A Surface Chemistry Approach to Enhancing Colloidal Quantum Dot Solids for Photovoltaics

by

Graham Hamilton Carey

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Edward S. Rogers Department of Electrical & Computer Engineering
University of Toronto

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Abstract

Colloidal quantum dot (CQD) photovoltaic devices have improved rapidly over the past decade of research. By taking advantage of the quantum confinement effect, solar cells constructed using films of infrared-bandgap nanoparticles are able to capture previously untapped ranges of the solar energy spectrum. Additionally, films are fabricated using simple, cheap, reproducible solution-processing techniques, enabling the creation of low-cost, flexible photovoltaic devices.

A key factor limiting the creation of high efficiency CQD solar cells is the short charge carrier diffusion length in films. Driven by a combination of limited carrier mobility, poor nanoparticle surface passivation, and the presence of unexamined electrically active impurities throughout the film, the poor diffusion length limits the active layer thickness in CQD solar cells, leading to lower-than-desired light absorption, and curtailing the photocurrent generated by such devices.

This thesis seeks to address poor diffusion length by addressing each of the limiting factors in turn. Electrical transport in quantum dot solids is examined in the context of improved quantum dot packing; methods are developed to improve packing by using actively densifying components, or by dramatically lowering the volume change required between quantum dots in solution and in
solid state. Quantum dot surface passivation is improved by introducing a crucial secondary, small halide ligand source, and by surveying the impact of the processing environment on the final quality of the quantum dot surface. A heretofore unidentified impurity present in quantum dot solids is identified, characterized, and chemically eliminated. Finally, lessons learned through these experiments are combined into a single, novel materials system, leading to quantum dot devices with a significantly improved diffusion length (enhanced from 70 to 230 nm). This enabled thick, high current density (30 mA cm$^{-2}$, compared to typical values in the 20-25 mA cm$^{-2}$ range) devices, and the highest reported solar power conversion efficiency to date.
Acknowledgments

I would like to begin by thanking my supervisor, Professor Edward Sargent. Ted brought me into his lab as an unproven undergraduate, welcomed me back as a doctoral candidate, and has consistently provided the opportunities and support that I have needed to succeed in the lab and beyond. He has helped to hone my critical thinking and communication, and to develop an entrepreneurial mindset that will serve me well as I move forward in life.

I feel honoured for the opportunity to work closely with a fabulous team of scientists and technicians, including Damir Kopilovic, Remi Wolowiec, Leny Palmiano, and not least Larissa Levina. Without them, the work that went into this thesis would have taken years longer to accomplish (if it had been possible at all). Thank you all for putting up with us, the transient grad students and postdocs, and for making a smooth-running lab seem effortless.

Several of my lab-mates through the years have had an outsized impact on my development as a scientist and as a person. I would like to thank, in particular, Dr. Susanna Thon, Dr. Illan Kramer, Dr. Sasha Voznyy, Dr. Riccardo Comin, Dr. Sjoerd Hoogland, Dr. Lisa Rollny, André Labelle and Alex Ip, as well as my collaborators at the King Abdullah University of Science and Technology, Ahmad Kirmani and Dr. Aram Amassian.

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Finally, I would like to thank my parents, Don and Joan, my siblings, Alexander and Hannah, and above all else my amazing partner, Anna. Without your love, support, and belief in me, I would never have been able to pursue all of the incredible opportunities that life has offered so far.
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<th>Description</th>
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<tr>
<td>3MN4P, 3MN5P, 3MN6P</td>
<td>3-mercaptopo-N-(butyl/propyl/hexyl)propanamide</td>
</tr>
<tr>
<td>ACN</td>
<td>acetonitrile</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>CdCl₂</td>
<td>cadmium chloride</td>
</tr>
<tr>
<td>CQD</td>
<td>colloidal quantum dot</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>DMAP</td>
<td>4-dimethylaminopyridine</td>
</tr>
<tr>
<td>EDC</td>
<td>1-ethyl-3-(3-dimethylaminopropyl)carbodiimide</td>
</tr>
<tr>
<td>EDT</td>
<td>ethanedithiol</td>
</tr>
<tr>
<td>ETL</td>
<td>electron transport layer</td>
</tr>
<tr>
<td>FF</td>
<td>fill factor</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>FTO</td>
<td>fluorine-doped tin oxide</td>
</tr>
<tr>
<td>GISAXS</td>
<td>grazing incidence small angle X-ray scattering</td>
</tr>
<tr>
<td>HTL</td>
<td>hole transport layer</td>
</tr>
<tr>
<td>HRTEM</td>
<td>high resolution transmission electron microscopy</td>
</tr>
<tr>
<td>IR-VASE</td>
<td>infrared variable angle spectroscopic ellipsometry</td>
</tr>
<tr>
<td>ITO</td>
<td>indium-doped tin oxide</td>
</tr>
<tr>
<td>J&lt;sub&gt;SC&lt;/sub&gt;</td>
<td>short circuit current</td>
</tr>
<tr>
<td>MeOH</td>
<td>methanol</td>
</tr>
<tr>
<td>MPA</td>
<td>3-mercaptopropionic acid</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>OA</td>
<td>oleic acid</td>
</tr>
<tr>
<td>PCBM</td>
<td>[6,6]-phenyl-C₆₁-butyric acid methyl ester</td>
</tr>
<tr>
<td>PbCl₂</td>
<td>lead chloride</td>
</tr>
<tr>
<td>PbS</td>
<td>lead sulfide</td>
</tr>
<tr>
<td>PCE</td>
<td>power conversion efficiency</td>
</tr>
<tr>
<td>QCM-D</td>
<td>quartz crystal microbalance with dissipation</td>
</tr>
<tr>
<td>R&lt;sub&gt;S&lt;/sub&gt;</td>
<td>series resistance</td>
</tr>
<tr>
<td>R&lt;sub&gt;SH&lt;/sub&gt;</td>
<td>shunt resistance</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>TiO₂</td>
<td>titanium dioxide</td>
</tr>
<tr>
<td>TOF</td>
<td>time of flight</td>
</tr>
<tr>
<td>UPS</td>
<td>ultraviolet photoelectron spectroscopy</td>
</tr>
<tr>
<td>VOC</td>
<td>open circuit voltage</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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Chapter 1  Introduction and Motivation

Humanity needs to balance the requirement of economic growth (crucial to stability and the alleviation of poverty) with the environmental impact of continued growth. Historically, the world economy has in significant part been enabled by the extraction and consumption of fossil fuels, such as coal, gas and oil, and these energy sources continue to generate the majority of electricity and power the majority of transportation worldwide (Figure 1-1). While attractive due to their high energy density, which has enabled technology ranging from power plants to the personal automobile, the combustion of fossil fuels generates significant harmful byproducts. The primary product of the combustion reaction, carbon dioxide, is a powerful greenhouse gas, and is generated in such quantities worldwide that the average atmospheric concentration recently exceeded 400 ppm. Climate scientists have warned of the potential impacts of such high levels of atmospheric CO$_2$, and have predicted that, in order to limit global temperature rise to 2°C over the preindustrial average (beyond which numerous climate catastrophes are predicted), carbon dioxide levels must be limited to 300-350 ppm. Given the long lifetime of carbon dioxide in the atmosphere, even if all emission were halted today, decades would pass before CO$_2$ concentration dropped back to the predicted safe level. Along with carbon dioxide, many fossil fuel sources (coal in particular) emit other pollutants which are more immediately harmful to human health, including soot particulate and sulfur/nitrogen oxides. Coal-dependent jurisdictions worldwide, in particular large Chinese metropolises, have been coming to terms with the cost to air quality and human health of continued large scale emission of pollutants in highly populated areas.
Global energy consumption is set to continue rising over the coming decades. To mandate zero consumption growth, particularly in developing nations, would condemn millions to continued poverty. This challenge suggests that we shift the means of production: economic growth must be decoupled from the production of greenhouse gases and other environmentally hazardous waste.

Fossil fuels are nothing more than sources of potential energy: they are solar energy that was stored via a conversion of carbon dioxide into organic compounds by photosynthesis millions of years ago. Rather than relying on the (ultimately very inefficient) process of extracting imbued solar energy from fossil fuel, we must shift our energy production closer to the source – the sun itself.

Solar energy is the most abundant and cleanest source of energy available on Earth; it is also the most underutilized. At a peak intensity of 1000 W/m$^2$, averaged over space and time, sunlight provides vastly more energy daily than the global population consumes.
Solar energy thus offers, in principle, a compelling option to power a sustainable and increasingly electricity-centric future. A robust photovoltaic industry is beginning to take shape worldwide, driven by early-generation solar technology based on silicon and compound semiconductors such as cadmium telluride. In order to compete with traditional energy sources, particularly with cheap and plentiful natural gas, solar photovoltaic systems must cost, fully installed, no more than $1 per watt-peak, which translates to a competitive $0.05/kWh energy cost over a system lifetime. While the cost of silicon solar panels has dropped precipitously in recent years (Figure 1-2), the field is still open to opportunities for new, cheap, lightweight materials and devices. Third-generation photovoltaic systems, including perovskite, organic, dye-sensitized, and colloidal quantum dot (CQD) solar cells, offer a path to low-weight, low-cost, and potentially high-efficiency solar energy capture and conversion. While third-generation technologies currently function at lower efficiency than commercial first-generation modules, significant pathways exist to reach and surpass the conversion efficiencies required to be commercially feasible.

![Figure 1-2 Solar module and system pricing](image)

While silicon solar cells maintain an advantage over new technologies simply due to economies of scale, they face several inherent limitations. First, silicon panels are bulky, inflexible, and require significant additional cost to install mounting racks to ensure long term stability. Second, the production of highly pure silicon requires expensive
manufacturing facilities, cleanrooms, and highly rigorous process control, boosting the overall cost of the product. Finally, while the bandgap of silicon is ideal for the capture and conversion of visible light, one fifth of the energy from the sun, in the form of near-infrared light, cannot be absorbed by silicon and is therefore wasted (Figure 1-3).

![Solar intensity spectrum](image)

**Figure 1-3 Solar intensity spectrum.** Red regions indicate photons which are not absorbed by standard silicon solar cells.

