sn}_2\text{S}_6^{4-}$ to $\text{Zn}(\text{NO}_3)_2$ and through vigorous stirring overnight, $\text{Zn}_2\text{Sn}_2\text{S}_6$ is formed. In the same manner, if the zinc nitrate ratio is doubled, a zinc-rich $\text{Na}_3(\text{ZnSn}_2\text{S}_6)$ compound is formed.

Because the QDs capped with the organic ligands are solvent in non-polar solvents such as chloroform or toluene and the $\text{Sn}_2\text{S}_6^{4-}$ compounds dissolve in water best, a classical ligand exchange in solution is not possible. Instead, an additional layer of metal chalcogenide ligands is spin-coated on top of the QDs. Thereby, ideally, some

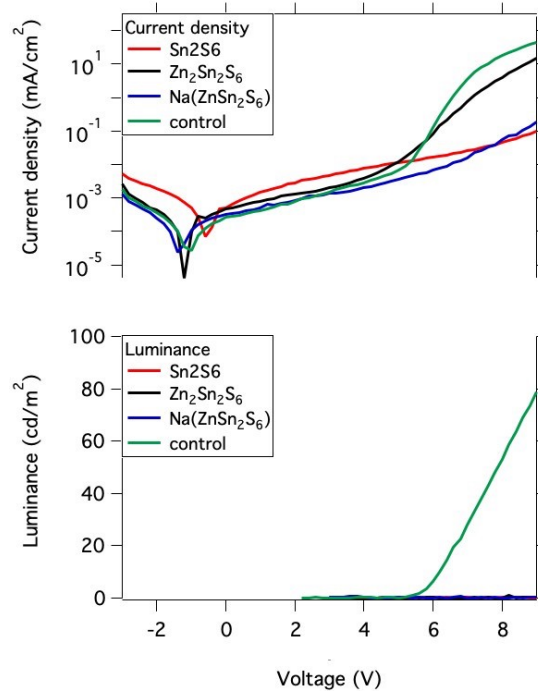


Figure 8.3: Voltage-current density-luminescence diagram for CdSe/CdS QLEDs with an additional MCC layer.

organic ligands are removed in a film or at least overcoated with their inorganic counterparts so that charges can travel more easily to the QDs.

Figure 8.3 shows a voltage-current density-luminescence plot of the QLEDs of respect to an additional MCC layer and a control device with triphenylamine capped QDs. The control device shows similar performance, both in terms of its electrical as well as light out-coupling performance, as described in chapter 3 and underlines the reproducibility of our work. With the addition of the MCC ligands, the device performance decreases: Compared to the control device, the current density is always lower and the radiative recombination becomes quenched. Interestingly, a Zn rich ligand enhances the current density whereas an Sn rich ligand acts almost like a charge injection barrier. This results further underlines the importance of a precise lattice tailoring of the QD/ligand interface. Because adding a metallic interlayer reduces the current density of the active layer, it appears that the electrically insulating ligands remain in the film and lead to a charge obstacle than cannot be overcome. Since the MCC ligands did not improve the light output but instead strongly encouraged non-luminescent recombination pathways the idea of using inorganic, electrically conductive ligands was not successful.

8.1.1 Nanoplatelets as bridging solution

Until the discovery of perfectly passivated but ligand-free QDs, novel synthetic pathways for quantum materials could lead the way towards less charge accumulation on the ligands in a device: Various concepts of anisotropic growth methods for QDs have led to a precise control of the shape of nano-sized crystals [21, 22]. These growth methods enable the shift from 0 dimensional to two-dimensional (2D) nanomaterials, which behave electronically as quantum wells [23] and show a directed [24], bright and spectrally narrow photoluminescence [25, 26]. In a film, nanoplatelets (NPLs) form a thin and flat surface where the thickness is determined by the number of monolayers [27]. These characteristics are particularly interesting for a light-emitting device as they may enhance the light-outcoupling efficiency.

Typically, NPLs are synthesised via a surfactant-based hot-inject method described in chapter 1.1.1. Just like their 0D counterparts, the surface of NPLs is passivated through long-chained ligands. Although the material composition, the size and shape of the core/shell of the nanoplatelet determine the optical properties of the NPL, surface ligands can influence the solubility and the position of the absorbance and photoluminescence peak [27, 28]. Giovanella *et al.* [29] have shown that through introducing a charge balancing interlayer and by exposing the devices to atmosphere the EQE of NPL-LEDs can be increased by 1 order of magnitude while maintaining good operational stability over hours. Their findings support the potential of NPLs for next-generation light-emitting material in electroluminescence devices. Despite advantages in film formation and photoluminescence, NPLs as emitting materials in light-emitting devices perform significantly worse than their spherical counterparts [29].

Because NPLs are larger in size than their colloidal counterparts, NPLs show a larger semiconductor-material and a smaller ligand ratio than classical QDs. Therefore, NPLs could be used as a bridging material towards ligand-free nanocrystals as NPLs form larger nanocrystals, thinner and more aligned films while decreasing the ligand impact of QDs.