The ideal solar material should be cheap, lightweight, highly manufacturable, and able to convert a broader range of solar energy into electricity than allowed by silicon. This thesis will highlight the potential of colloidal quantum dots to fill this niche. In brief, CQDs are nanoscale semiconductor particles, capped with stabilizing surface molecules and suspended in solution. This solution can then be employed as an ink, allowing the fabrication of thin, solution-processed photovoltaic films. Additionally, the nanometer scale of the particles switches the materials physics regime from bulk properties to a quantum confined state, where the optoelectronic properties of the semiconductor can be tailored by slight adjustments to the particle size. This allows a given semiconductor to
exhibit a custom-selected bandgap energy to capture infrared solar energy when synthesized in nanoparticle form.

CQD solar cells represent a potentially interesting alternative or additive to first generation silicon solar panels, yet in order to produce efficient devices with meaningful output capacity, a key material limitation must be addressed and overcome. Diffusion length, the average distance an electrical charge carrier can travel through the active film from its point of generation before recombining, is a critical materials parameter. A longer diffusion length allows for thicker films, higher light absorption potential, and improved electrical transport through the film leading to overall more efficient devices. In single crystalline silicon solar cells, diffusion length is typically in the hundreds of micrometers,\(^\text{11}\) while the typical measured value for colloidal quantum dot solar cells is roughly 75 nm.\(^\text{12}\) This three-orders-of-magnitude difference is a key limitation holding back progress in the CQD photovoltaic field. This thesis details a multi-pronged approach to improving the diffusion length in CQD solids.

A brief outline of this thesis is as follows: Chapter 1 describes the motivation for studying colloidal quantum dot photovoltaics and a key challenge facing the field. Chapter 2 examines existing research in the CQD field, introducing the material system in greater detail, discussing the three-facet impact of electrical transport, surface passivation and film impurities on diffusion length in CQD films, and outlining the benefits and limitations of existing CQD surface chemistry approaches. Chapters 3 through 6 focus on the novel work produced for this thesis. As indicated by Figure 1-4, Chapter 3 will outline strategies for measuring and improving electrical transport in CQD films, Chapter 4 will address techniques for improving CQD surface passivation, and Chapter 5 will highlight the impact of impurities in CQD solids and suggest impurity management strategies. Chapter 6 draws on the lessons learned in the three preceding chapters, combining improvements in impurity management, passivation, and electrical transport to design a CQD solar cell with the longest diffusion length reported to date in this material – four times greater than previously observed values. Chapter 7 draws together the overall conclusions and findings generated in this thesis, highlighting the relevance and impact on future research directions.
Figure 1-4 Thesis outline. Lessons are drawn from initial studies to improve electrical transport, quantum dot passivation, and impurity management in quantum dot films, and are integrated into a single elegant method of creating quantum dot solids with record carrier diffusion length.
Chapter 2  Background

The first solar cell constructed using colloidal quantum dots was created in 2005; in the decade since that initial discovery, the field has progressed significantly, with major material and architectural improvements that have seen device efficiencies escalate from sub-1% solar power conversion efficiency to certified efficiencies of near-10% today.

This chapter will examine in detail the research that has led up to and informed the novel work presented later in this thesis. First, the underlying theory of photovoltaic devices will be briefly covered, to set out the context for the remainder of the thesis. Second, colloidal quantum dots will be described in greater detail, laying out the structure, chemistry and synthesis of these nanoparticles, and surveying the techniques that have been developed to convert colloidal solutions into high quality films and devices. Finally, previous research into the three factors which limit the diffusion length in CQD solids (transport, passivation and impurities) will be outlined.

Some content in this chapter has been adapted from a previously published review article (G.H. Carey, K.W. Chou, B. Yan, A.R. Kirmani, A. Amassian, E.H. Sargent, Materials processing strategies for colloidal quantum dot solar cells: advances, present-day limitations, and pathways to improvement, MRS Communications 3, 1-8, 2013) and from a to-be-published, invited review in Chemical Reviews titled Colloidal Quantum Dot Solar Cells.

2.1 Photovoltaic Theory

Every photovoltaic device can be reduced, in its simplest form, to the combination of three key components: a light absorbing material, a charge separating and/or transporting material, and asymmetric electrodes for charge extraction (Figure 2-1). In practice, solar cell design can become quite complex, as there exist numerous ways to fulfill the three requirements with a wide variety of mixed material systems. In some systems, the light absorber and the charge transporting material are a single component (for instance, in silicon, compound semiconductor, and many quantum dot solar cells), while other systems rely on separate materials to absorb light and transport photogenerated carriers (dye-
sensitized and many organic solar cells). Further complicating the picture, the electrodes can be chosen to allow or reflect light; typically, the front electrode in a cell is a transparent conductive material, while the back electrode includes a highly reflective metal, to reflect any remaining unabsorbed light back through the absorbing material for a second pass.

![Basic photovoltaic device schematic](image)

**Figure 2-1 Basic photovoltaic device schematic.** A standard solar cell consists of an absorbing/charge separating layer, sandwiched between electron and hole transporting materials (ETL and HTL respectively); the front layer is transparent, while the back layer is typically reflective to allow a second pass of unabsorbed light.

Once a photon has been absorbed by the active layer of the solar cell, an exciton (a tightly-bound electron-hole pair) is generated at the point of absorption. This exciton has equivalent energy to the absorbed photon (i.e. any energy greater than the material bandgap), and relaxes over a short period of time to the bandgap energy of the absorber. In order to generate a useful output, the exciton must be separated into its constituent carriers, which must then be transported and removed via the opposing electrodes. Depending on the properties of the absorber/transporting material(s), various trap states and recombination processes can intervene in the full extraction of every photogenerated carrier, limiting the output current.

Extraction of the charge carriers depends on the presence of either an electric field produced by an external bias, or a built-in electric field generated by a metal-semiconductor or semiconductor-semiconductor interface. Many solar cells (including all CQD devices described in this thesis) are driven by a pn junction – the junction formed by
the interface of a p-doped semiconductor (e.g. CQD solid) and an n-doped semiconductor (e.g. titanium dioxide). At such a junction, the large carrier concentration gradient across the interface causes electrons to diffuse from the n-type to the p-type semiconductor, and holes to diffuse in the opposite direction (Figure 2-2). This establishes a quasi-neutral region in each semiconductor, and sets up a built-in electric field in the depletion region at the interface. The depletion region width, $W$, is the total of the depletion region in each semiconductor ($x_p$ and $x_n$ respectively), as described by equation 2.1,

$$W = x_p + x_n = \left[ \frac{2\varepsilon k T}{q^2} \ln \left( \frac{N_A N_D}{n_i^2} \right) \left( \frac{1}{N_A} + \frac{1}{N_D} \right) \right]$$

where $\varepsilon$ is the permittivity, $k$ is the Boltzmann constant, $T$ is the temperature, $q$ is the elementary charge, $n_i$ is the intrinsic charge, and $N_A$ and $N_D$ are the acceptor and donor concentrations in the p-type and n-type semiconductors, respectively; the individual depletion widths are calculated by multiplying $W$ by $N_A/(N_A + N_D)$ or $N_D/(N_A + N_D)$ – giving $x_n$ and $x_p$, respectively. The depletion region is therefore thickest on the lower doped side of the pn junction. For heterojunctions between lightly doped nanoparticles and highly doped titanium dioxide, this generates a sizeable depletion region in the quantum dot layer.

**Figure 2-2 Schematic of a pn junction.** In this example, a lightly p-doped semiconductor is connected with a heavily n-doped semiconductor. A large carrier concentration gradient causes charge diffusion across the interface until equilibrium is established, setting up a depletion region (centre) and quasi-neutral regions (far left and right).
In an active layer with both a depletion region and a quasi-neutral region, two distinct electrical transport mechanisms are in effect. The depletion region is dominated by drift current (determined by carrier mobility and magnitude of the electric field), whereas transport is dominated by diffusion in the quasi-neutral region (determined by mobility and recombination lifetime). For a solar cell thick enough to absorb a significant fraction of any incident light, both region types are typically present, and therefore it is desirable for both drift and diffusion to be highly efficient processes.

Solar cell performance is characterized under one sun simulated illumination, typically using the American Society for Testing and Materials AM 1.5 G standard spectrum. Device behavior is compared by plotting the current-voltage profile under illumination, typically plotting current density \( J \) (mA cm\(^{-2}\)) versus applied bias \( V \) (V) – a representative curve is shown in Figure 2-3. Several key metrics are used to characterize the performance of any given solar cell from a plot such as Figure 2-3. Most obviously, open-circuit voltage \( V_{OC} \) is the voltage at zero current, while short-circuit current \( J_{SC} \) is the current observed at zero bias. On the curve between these points, the point at which the current-voltage product maximizes is called the maximum power point (MPP). This point has related current and voltage values, \( J_{MPP} \) and \( V_{MPP} \), respectively. The difference in area between the J-V curve and the rectangle outlined by the maximum power point coordinates is known as fill factor (FF), and is defined by equation 2.2.

\[
FF = \frac{J_{MPP} \cdot V_{MPP}}{J_{SC} \cdot V_{OC}}
\]  \hspace{1cm} (2.2)

This factor describes the squareness of the J-V curve, with an ideal value of 1. Lower fill factor reduces the overall efficiency of the solar cell \( \eta \), the ratio of electrical power output to solar power input \( P_{IN} \), described by equation 2.3.

\[
\eta = \frac{FF \cdot J_{SC} \cdot V_{OC}}{P_{IN}}
\]  \hspace{1cm} (2.3)

Fill factor is determined by the parasitic series and shunt resistances \( R_{S} \) and \( R_{SH} \) present in the device. These values can be extracted from the J-V curve by calculating the slope near \( V_{OC} \) and \( J_{SC} \), respectively – in an ideal diode, series resistance would be zero, and shunt resistance would approach infinity.
Figure 2-3 Representative current-voltage curve. Characteristic points of interest are short-circuit current ($J_{SC}$), open-circuit voltage ($V_{OC}$), and the maximum power point (MPP), with its corresponding current and voltage values. Series and shunt resistances ($R_S$ and $R_{SH}$) are calculated from the slopes of the curve near the axes. Reprinted by permission from Macmillan Publishers Ltd: Nature, copyright 2012.

2.2 Colloidal Quantum Dots

Colloidal quantum dots, or CQDs, are semiconductor nanocrystals capped with surface molecules (ligands) which allow suspension in solution via steric or electrostatic factors. This section will detail the process of quantum dot synthesis, followed by a discussion of film formation – the process by which a colloidal solution is converted to a well-packed solid film of nanoparticles. The section concludes with a brief overview of the device architectures that have been employed to create successful CQD photovoltaic devices to date.

2.2.1 CQD Synthesis

The primary synthesis used for CQDs (in particular those employed throughout this thesis, lead sulfide (PbS) nanoparticles) relies on the LaMer model,$^{17,18}$ which is depicted in Figure 2-4. Nanoparticle precursors (e.g. a lead and sulfur source) are injected into a stabilizing solvent at elevated temperature. At elevated concentrations (above the
nucleation threshold), nucleation will occur, forming small, plentiful nanocrystals. After the initial nucleation phase, the concentration of remaining precursors will be below the nucleation threshold, ensuring a constant population of quantum dots, and allowing the remaining precursors to solely react with the existing particles, rather than forming new small nuclei. This generates a consistent, high quality, monodisperse set of nanoparticles.

![LaMer model schematic](image)

Figure 2-4 LaMer model schematic showing the process of nanocrystal nucleation and growth over time. Reproduced with permission from The Royal Society of Chemistry.

Depending on the reaction temperatures used and the duration of ripening allowed before the reaction is quenched, a wide variety of quantum dot sizes can be achieved. Combined with the quantum confinement effect, this allows for a broad range of effective bandgap energies. The Brus equation (equation 2.4) details the quantum confined bandgap, $E$, as a factor of the bulk bandgap, $E_g$, Planck’s constant, $h$, the quantum dot radius, $r$, and the effective mass of the electron and hole in the material ($m_e^*$ and $m_h^*$).

$$E = E_g + \frac{h^2}{8r^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right)$$
Figure 2-5 shows the impressive amount of control over optoelectronic properties possible in a single material, with quantum dots with diameters from 3 to 10 nm and excitonic absorbance peaks (related to the optical bandgap of the material) ranging from 900 to 2100 nm.

![Absorption spectra for various PbS quantum dot sizes](image)

**Figure 2-5 Absorption spectra for various PbS quantum dot sizes**, ranging from 3-10 nm in diameter. Reprinted with permission, copyright 2011 American Chemical Society.

### 2.2.2 CQD Film Formation

While the physical process of converting a solution of quantum dots into a solid film consistently involves solution deposition and solvent evaporation, the method of deposition has significant impacts on the physical morphology and macroscopic properties of the resultant film. All methods rely on depositing a small volume of solution onto a substrate and evaporating the solvent, leaving behind a collection of immobile quantum dots. Typically, a low boiling point solvent is chosen to facilitate a rapid drying step, in order to quickly and reproducibly obtain quantum dot solids for further processing. This process varies minimally between methods; the key point of variation is the means of depositing the initial solution on a given surface.
The majority of studies to date have focused on small-scale, batch-driven deposition methods. These methods tend to favor minimizing material use over scaling up the final film dimensions; for process development studies, batch processing is sufficient to discover and study characteristics and trends. The three batch deposition methods most commonly employed are drop-casting, spin-coating, and dip-coating. Drop-casting is the simplest of the three; a drop of solution is deposited on a substrate and simply left to dry without further physical impetus. Drop-casting is typically employed when the quantum dots are dispersed in a high boiling point solvent such as dimethylsulfoxide or formamide; such solvents are generally only used to disperse quantum dots capped with short, polar ligands, rather than the native long chain organic ligands. Depending on the boiling point of the chosen solvent, drop-casting can be performed on a hotplate at elevated temperature, to speed the evaporation process; however, adjusting the deposition temperature could alter the morphology and characteristics of the final film, as well as introducing chemical reactions such as oxidation into an otherwise purely physical process. The long timescales typically involved in drop-cast film formation can lead to low quantum dot packing density in the final film and negatively impact film characteristics.

Spin-coating is a variation on drop-casting; the substrate is mounted on a rotating vacuum stage, and after deposition of the initial solution, the stage is spun at typical speeds of 1000-5000 rpm, leading to spreading and shearing of the deposited solution. A constant spin-coating speed leads to reproducible, uniform thin films; to build up a film of desired thickness, the deposition and spinning process is typically repeated several times (layer-by-layer deposition). This method tends to consistently generate the highest quality film morphology. Spin-coating is input-intensive, and wastes a significant fraction of the total quantum dot solution used; additionally, the process can be highly sensitive to spin speed and ambient conditions such as temperature and humidity. Solvent choice is important; relatively low boiling point solvents such as toluene or octane must be chosen to balance colloidal stability with quick evaporation to ensure high quality morphology thin films. While the process is useful for small-scale device development, it is incompatible with scaled-up device fabrication.
Dip-coating applies a different mechanism for film deposition; rather than depositing solution on a substrate, the substrate is dipped into a stock solution of quantum dots, and withdrawn at a constant rate (typically using an automated system to ensure precision and repeatability). Based on the viscosity and surface tension of the solution, a thin layer is deposited on the substrate after evaporation. This process wastes less of the initial inputs, and is slightly more scalable than spin-coating; however, it generates slightly less uniform films, and requires the use of lower boiling point solvents such as hexane to ensure proper deposition at the liquid/substrate interface. Dip-coating is also susceptible to changes in ambient processing conditions.

Small-scale batch processing is acceptable for initial research purposes, but as the field matures, researchers are increasingly examining the feasibility of scaled-up deposition methods. Such techniques must be able to deposit material over much larger areas, and are typically compatible with roll-to-roll processing schemes. Two such methods which have gained increasing attention in recent years are ink-jet printing and spray-coating. Each technique uses automated setups to reproducibly deposit very small volumes of colloidal quantum dot solution over a large area, and can be integrated into a setup with a continuous, rolling substrate for increased throughput and manufacturability.

Long-chain ligands facilitate solution processing by allowing consistent, stable dispersions of capped quantum dots in low boiling point non-polar solvents such as octane or toluene; however, in a deposited film, the length of the capping molecule greatly increases the spacing between individual quantum dots. There is some debate in the field surrounding the nature and mechanism of electronic transport between quantum dots; some researchers report band-like transport, while others indicate that a carrier hopping mechanism dominates. It is not disputed, however, that widely-spaced dots suffer from low carrier wavefunction overlap and consequently low carrier mobilities in film.

To minimize dot-to-dot spacing and thereby maximize carrier transport, a layer-by-layer treatment, applied as a post-film-formation treatment to a quantum dot film, has dominated all promising device reports. This approach, termed the solid-state exchange, is depicted in Figure 2-6. An initial film of long-chain-capped quantum dots is deposited
on the substrate. The processing conditions can be optimized to achieve a solid film with initial thickness ideally no more than 40-50 nm, and with reasonably close packing and, potentially, mesoscale order. This film is subsequently treated using a solution containing a second, shorter molecule or atom. By introducing an overconcentration of this shorter ligand in a solvent that does not disperse the long-chain-capped quantum dots, and by selecting a substituting molecule that will bind more strongly the quantum dots than does the original long-chain ligand, the original long molecules can be removed and replaced with the new ligand. The quantum dots are thus rendered insoluble, and the film is typically rinsed to remove any remaining unbound ligands and byproducts. The entire process is then repeated until the desired total thickness of film has been deposited.

Figure 2-6 Layer-by-layer solid state exchange. Clockwise from the top, a thin layer of long-chain ligand capped CQD is deposited on the substrate and rapidly dried. This film is subsequently treated in a solution of a second, shorter ligand; concentrations and treatment times vary depending on the experiment. A rinsing step with a pure solvent generally follows the exchange to remove any remaining unbound ligands. The entire process is repeated until the desired thickness of film has been built up. Reprinted with permission from Cambridge University Press, copyright 2013.

2.2.3 CQD Photovoltaic Devices

Since the conception of infrared-capable CQD solar cells in 2005, the field has made rapid progress, improving from initial sub-1% to 9.9% certified solar power conversion efficiencies in 2015. Major advances can be categorized into two broad headings:
improvements in materials science and engineering, and improvements in device architecture, wherein the best is made of the quantum dot solid’s available electronic materials properties by rational choice of electrodes and optimization of the overall materials stack from a joint optical and electronic perspective.

In reference to progress in device architecture (Figure 2-7), formative research in the field was carried out on the relatively simple Schottky architecture. Devices consist of a layer of p-doped quantum dots sandwiched between an Ohmic conductive transparent electrode such as indium tin oxide and a metal electrode with a shallow work function. In this layout, a Schottky junction is formed at the quantum-dot-to-metal interface, giving rise to charge separation via the formation of a depletion region with a built-in field that separates and drives out electrons and holes. This architecture suffers when, in an attempt to increase total light absorption, the thickness of the active layer is increased well beyond the thickness of the depletion region. In this case, the strongest rate of generation occurs in the undepleted quasi-neutral material, in which minority carrier diffusion proceeds inefficiently in today’s CQD solids.

**Figure 2-7 CQD PV device schematics.** Each device is constructed on glass coated with a transparent conductive oxide (either indium tin oxide (ITO) or fluorinated tin oxide (FTO)). The Schottky cell, left, has a layer of p-doped CQD directly on the substrate, with a shallow work function metal (aluminum or magnesium) forming the top contact. The depleted heterojunction, middle, has a layer of mesoporous, n-doped titania between the substrate and the CQD layer, with a deep work function hole acceptor as the top electrode (either gold or molybdenum oxide). The quantum junction cell, right, employs layers of p- and n-doped QDs to form a p–n junction using one base material system. Reprinted with permission from Cambridge University Press, copyright 2013.
The field addressed this limitation by designing architectures that shift the charge-separating interface closer to the source of illumination. The first and, to date, most efficient architecture designed is the depleted heterojunction, which flips the Schottky structure and layers the quantum dots atop a shallow work function, transparent electron acceptor such as titania or zinc oxide.\textsuperscript{48-52} The Ohmic contact is now formed at the back of the cell, the top electrode made using a deep work function metal or, most promisingly, a metal oxide such as molybdenum oxide. In a similar vein, the recently reported quantum junction architecture replaces the thick oxide electron acceptor layer of the depleted heterojunction with a pn junction fully comprised of appropriately-doped quantum dots.\textsuperscript{53,54} In this architecture, which relied on improved control of doping type and amplitude in quantum dot solids, light passes through a thin p-doped layer followed by a thicker n-doped film, with the desired charge separation occurring at the interface. A blend of these two methods has also been reported, creating a p-i-n structure by sandwiching a thick intrinsic layer of quantum dots between a thin p-doped layer and an n-doped transparent conductive oxide.\textsuperscript{55} Present-day performance records for each platform are outlined in Table 2-1.