The incorporation of NPLs in QLEDs in preliminary experiments points towards a decreased accumulation of charge carriers on the ligands: CdSe/ZnS NPLs capped with oleic acid as a ligand did not show a transient overshoot as a response to a rectangular input signal. In a similar manner, capacitance was decreasing and becoming negative due to a strong recombination but did not show an oscillating behaviour. As oleic acid is a long-chain ligand, the lack of two charge accumulation features is a strong indicator towards the increased performance of NPLs over QDs in terms of

charge accumulation and storage.

At the same time research towards completely ligand-free nanocrystals could be a solution: carbon dots combine a spectrally sharp emission without charge trapping on stabilising ligands.

8.1.2 Summary

The results of the previously described experiments suggest that the problem of organic ligands trapping charges cannot be solved by overcoating them with another semiconductor or metal chalcogenide. Instead, the device performance exacerbates, charges accumulate even more and non-luminescent recombination pathways become strengthened.

Removing the ligands without damaging the QDs while maintaining their colloidal shape and size could solve the ligand problem. Physical removal techniques, such as ozone plasma treatment can potentially remove ligands but causes severe damages: the QDs suffer from bleaching effects, pinholes in the underlying charge transport layers reduce the stability as a whole and finally enhance the degradation and burn-ins.

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Chapter 9

Concluding Remarks

Over the past 8 chapters, the impact of ligands of purple emitting II-VI semiconductor quantum dots and their incorporation into electroluminescent devices have been explored. Through slightly changing the surface of the semiconductor, the device performance changes significantly and makes a body of work that spans from chemistry into device physics. This thesis is another example that the development of a next-generation blue emitter requires a joint effort between material chemistry and device engineering. For the realisation of a stable and bright Quantum Dot LED new materials with advanced charge transport and injection properties have to be developed but maybe even more important will be a stronger understanding of the operational principles of a device. Thereby, not only brightness but also efficiency and more conceptional issues such as device lifetime can be improved to bring true QD displays into the market. To do this the electronic and photo-physical properties of a quantum dot and its surfactants in an electromagnetic field must be well understood. Mono-sized, bright and stable quantum dots are fundamental for the incorporation into an optoelectronic device. While the surrounding ligands might not change the optical properties of the nanocrystal, chapter 3 shows that by changing the chain length of the ligand the inter-particle in a film can be changed. Further, electrically conductive ligands can enhance the conductivity of the film whereas their insulating counterparts decrease the conductivity. Thereby, the optoelectronic properties of a LED such as light output and turn-on voltage are changed. To study the ligand-dependent effects on a QLED, a set of five organic, amine-based ligands of various lengths and electrical conductivity is core to this thesis.

Because changes in electrical conductivity are rather small and the impact of the ligands on the device performance is comparably big, chapter 4 looks at changes in the charge population during device operation. At low frequencies and under bipolar injection, the capacitance can drop below 0 before it becomes positive again for

even smaller frequencies. Together with chapter 5, ligand-dependent changes in both the capacitive and resistive plane are related to recombination pathways. With an equivalent circuit, delay times of charges on the ligands surrounding the QDs are modelled and linked to the luminescent recombination efficiency of the device. Chapter 6 optically proves the accumulation of charges: by pulsing the device with a rectangular bias, trapped charges are released and respond with a delayed luminescence spike when the bias is already turned off. By adding a 5 nm thick aluminium interlayer, chapter 7 makes use of trapped charges and introduces a memory functionality to a light-emitting device.

While the field of QLED research naturally focusses on device improvement, little understanding has been gained on the impact of the surface chemistry on the device performance. The results from chapters 3 to 7 suggest that the ligands surrounding the QDs strongly impact the performance of a quantum dot light-emitting diode. Because charges get trapped and accumulate on the ligands, we consider the organic stabilisers a major obstacle for the realisation of stable and true quantum dot emitter. Inorganic ligands with a mediocre length and electrical conductivity beyond $\text{Sn}_2\text{S}_6^{4-}$ could be more stable; alternatively, ligand-free QDs with superior surface passivation could eliminate charge trapping completely. So far, ligand-free QDs with comparable photo-physical properties are not available; research towards these could enhance the understanding of QDs even more.

A better understanding of QDs in an electric field could also be achieved by pushing towards 3 electrode devices: Light-emitting transistors combine charge transport and the emission of light. Through the gate electrode, the electric field in the active layer can be changed towards electron or hole rich. Thereby an understanding of the optoelectronic properties in particular with regards to field-induced quenching could be achieved which could then further improve a quantum dot light-emitting diode.

When a precise control over the surface chemistry of the quantum is combined with advanced device architectures and numerical modelling, a detailed understanding of a simpler light-emitting diode is achieved. In such an interdisciplinary approach electronics of tomorrow can be designed that outreach the performance of their organic counterparts: a precise, well-tailored and almost monochromatic emission together with an increased efficiency and an enhanced lifetime will revolutionise the way we will see colours on a screen.