<table>
<thead>
<tr>
<th>Architecture</th>
<th>Voc (V)</th>
<th>Jsc (mA cm\textsuperscript{-2})</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schottky\textsuperscript{41}</td>
<td>0.46</td>
<td>19.3</td>
<td>58</td>
<td>5.2</td>
</tr>
<tr>
<td>Quantum junction\textsuperscript{53}</td>
<td>0.52</td>
<td>23.3</td>
<td>50</td>
<td>6.1</td>
</tr>
<tr>
<td>Depleted heterojunction\textsuperscript{52}</td>
<td>0.55</td>
<td>29.9</td>
<td>58</td>
<td>9.2</td>
</tr>
<tr>
<td>p-i-n junction\textsuperscript{55}</td>
<td>0.55</td>
<td>24.2</td>
<td>64</td>
<td>8.6</td>
</tr>
</tbody>
</table>
2.3 Performance Limitations in CQD Solids

When one compares performance characteristics from Table 2-1 with theoretical performance limits, it is clear that today’s best devices operate well below their inherent potential. Each of their open-circuit voltage; their short-circuit current; and their fill factor are 1.4-1.6x lower than the optimum. Numerous research groups have worked to quantify these limitations, and consistently arrive at a similar conclusion: major further quantitative improvements in electronic transport are required to continue rapid progress for the field. Improved electronic transport must include, but go well beyond, reporting higher carrier mobilities for electrons and holes. Only once carrier lifetime, limited by the presence of recombination centres, is also dramatically improved, can the sum of the diffusion length and drift length become comparable to, and ultimately exceed, the absorption length for light of all solar wavelengths of interest.

2.3.1 Electrical Transport

Electrical transport characteristics for a number of different quantum dot film systems are summarized in Figure 2-8. Figure 2-8a and b show mobility measurements for field-effect transistor (FET) architectures generated by the Sargent\textsuperscript{61} and Law\textsuperscript{34} groups, respectively. Mobility extracted in this manner does not correspond directly to carrier mobility in an active solar cell, since the properties of a transistor channel are quite distinct from the path traveled by carriers in a photovoltaic device. Further, in the FET mobility measurement, electronic trap states that can limit average mobility in an operating solar cell can be filled, and thus overcome, through gate-electrode control over the Fermi level in the transistor test structures. Nevertheless, this technique can be instructive in identifying promising ligands and treatments, and can be used as a comparative tool, as shown in both Figure 2-8a (comparing mobilities for various inorganic ligands attached to PbS dots) and Figure 2-8b (comparing mobilities for similar ligands of various lengths attached to PbSe dots).
Figure 2-8 Carrier mobility values in CQD films. Values are extracted for a variety of QD and ligand types, consistently showing low mobility: (a) mobility and carrier density measured using FETs composed of PbS QDs capped with halide ligands from tetrabutylammonium-chloride, -bromide, and -iodide. (b) Mobility measured using FET layouts for PbSe QDs capped with dithiols of varying length (EDT, ethanedithiol; PDT, propanedithiol; BuDT, butanedithiol; PenDT, pentanedithiol; HDT, hexanedithiol), showing an inverse trend in mobility with increasing ligand length. Adapted with permission from Cambridge University Press, copyright 2013.40

The solid-state exchange method detailed in Figure 2-6 presents a second key limitation: exchanging from a very long-chain capping ligand to a very short ligand inevitably leads to a large volume contraction in the deposited film. This can lead to cracking on either a micro- or macroscopic scale; cracking reduces film density, lowering absorption per unit length, while simultaneously creating potential electrical shorts through the film and lowering conductivity compared to a continuous film. This problem is typically reduced or eliminated by creating many-layered films, rather than depositing a single, thick layer.

Researchers have shown the positive influence of ordering or superstructures on electrical transport characteristics in nanocrystalline films.62,63 The solid-state exchange reduces the ordering found in the originally deposited film. Instead of a film of tightly-packed quantum dots limited only by the length of the ligands between dots, the solid state exchange leads to films with highly variable dot-to-dot spacing. While the solid-state exchange to a short ligand leads to significantly shorter average interparticle spacing than the initial film, disorder tends to be high. Disorder is expected to work to the detriment of electronic transport: rather than taking the straightest path available in a film consisting of
evenly-spaced quantum dots (Figure 2-9, left), charge carriers will travel a more tortuous percolation path (Figure 2-9, right).

**Figure 2-9 Effect of disorder on carrier transport.** Schematic diagram portraying a simplified, two-dimensional argument for the importance of uniform, tightly packed QDs in a final film, shown on the left. In this film, any given carrier has a simple, direct path from generation site to extraction (path shown in red). By contrast, a film with a broader distribution of dot to dot distances (right) forces carriers to account for both spacing and field when being extracted, leading to longer effective extraction lengths. Adapted with permission from Cambridge University Press, copyright 2013.

### 2.3.2 Nanocrystal Surface Passivation

One potential reason for low photovoltaic performance in such systems may be related to the second function of capping ligands – reducing trap state density by passivating surface states. It is well known that dangling bonds at surfaces in bulk semiconductors represent significant trap states; the large surface-to-volume ratios in quantum dot films magnify this effect. Various ligand strategies have been examined to minimize this effect. To date, the most successful strategies include purely atomic ligands such as iodine or bromine, or a hybrid of atomic ligands and short organic ligands such as mercaptopropionic acid or ethanedithiol. Full ligand coverage has been attempted via ligand exchange or via a mixture of passivation in solution and solid state ligand exchange.

A recent alternative to solid-state ligand exchange is fully solution-exchanged quantum dots. Such strategies exchange fully from long aliphatic capping ligands to the desired final short species while adjusting the stabilizing solvent from non-polar to polar to maintain colloidal stability. Examples include metal chalcogenide complex ligands and short organic ligands similar to those used in solid state exchanges mixed with
stabilizing molecules. Devices using fully solution-exchanged nanoparticles have, to date, demonstrated limited photovoltaic efficiency, due in large part to deficiencies in film formation.

Ligand exchange in metal chalcogenides (the dominant CQD materials for photovoltaic systems) has tended to focus on passivation of exposed metal centres, with minimal research on the impact of sulfur/selenium passivation. Two binding modes have recently been proposed for thiol ligands in metal/sulfur quantum dots, with the sulfur bound either within the nanocrystal or to a surface metal, as shown in Figure 2-10. Such a strategy could lead to improved overall passivation and enhanced photovoltaic performance. Additionally, a model has been proposed wherein excess metal carboxylate complexes in solution (Z-type ligands) bind reversibly to surface chalcogens, leading to dynamic surface passivation.

Figure 2-10 Chalcogen passivation in quantum dots. Thiol ligands shown incorporated into the crystal structure of a nanoparticle or surface-bound to metal atoms. Adapted with permission, copyright 2014 American Chemical Society.
2.3.3 Impurities and Their Removal

Due to the overwhelming impact of the surfaces on overall properties of a quantum dot solid, only limited attention has been paid to the impact of non-surface-bound chemical impurities on film characteristics, in contrast with related bulk semiconductor fields. The majority of intentional impurity (and related quantum dot stoichiometry) studies have focused on adjusting synthesis parameters and conditions; recent evidence indicates that impurities may also be introduced in post-synthesis processes, such as the carbon-rich stripes observed between quantum dot layers in Figure 2-11. Some inclusions may be inert within the film, while others appear to be electronically active, increasing the trap state density in the film. Additionally, the effect of quantum dot size polydispersity is significant; because optoelectronic properties are governed by dot size, overall film properties can be pinned by a relatively low population of differently-sized quantum dots. Novel approaches have been developed to purify films, eliminating all species other than quantum dots of a single size and ligands directly passivating surface sites.

![Cross-sectional TEM images of layer-by-layer fabricated CQD films](image)

**Figure 2-11 Impurities in CQD films.** Cross-sectional TEM images of layer-by-layer fabricated CQD films (top) indicate the presence of impurities, which vary depending on deposition technique. Electron energy loss spectroscopy (EELS) further elucidates that such impurities are sulfur-poor and carbon-rich (bottom). Reprinted with permission, copyright 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
Chapter 3  Electrical Transport in CQD Solids

Electrical transport through quantum dot films, particularly charge carrier mobility, is a significant limiting factor in the search for long diffusion length material systems. By reviewing existing research, it is clear that a driving factor for improved mobility in CQD solids is improved film packing density – the higher the overlap in electron wavefunction between adjacent quantum dots, the greater the observed mobility, typically. This chapter will address two distinct paths to improving the packing density of quantum dots in a film: a solution-based partial ligand exchange, and a novel ligand that can be cleaved in situ rather than exchanged.


3.1 Multi-Ligand Mobility Enhancement

Previous research in the field of colloidal quantum dot photovoltaic devices has attempted to create denser quantum dot films by exchanging the initial stabilizing surface ligand (typically oleic acid, an 18-carbon long organic molecule) with the shortest possible surface passivant, single atom ligands such as chlorine, iodine or bromine. While this approach led to moderately successful device efficiencies, electrical transport in such films was limited, and fell below expected conditions for highly densified films. In this section, a variant of the atomic ligand approach is introduced, combining atomic ligands with short bifunctional organic molecules to produce an actively densifying process and improved carrier mobilities in CQD films.
A hybrid ligand passivation strategy was developed to combine the benefits of strong surface passivation observed in inorganic, atomic ligand passivation, with the active densifying capabilities of short bifunctional molecules such as 3-mercaptopropionic acid (MPA). Metal halide salts were introduced during the synthesis process, with CdCl₂ or PbCl₂ dissolved in tetradecylphosphonic acid and oleylamine added to the synthesis mixture following termination of the nanocrystal growth stage. It was observed by X-ray photoelectron spectroscopy (XPS) that both the cation and anion in the salt attach to unpassivated surface sites, and are responsible for displacing a fraction of the initial long chain surface ligand (oleic acid).

Films were fabricated using the partially solution-exchanged quantum dots; thin layers were deposited by spincoating and treated with a solution of MPA in methanol, exchanging the remaining oleic acid ligands with the shorter, bifunctional ligand. Synchrotron grazing-incidence small-angle X-ray scattering (GISAXS) measurements were used to compare the dot-to-dot spacing between the hybrid films, films of unexchanged (oleic acid capped) quantum dots, and films of the previously described inorganic-exchanged, atomic ligand capped quantum dots (Figure 3-1). Intensity maps (Figure 3-1a-c) show that, while the strongest order is observed for unexchanged quantum dots, the closest interparticle spacing is obtained in the hybrid exchange case. Indeed, as shown in Figure 3-1d, for nanoparticles of ~3.1 nm in diameter, the inorganic ligand only approach led to, if anything, slightly less well packed films, on average, than unexchanged films, while the hybrid approach led to an average decrease in dot-to-dot spacing of roughly 1 nm.
Figure 3-1 Film density comparison via GISAXS. a–c, GISAXS patterns of as-cast, unexchanged CQDs (a) and films treated using fully inorganic passivation (b) and hybrid passivation (c). The x- and y-axes represent the scattering wave vector in the y (scattering in the direction along the sample surface perpendicular to the X-ray beam) and z (scattering normal to the sample surface plane) directions, respectively. The colour scale represents the log of the scattering intensity as recorded by the CCD. Blue represents lower intensity and red represents higher intensity, with each spectrum normalized to show the full dynamic range of each data set. d, By integrating the intensity in a–c azimuthally, the average interparticle spacing can be found. Inorganic passivation (green curve), in spite of minimally sized atomic ligands, does not increase the film density compared with initially cast dot films (red curve). An exchange using short bidentate organic thiols (blue curve) results in a significant reduction in average interparticle spacing.

A charge carrier time of flight (TOF) measurement setup was constructed to measure the hole carrier mobility in these films. Samples were optically excited using 1 ns
pulses from a 355 nm laser (to ensure full light absorption very close to the pumped interface). The sample was held under a range of applied biases, with the transient current output observed with an oscilloscope. A thick (~500 nm) film was used to minimize the effect of RC limitations on the output signal. Transient signals for MPA-only films, and hybrid devices using PbCl$_2$ and CdCl$_2$ are shown in Figure 3-2a-c. As expected, increasing bias led to shorter carrier transit times through a film (indicated by the knee on a log-log plot). Plotting the inverse transit time versus applied bias (and correcting for sample thickness) led to Figure 3-2d; the slope of these curves is equivalent to the hole mobility in the film. The mobility varied with the hybrid passivant (discussed in greater depth in Chapter 4), but in general, was measured to be in the mid $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ range, a significant improvement for this characteristic transport property.
Figure 3-2 Carrier mobilities measured by time-of-flight (TOF). a–c, TOF measurements showing the hole current versus time (both on log scales) for six different bias voltages between 0 V (bottom line) and 0.6 V (top line, for a) or 1 V (top line, for b and c) for CQD films using organic passivation (a), hybrid passivation with a PbCl$_2$ in-synthesis treatment (b) and hybrid passivation using a CdCl$_2$ in-synthesis treatment (c), which we have found to work best in this study. Green lines (only shown for one curve in each panel for clarity) demonstrate the fits to the linear regimes used to extract the carrier transit times. d, Extracted carrier velocity plotted versus field to calculate the majority carrier mobility for the organic (red), PbCl$_2$ hybrid (pink) and CdCl$_2$ hybrid (blue) cases. A steeper slope (and thus higher mobility) implies improved trap passivation.
3.2 Ligand Cleavage

As demonstrated in the previous section, the pursuit of high mobility, photovoltaic-applicable colloidal quantum dot solids has typically been driven by attempts to increase film packing density through the use of short replacement ligands.\textsuperscript{65,66} While this line of research has produced interesting, relevant results, progress has been hampered by one of two factors. On one hand, in the majority of processing conditions, quantum dots are kept colloidal stable in solution with long organic ligands, which are subsequently exchanged in the solid state with shorter ligands. This is a chaotic process and inherently involves a dramatic volume change in the film, limiting potential for order and very high packing density. Alternatively, short ligand capped quantum dot solutions have been developed with some limited success.\textsuperscript{23,24} However, this approach depends on the addition of a second, stabilizing chemical species in the solution, which either remains in film (limiting density) or must be removed after the fact (again, potentially destroying order in the film).

In order to progress, a fundamental shift in the solution set is required. Rather than requiring a short initial capping ligand, or being limited by a massive volume change to exchange oleic acid ligands with short final ligands in film, an appropriate solution seems to exist in an intermediate space between the two extremes. This section lays out the design and implementation of a novel ligand in the colloidal quantum dot field, a short thioamide, which is strongly bound to lead sulfide quantum dots, generates a sufficiently non-polar surface to ensure colloidal stability in standard organic solvents, and crucially can be shortened by cleaving the ligand with a simple weak acid treatment, rather than relying on full ligand exchange. The removal of 4-6 carbons, rather than 15, as in a typical ligand exchange, provides a much gentler densification environment and represents a highly relevant path to creating high mobility, high efficiency CQD photovoltaic devices.

The search for an ideal ligand was informed by the following desired characteristics:

- Functional termination able to readily displace a carboxylic acid in solution (i.e. SH-).
- Medium length ligand (sufficient chain length to preserve colloidal stability, short enough to minimize volume change).
- Easily cleaved molecule (central functional group such as ester or amide which responds quickly to simple hydrolysis cleaving mechanism, leaving behind desired final ligand).

This search was quickly narrowed to esters or amides created using 3-mercaptopropionic acid (MPA - a common CQD ligand) as the carboxylic acid source. Further, amides were identified as the most promising candidate, due to the potential to cleave in a methanolic rather than aqueous solution, given the known sensitivity of PbS quantum dots to excessive moisture. A commercial source of such ligands was not available, thus a synthesis process was designed in-house to produce a number of promising ligand options.

Figure 3-3 depicts the synthetic process used to create the thioamide ligands. This procedure is described in greater detail in Appendix A, but in brief, MPA and a primary amine (butyl, pentyl or hexyl-amine) were mixed in solution in the presence of a catalyst, forming an amide bond between the carboxylic group of the MPA molecule and the amine. The catalyst and any remaining byproducts were removed from the solution by rinsing with concentrated citric acid. The solution was then dried and evaporated via rotary evaporation, leaving a waxy solid. These solids were redispersed in dichloromethane and analyzed for purity and correct molecular structure.

![Figure 3-3 Thioamide synthesis](image)

**Figure 3-3 Thioamide synthesis** combining MPA and a primary amine, catalysed via 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and 4-dimethylaminopyridine (DMAP).

Mass spectrometry was performed on the products (Figures 3-4a-c), resulting in mass peaks at the appropriate m/z values – 3-mercapto-N-butylpropanamide (3MN4P), 162.1; 3-mercapto-N-pentylpropanamide (3MN5P), 176.1; 3-mercapto-N-hexylpropanamide (3MN6P), 190.1. Formation of by-product species was negligible. In addition to mass spectrometry, NMR studies were performed to confirm that the desired ligand structure was achieved. $^1$H-NMR (400 MHz; CD$_2$Cl$_2$; 3MN4P): $\delta$ 5.35 (s, 1H), 3.23
(m, 2H), 2.76 (m, 2H), 2.47 (m, 2H), 1.64 (t, 1H), 1.48 (m, 2H), 1.34 (m, 2H), 0.92 (t, 3H); (400 MHz; CD₂Cl₂, 3MN5P): δ 5.35 (s, 1H), 3.22 (m, 2H), 2.76 (m, 2H), 2.47 (m, 2H), 1.64 (t, 1H), 1.49 (m, 2H), 1.32 (m, 4H), 0.90 (t, 3H); (400 MHz; CD₂Cl₂, 3MN6P): δ 5.35 (s, 1H), 3.22 (m, 2H), 2.77 (m, 2H), 2.47 (m, 2H), 1.64 (t, 1H), 1.50 (m, 2H), 1.30 (m, 6H), 0.89 (t, 3H).

**Figure 3-4 Ligand synthesis and solution exchange.** a-c) mass spectra for thioamides synthesized with butyl-, pentyl- or hexylamine. Expected peaks are found at m/z 162.1 (a), 176.1 (b), and 190.1 (c), with minimal evidence of extraneous compounds. d) Solution ligand exchange characterized via FTIR. Oleic acid capped PbS quantum dots (black) are exchanged with a solution of 3MN6P in toluene, leading to full replacement of surface ligands (red), evidenced primarily by the disappearance of the C=C stretch peak at 3000 cm⁻¹.

Having successfully generated a suite of ligands with the desired features, the new molecules were then mixed in solution with oleic acid capped quantum dots. The CQDs were precipitated with methyl acetate, dried under mild vacuum, and redispersed in
toluene. Figure 3-4d shows Fourier transform infrared spectroscopy (FTIR) results before and after solution ligand exchange, indicating that, as expected, the strongly bound thiols fully replace oleic acid as the surface ligand – in particular, the C=C stretch at 3000 cm\(^{-1}\) characteristic of oleic acid is fully eliminated after the exchange. Colloidal solutions retain high stability, confirming the suitability of the new ligands for colloidal dispersability.

Following ligand synthesis and successful solution ligand exchange, it remains to prove ligand cleavage in film and the construction of multi-layer, device-ready solids. The ligand cleavage process (termed acidic methanolysis) is depicted in Figure 3-5. A 1% v/v solution of lactic acid in methanol was chosen as the acid source. Films of thioamide-capped quantum dots were spincoated, then soaked with the acid solution for 5-10 seconds per layer. Multiple layers were deposited and treated to build up a thick film.

![Figure 3-5 Ligand cleavage process catalyzed by acid and methanol.](image)

X-ray photoelectron spectroscopy (XPS) measurements were used to confirm a successful cleaving process in film; Figure 3-6 compares films before and after exposure to the cleaving solution, showing complete elimination of the nitrogen-containing amide centre.
Figure 3-6 XPS spectra before and after ligand cleavage. The nitrogen signal (right) indicates the presence of an amide group. After acidic methanolysis, this signal is fully eliminated (red curve). The cadmium signal (left) is unaffected by the acidic treatment (slight shift in peak position can be attributed to sample-to-sample variation).

Cleaved films were analyzed using grazing incidence small-angle X-ray spectroscopy (GISAXS) to determine the film packing density. Figure 3-7 shows an azimuthal integration for a film of 3MN6P-capped quantum dots, post-ligand-cleavage. The average d-spacing in this film is comparable to previous findings for typical, ligand-exchanged films (3.3 nm, as shown by Figure 3-1). However, comparing peak breadth to previous measurements (FWHM ranges extracted from Figure 3-1 are shown in Figure 3-7), the ligand cleavage procedure leads to a significantly narrower distribution of particle separation lengths than observed in either oleic acid-capped or ligand-exchanged films.
Figure 3-7 d-spacing extracted from GISAXS measurements. Cleaved 3MN6P-capped PbS quantum dot films (red curve) exhibited an average d-spacing comparable to MPA-exchanged films (3.3 nm). FWHM ranges are shown for previously reported data (black lines, peak maxima indicated by red circles), showing a narrower distribution for the ligand cleavage method.

Fully cleaved films were used to fabricate photovoltaic devices. As shown in Figure 3-8, device efficiency is appreciable for a new ligand system and film fabrication process (device data shown for 3MN6P films). Performance was somewhat limited by the thickness of the device – particularly current densities; it is hypothesized that the post-cleavage short thioester ligands may retain mild solubility in toluene, somewhat complicating the build-up of the thicknesses necessary for high current output. Nevertheless, a power conversion efficiency of 5.6% provides a promising baseline for further optimization and study for a substantially altered device fabrication process.
**Figure 3-8 Photovoltaic device performance.** Current density (blue line) and power density (red line) versus bias voltage for cleaved, 3MN6P-capped quantum dots.

Further studies will optimize the solution ligand exchange, ligand cleavage and film formation steps to generate high mobility, high efficiency colloidal quantum dot photovoltaic devices. This study has shown a simple synthetic procedure for the creation of theoretically interesting new ligands, and the viability of ligand cleavage rather than ligand exchange, for the creation of well-passivated, well-packed colloidal quantum dot solids.
Chapter 4  Surface Passivation

Assuming high mobility in a quantum dot solid, in order to achieve a large diffusion length, carriers must also encounter a minimal concentration of recombination centres in their diffusion path. In the presence of significant trap states, high carrier mobility simply leads to more efficient transport to recombination, rather than higher carrier extraction and current generation. A significant source of trap states in colloidal quantum dot solids is improperly passivated surface sites; given the very high surface to volume ratios present in nanoparticle films, this presents a substantial challenge. While quantum dot surfaces, as-synthesized, tend to be very well passivated by the native long chain ligands, all subsequent physical and chemical processing steps degrade the quality of passivation and lead to less robust materials and higher trap state densities. This chapter highlights two strategies for increasing or maintaining high levels of surface passivation – through a hybrid organic-inorganic passivation method, introduced in Chapter 3, and by manipulating the solvent environment to better retain surface passivants.

Section 4.1 contains ideas and content which I contributed to the previously discussed Nature Nanotechnology paper, Hybrid passivated colloidal quantum dot solids. Section 4.2 contains material from the co-authored: A.R. Kirmani, G.H. Carey, M. Abdelsamie, B. Yan, D. Cha, L.R. Rollny, X. Cui, E.H. Sargent, A. Amassian, Effect of Solvent Environment on Colloidal-Quantum-Dot Solar-Cell Manufacturability and Performance, Advanced Materials 26, 4717-4723, 2014. Figures are reprinted with permission, copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. I was responsible for the original experimental conception and design, as well as fabrication and characterization of devices, while A.R. Kirmani performed the secondary materials characterization.

4.1 Hybrid Passivation

The traditional approach to passivating the surfaces of colloidal quantum dots focused nearly exclusively on single molecule ligand solutions. The highest level of surface ligand coverage and lowest level of observed trap states tends to occur immediately following synthesis, the quantum dots capped exclusively with a long chain organic molecule such
as oleic acid. However, numerous studies which fabricated films by exchanging oleic acid with a variety of single ligands (such as 3-mercaptopropionic acid – MPA, ethanedithiol – EDT, and cetyl trimethylammonium bromide – CTAB) consistently found higher than expected concentrations of trap states within CQD films, and evidence of only partial surface passivation.\textsuperscript{42,65,73,74}

Theoretical studies, particularly density functional theory (DFT) experiments, were used to explore the capacity for single ligand systems to achieve full passivation on nanoparticle surfaces. It was found that, on certain nanocrystalline facets, metal surface sites exist in “trenches” between outer layer metal cations – due to steric factors, it is not feasible to passivate all surface and “trench” atom sites with a single ligand, while achieving the necessary film densification mentioned in Chapter 3. Consequently, the hybrid ligand approach previously introduced, using both a short bifunctional organic molecule and a metal halide source, was posited as an elegant solution, with the metal halide passivating both surface chalcogen sites and “trench” metal sites, and the organic ligand passivating the remaining metal cation sites and providing a densifying effect.

As previously demonstrated (Figure 3-2), the introduction of a metal halide to the hybrid mixture led to improvements in mobility over a single-ligand strategy. Trap-state density measurements further confirmed the impact of a mixed ligand system on passivation – the hybrid passivated film was found to have a mid-gap trap density of $2 \times 10^{16} \text{cm}^{-3}\text{eV}^{-1}$; this represented a five-fold decrease over levels observed in single ligand systems. The choice of cation in the metal chloride (either lead or cadmium) also played a minor role in surface passivation and electrical transport parameters – as shown by Figure 3-2, cadmium leads to a slight improvement in carrier mobility in film compared to lead.

The central finding of this research was the critical importance of maintaining high levels of halide co-passivation in order to minimize mid-gap trap states in colloidal quantum dot films. This factor becomes increasingly evident in the following section, where changes to the film processing environment are shown to dramatically affect levels of halide retained by the quantum dot surfaces in the final film, and hence photovoltaic device performance.
4.2 Impact of Solvent Environment on Passivation

The current colloidal quantum dot film fabrication process is tedious, wasteful and generally incompatible with scalable solution processing methods which can be applied in a roll-to-roll manner. Solution-phase ligand-exchange strategies have recently been reported that allowed a single-step deposition of the QD absorber layer thereby avoiding material waste. However, device performance was found to still be limited by the reduced ligand coverage that resulted in a high density of charge carrier traps, and performance was therefore significantly lower than state-of-the-art devices prepared by the layer-by-layer (LbL) build-up method. We have taken the view that significant improvements are still possible in the LbL process which may lead to the successful implementation of a single step CQD thin film followed by ligand exchange, with the important requirement of maintaining benchmark solar-cell performance.

The absence of any studies reporting efficient solar cells fabricated with fewer than 10 LbL steps highlights possible limitations of the current scheme. To illustrate the problem, we have fabricated a typical device with ca. 7% power conversion efficiency (PCE), made with a 300 nm absorbing layer fabricated in 80 nm/30 nm (pristine/exchanged) layers including a three-second-long ligand exchange per layer (see Figure 4-1 for J–V characteristics and Table 4-1 for device characteristics). We then fabricated a similar device with a reduced number of steps (3 instead of 10), effectively building up the absorbing layer in ca. 250 nm/100 nm steps, but without extending the ligand-exchange duration; not surprisingly, we observed a significant performance loss (down to ca. 5% PCE), likely due to incomplete ligand exchange within the thicker QD films, as evidenced by low Jsc. We therefore extend the ligand exchange and find, to our surprise, the devices perform even worse (ca. 3.7% PCE), due in large part to a reduction in Voc, indicative of trap formation. It should be noted that the limitation to three layers was dictated by the fact that spin-coating could not achieve QD films thicker than 250 nm/100 nm (pristine/exchanged).
Figure 4-1 Typical current–voltage profiles for a standard processed device – a solid-state exchange using 3-mercaptopropionic acid (MPA) in methanol, treated for 3 s per 30 nm layer (black) and reduced material devices, treated for 3 s per 100 nm layer (blue) and for 60 s per 100 nm layer (red).

Table 4-1 Device properties for CQD thin films processed according to three different recipes. A solid-state exchange using 3-mercaptopropionic acid (MPA) in methanol, treated for 3 s per 30 nm layer for a total of 10 layers, 3 s per 100 nm layer for a total of 3 layers, and 60 s per 100 nm layer for a total of 3 layers.

<table>
<thead>
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<th></th>
<th>Voc [V]</th>
<th>Jsc [mA/cm²]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
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<td>16.4</td>
<td>52.8</td>
<td>4.99</td>
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<tr>
<td>MeOH – 60 s/100 nm</td>
<td>−0.409</td>
<td>18.1</td>
<td>49.6</td>
<td>3.67</td>
</tr>
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</table>

We take the view that extended solvent–QD interactions during the ligand-exchange step may be the culprit of the device performance degradation. Our evaluation
of solvent effects reported in this section reveals indeed that methanol (MeOH), the ligand-exchange solvent, chemically damages the QDs by leaching the chlorine (Cl) atomic passivant when the ligand exchange is extended beyond a few seconds. Next, we demonstrate this chemical damage can be avoided entirely by using an aprotic and high-dipole-moment organic solvent, such as acetonitrile (ACN), which leaves the QDs physically and chemically intact even after extended exposure. Using ACN, we successfully demonstrate a state-of-the-art QD solar cell employing an active layer fabricated in only 3 steps. The new insight into the role of the solvent in the ligand-exchange process is expected to lead to single step preparation of QD absorber, paving the way for large area roll-to-roll manufacturing of efficient CQD solar cells.

It has been long known that the carboxylic hydrogen atom plays a decisive role in the solubility of oleic acid (OA).\(^ {75} \) In hydroxyl group-containing solvents such as MeOH the carboxylic hydrogen of OA can compete with the internal hydrogen bonding in the solvent giving rise to high solubility of OA in MeOH. For nitrogen-containing solvents such as ACN, wherein the intermolecular dipole moments are very high, the carboxylic hydrogen of OA is unable to form hydrogen bonds with the solvent and hence OA is poorly soluble. Both MeOH and ACN dissolve the MPA ligand effectively and thus allow us to focus the first part of our investigation on solvent-QD interactions. A key difference in the solvent-QD interactions is illustrated in Figure 4-2a-b, where we have compared Fourier transform infrared (FTIR) transmittance spectra of a pristine QD film with that of a film exposed to MeOH and ACN for 10 min. The spectra reveal significant loss of oleic acid from the QD surface upon extended interaction with MeOH. Atomic ratio of OA to lead for the pristine and solvent treated films as measured from XPS are shown in the insets of Figure 4-2a-b. MeOH treatment results into a decrease of the capping OA content, whereas ACN treatment seems benign in comparison. It should however be noted that since the carbon signal in XPS includes the adventitious surface carbon footprint, the C:Pb ratio should be considered to be depicting only a qualitative rather than a quantitative trend.
Figure 4-2 Comparison of methanol and acetonitrile on CQD films. Fourier transform infrared (FTIR) spectra showing the C–H stretching vibration for quantum dot thin films before and after exposure to: a) MeOH and b) ACN, for a duration of 10 min, indicating significant loss of OA from quantum dots upon extended MeOH exposure, whereas minimal change is detected following exposure to ACN. The insets in (a) and (b) show the carbon-to-lead atomic ratio highlighting the effect of MeOH and ACN exposures, respectively. c) Quartz-crystal microbalance (QCM-D) measurements of mass change upon exposure of pristine quantum dots to MeOH and ACN, revealing loss of mass in MeOH films as a result of OA loss. d) QCM-D measurements of the mass change upon drop-casting octane on the quantum-dot films after their exposure to MeOH and ACN for 100 s, revealing the MeOH-treated quantum dots are rendered insoluble. e) Time evolution of the fraction of OA remaining with respect to exposure time to MeOH and ACN. f) Time evolution of the fraction of QDs dissolved in octane as determined from QCM-D measurements, revealing the QDs are rendered insoluble by exposure to MeOH for nearly 90 s.
We have probed the interaction of the MeOH and ACN solvents with QDs in detail using a quartz crystal microbalance with dissipation (QCM-D) capability. QCM-D measures the mass loading/unloading on the surface of a quartz sensor in terms of a shift in its resonance frequency.\textsuperscript{76–78} Due to the strong impedance mismatch between the quartz crystal and the solution medium, only a shallow evanescent wave propagates into the solution, making the QCM-D technique only sensitive to the addition or loss of mechanically bound mass. It is also insensitive to evaporative loss of solvent from the bulk solution for the same reason. As such, it should be sensitive to OA removal as well as to the loss or not of QDs when solvent-treated QDs are exposed to octane, a good solvent for CQDs. QCM-D reveals significant mass loss upon dropping MeOH onto a QD-coated QCM-D crystal, indicating exponential decay of mass (Figure 4-2c). The mass loss detected by QCM-D suggests the detachment of OA from the QD surface and its subsequent dissolution into the solution above the sensor. The process appears to stabilize within 200 s, with most of the mass loss observed in the initial 100 seconds of MeOH exposure, whereas no noticeable change is detected in case of ACN-treated QD films. Following a 100 second exposure to MeOH or ACN, octane was dropped upon the surface of the N-2-dried QD film. The ACN-treated QDs dissolved nearly completely (Figure 4-2d) in a matter of seconds, whereas the MeOH-treated QDs remained immobilized on the surface. Infrared variable-angle spectroscopic ellipsometry (IR-VASE) measurements were performed in reflection mode on QD films (see Figure 4-3) to probe the extent of OA loss with solvent exposure time. The IR signature of the C–H stretching vibrations in OA at 2852 cm\textsuperscript{−1} and 2922 cm\textsuperscript{−1} were followed over successive solvent treatments to track the evolution of OA content.\textsuperscript{65}
Figure 4-3 C-H stretching vibrations of OA studied using IR-VASE for successive treatments of solvents (a) ACN and (b) MeOH. For the case of MeOH, the signal decreases with treatment time indicating OA removal. For the inert solvent ACN, the signal remains unchanged in intensity.

Over a period of 10 min, MeOH removes approximately 80% of the OA whereas ACN shows only a 10% decrease (Figure 4-2e). IR-VASE measurements reveal the time-evolution of OA content in the QD films and indicate that 40% overall loss of OA is required to render the QD film entirely insoluble in octane. During this period, the MeOH-treated film collapses to ca. 60% of its initial thickness accompanied by densification, as suggested by significant increase of the refractive index as per UV–vis–NIR VASE measurements (Figure 4-4).
Figure 4-4 Solvent-dependent film thickness (normalized to pristine, time zero film thickness) – thickness decreases upon MeOH exposure, and does not change upon ACN exposure. The inset shows the change in refractive index of the film at $\lambda = 1200$ nm indicating significant densification accompanying volume change.

When treated for shorter times, MeOH is believed to remove OA predominantly from QDs near the top surface of the film, which renders parts of the film insoluble in octane with the OA-rich QDs still breaking through the crust and dissolving in octane, as suggested by SEM and AFM images (see Figure 4-5).
Figure 4-5 High resolution cross-sectional TEM images showing the film morphology for (a) pristine film and (b) 600s MeOH treatment. The insets show the higher resolution images near the top regions. The film seems to densify with increasing MeOH treatment with agglomeration setting in. (c) Top-view SEM and (d) AFM images for 40s MeOH-treated samples followed by a two minute octane wash to remove all but insoluble material.

The optical properties of the QD films reveal a blue-shift of the quantum confinement peak at ca. 950 nm upon MeOH exposure (see Figure 4-6).
Figure 4-6 Shifts in the quantum dot absorption peak position with solvent exposure. Long exposure to acetonitrile (red) has little effect on peak position, while methanol exposure (blue) leads to significant blue shift over time.

With time, as MeOH removes OA, the dots come closer thereby reducing the inter-dot spacing from ca. 4.6 nm in pristine films to ca. 4.4 nm after 10 min of MeOH exposure, as demonstrated by grazing incidence small angle X-ray scattering (GISAXS) measurements (see Figure 4-7).
Figure 4-7 Average interdot spacing in quantum dot thin films exposed to MeOH and ACN. Long exposure to methanol (blue) leads to a gradual decrease in the average interdot spacing, whereas little statistical difference is obvious with acetonitrile exposure (red).

In addition to the loss of OA, X-ray photoelectron spectroscopy (XPS) measurements reveal a significant loss of chloride (Cl) from the surface of the QDs when exposed to MeOH for 600 seconds (see Figure 4-8). By contrast, the ACN-treated film shows almost no change in terms of OA fraction, solubility, thickness, optical properties, inter-particle spacing, or halide content.
The films were treated with the solvents for 600s. Figures (a), (b) show changes to the Pb 4f peak; figures (c), (d) show changes to the S 2p peak; and (e), (f) highlight changes to Cl 2p peak for ACN and MeOH treatments, respectively. A strengthened lead and sulfur signals in b) and d) are attributed to a greater exposure of surface atoms (both Pb and S) after significant ligand removal by the solvent system.

The halide atoms on the surface of QDs are crucial for assuring effective atomic passivation and mitigating the sub-gap trap state density, which strongly influences carrier recombination in QD solar cells. Thus, we speculate that loss of halide atoms when exposing QDs to MeOH may be the main reason for the degradation of photovoltaic performance upon extending the ligand-exchange duration. This effect may not have been discovered earlier, because solar cells fabricated in 10 LbL steps either with MeOH or ACN yield nearly identical power conversion efficiencies, as will be shown below. This is probably because ligand exchange is completed on a sub-second timescale for the low QD film thicknesses involved in the 10 LbL process, irrespective of the solvent choice (Figure...
4-9), and thus state-of-the-art device fabrication recipes do not require extended exposure to MeOH for longer than 3 seconds.

![Figure 4-9 Mass change during ligand exchange process](image)

**Figure 4-9 Mass change during ligand exchange process** as a function of treatment time for (a) ACN and (b) MeOH. A variety of MPA concentrations have been tested. At higher MPA concentrations, solvent has minimal impact on mass change kinetics, while at low concentration, a methanol-based exchange proceeds similarly to the pure solvent case.

Turning our attention to the loss of halide during ligand exchange, we use XPS to look at the differences in the elemental composition of ligand-exchanged films using MeOH and ACN-based treatments for durations longer than 3 seconds (Figure 4-10 and Figure 4-11). XPS reveals loss of surface halide (Cl) with extended ligand exchange when MeOH is used as the solvent, evident by the decreasing Cl:Pb atomic ratio. No such loss is observed for the case of ACN-based treatments (Figure 4-10a). Also shown in Figure 4-10a are the effects of pure solvents MeOH and ACN, previously discussed, revealing the Cl:Pb ratio is the same regardless of whether MPA is present or not in MeOH. This demonstrates that halide loss can be directly linked to MeOH exposure.
Figure 4-10 X-ray and ultraviolet photoelectron spectroscopy were used to study the solvent–quantum-dot interactions. a) Evolution of the Cl/Pb atomic ratio with increasing ligand-exchange process duration using MeOH (red bars) and ACN (black bars). Also shown is the case for an extended exposure (600 s) to the respective pure solvent. b) UPS spectra showing an increased near-Fermi density of states for a MeOH-treated thick film as compared to an ACN-treated thick film for the same duration (60 s). The enhancement of sub-gap trap state density in case of MeOH treated devices is believed to affect the device performance. An increase in the VB maxima by ca. 0.2 eV is observed for the MeOH-treated film as compared to the ACN-treated film.
Figure 4-11 Ligand exchange on pristine QD films studied using XPS. Each figure shows the films under four conditions – pristine, 3s, 60s and 600s exchanges. Figures (a), (b) show changes to the Pb 4f peak; figures (c), (d) show changes to the S 2p peak; and (e), (f) highlight changes to Cl 2P peak for ACN and MeOH treatments, respectively.

We combine the XPS study detailed above with UPS in order to study the valence bands of the extended ligand-exchanged QD films (Figure 4-10b). Enhanced near-Fermi level DOS in PbS QDs have been suggested to behave as charge carrier traps which are detrimental to device performance.\textsuperscript{47,79} Katsiev et al. recently demonstrated that synchrotron-based UPS can be effectively used to study the near-Fermi level carrier trap states in PbS-QD-based solar cells.\textsuperscript{80} We find a higher density of electronic states near the Fermi level for films exchanged using MeOH. This proves that MeOH-induced Cl-loss leading to charge carrier traps is the reason behind device-performance loss and that ACN is gentler even after extended exposure. We also observe a ca. 0.2 eV shift of the valence band edge towards the Fermi level as shown in Figure 4-10b by the black dashed lines. We
suspect this to be the reason for the reduction of the VOC for the MeOH-based 3 LbL device (see Table 4-1). While the high dipole moment is believed to make ACN gentle on the OA, it is not clear at this time whether this or the aprotic nature of the solvent is to credit for preventing Cl-loss.

We now seek to demonstrate that ACN can be used to perform effective ligand exchange for longer duration on the thicker films, allowing the absorbing layer to be fabricated in fewer steps. As thicker films are believed to require longer ligand-exchange duration to achieve the same level of exchange as in case of thinner films, we have used VASE to monitor the thickness and optical properties of thin (ca. 80 nm) and thick (ca. 180 nm) films as a function of ligand-exchange time (see Figure 4-12).

![Graph showing VASE data](image)

**Figure 4-12 Variable-angle spectroscopic ellipsometry (VASE) data** showing a comparison of: a) thickness variation and b) refractive index for extended ligand-exchange times on thin (ca. 80 nm) and thick (ca. 180 nm) films using the solvents ACN and MeOH. The results show that the ligand-exchange process requires more time for thicker films as compared with the sub-second timescale required for ligand exchange in the standard-thickness films. The ligand-exchange kinetics appear to be independent of the solvent used.
VASE analysis of even thicker films (ca. 250 nm) was complicated by virtue of thin film uniformity and roughness issues, thus we have limited our comparison to films of nearly ca. 180 nm, which after ligand exchange shrink down to ca. 75 nm. Several important conclusions can be drawn from these results. First, for both thin and thick films, ligand-exchange dynamics seem to be independent of the choice of solvent as was suggested above on the basis of QCM-D studies on ligand exchange on thin films. Second, ligand exchange leads to film densification as suggested by the increase in refractive index. This is accompanied by a massive decrease in the inter-dot spacing and an expected red-shift in the peak absorption.\textsuperscript{81,82} Interestingly, MeOH-based ligand exchange leads to smaller interdot spacing than ACN-based ligand exchange. Third, the thicker films show a slowed ligand exchange nearing completion after ca. 20 s, a duration nearly 6–7 times greater to fully exchange a film only 2.3 times thicker.

We naturally anticipate that thicker films will require even more time to complete the ligand exchange. Our optimization efforts show that a ligand-exchange duration of ca. 60 seconds is sufficient to complete the ligand exchange of QD films with a exchanged/pristine thickness of ca. 100 nm/ca. 250 nm. The device performance shown in Figure 4-13 validates this hypothesis (see Table 4-2).
Figure 4-13 Champion devices. Three-layer devices processed using 60 s ligand exchange in methanol or acetonitrile solvent environments are compared. For comparison, we have included a ten-layer device using 3 s ligand exchange in acetonitrile.

Table 4-2 Champion device characteristics for CQD thin films processed according to two different recipes. A solid-state exchange using 3-mercaptopropionic acid (MPA) in methanol versus acetonitrile, for 60 s treatments per 100 nm layer for a total of 3 layers.

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<th>( J_{sc} ) [mA/cm(^2)]</th>
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<th>PCE [%]</th>
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<td>MeOH – 60 s/100 nm</td>
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<td>49.6</td>
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</table>

The ACN-based 3 LbL device (black) employing a 60 second exchange shows much better performance than the MeOH-based 3 LbL device (red) and closely approaches the performance observed in standard MeOH- and ACN-based 10 LbL devices shown in Figures 4-1 and 4-13, along with significant process simplification and consuming ca. 40% less CQD solution than the latter (see Figure 4-14). The ACN-based devices behave well
despite the fact that interdot spacing is larger than when MeOH-based ligand exchange is used. This may be due to the OA washing step just following the ligand exchange and performed using the same solvent. ACN being a poor solvent to OA may not remove all the excess OA from the QD film, resulting in a slightly larger interdot spacing. This, however, does not appear to harm device characteristics.

**Figure 4-14 Material use reduction.** Quantity of QDs used for the fabrication by spin-casting a 300 nm absorber layer for a standard 10 LbL device and a 3 LbL device, on a 2x2 cm FTO substrate. The latter utilizes at least 40% less material than the standard strategy. Inset shows the fraction of the CQD solution utilized per layer for the two architectures. The 3 LbL architecture makes use of ~56 % more of the CQDs solution per layer that otherwise gets wasted in the 10 LbL strategy.

In summary, we have identified that the ligand-exchange solvent, MeOH, leads to device performance degradation by chemically damaging the surface passivation of CQDs for extended exposures, whereas ACN has been shown to be inoffensive. This is the reason for the CQD solar cells made with MeOH requiring several tedious and wasteful steps as
part of the LbL buildup of the absorbing layer. Understanding of solvent interactions with QD films has led to the development of more efficient processing conditions based on use of ACN, which allows us to achieve state-of-the-art performance using only three steps for active layer deposition. The results presented herein fit well within the context of recent work in the field as a whole - in particular, recent studies by Weiss and Owen. Weiss et al studied surface ligand states on lead sulfide quantum dots, and the chemical and physical impact of solvent exposure.\textsuperscript{83,84} Owen et al have performed in-depth characterizations on ligand binding modes, and the impact of various binding modes and solvent environments on nanoparticle behavior.\textsuperscript{71,85} Such studies have highlighted both the critical impact of the solvent system, as described in this chapter, and the importance of X-type ligands (such as halides) to the electrical properties of quantum dots solids. By taking the solvent system into account to preserve high chloride passivation, the results presented in this chapter shed light on ways to achieve a single-step deposition by other solution processing methods and solid-state ligand exchange, greatly enhancing the opportunity to fabricate solar cells in a scalable manner.
Chapter 5  Impurity Management

While the impact of nanocrystal surface passivation defects have been frequently studied as a source of trap states and recombination centres in colloidal quantum dot films, the presence and effect of extraneous, non-surface-bound compounds in such films has received minimal attention. Given the complex synthesis and chemical processing processes involved in the fabrication of CQD films, it is quite reasonable to expect less than perfect purity and to find observable levels of organic or inorganic impurities intercalated between the quantum dots. Since the basic nature of such impurities is poorly understood, it is unsurprising that the potential impact on overall film trap state density and carrier diffusion length properties has not been studied in any depth. This chapter initiates that research path, characterizing one of the most obvious impurities in CQD films and devising a simple impurity management strategy, leading to higher quality nanocrystal solids.

Section 5.1 includes content from: G.H. Carey, I.J. Kramer, P. Kanjanaboos, G. Moreno-Bautista, O. Voznyy, L.R. Rollny, J.A. Tang, S. Hoogland, E.H. Sargent, Electronically Active Impurities in Colloidal Quantum Dot Solids, ACS Nano 8, 11763-11769, 2014. Figures are reprinted with permission, copyright 2014 American Chemical Society. I performed the chemical and device processing and characterization, while other authors were responsible for NMR measurements and DFT simulations.

5.1 Electronically Active Impurities

Colloidal quantum dots (CQDs) are an attractive option for low-cost, high-efficiency optoelectronic applications such as light-emitting devices\textsuperscript{86,87} photodetectors\textsuperscript{88} and solar cells\textsuperscript{13,66}. CQDs are solution-processed nanoparticles (typically semiconductor materials such as PbS, PbSe, CdS, etc.) which, through quantum size effect tuning, enable a broad range of bandgaps compared to the compositionally determined bandgap of the constituent bulk material\textsuperscript{89}. This characteristic is particularly useful for photovoltaic applications since it allows even a single materials system to become spectrally versatile\textsuperscript{90–92}. 
CQD photovoltaic device performance has progressed quickly in the past decade of research. Recent studies have begun to address CQD device properties beyond instantaneous power conversion efficiency, looking, for example, at manufacturability. A key metric for manufacturability is the reproducibility of performance: consistency from device to device, substrate to substrate, and CQD synthesis batch to batch. A statistically repeatable process is an important ingredient in achieving a scalable end product.

The method of CQD film deposition influences device performance and repeatability. Recent reports have revealed notable differences between the standard spin-coated layer-by-layer film formation technique and a more controlled spray-coating deposition method, the latter employing near-monolayer control of CQD buildup and termed sprayLD.

In the present work, we investigate the origins of performance variability in CQD photovoltaic device performance based on legacy layer-by-layer methods; and we then develop a chemical method that overcomes this variability. The method is applicable to films formed using a wide suite of deposition methods.

We began with analytical studies of the composition of high-performing films, seeking possible correlations between materials composition and performance. Solid-state nuclear magnetic resonance (NMR) (Figure 5-1a) revealed that the signal associated with the presence of COOH groups, potentially associated with protonated 3-mercaptopropionic acid (MPA) used in crosslinking, was present at a higher concentration in better-performing films. Similarly, Fourier transform infrared spectroscopy (FTIR) studies showed a marked difference between bound and unbound carboxylate signals (Figure 5-1b), with the higher-variability processes showing greater evidence of a bound (and thus deprotonated) COO- group (1500-1550 cm$^{-1}$ range).
**Figure 5-1 Impurity characterization.** (a) Proton solid-state NMR measurements of our typical (spin, top) films and of our films exhibiting a tighter photovoltaic performance distribution (sprayLD, bottom) (solid lines). Peak fits indicating phosphonic acid (∼12 ppm), the MPA carbon chain (∼0–2 ppm), and residual methanol and water (∼3 ppm and ∼5 ppm, respectively) are represented by dashed lines. The presence of a protonated carboxylic acid is observed in the sprayLD case at ∼8 ppm (highlighted in green). (b) FTIR spectroscopy of the same films as (a). The acid peak shifts toward a deprotonated carboxylate (shoulder at ∼1500–1550 cm$^{-1}$) in the spin case, whereas the increase at 1600–1700 cm$^{-1}$ for sprayLD indicates the enhanced presence of carboxylic acid.

In each case, the films in question had been fabricated by depositing oleic acid-capped PbS CQDs and exchanging surface ligands with a shorter bifunctional molecule, MPA. The film is then rinsed with methanol to remove any unbound MPA and oleic acid. Since both the initial and final ligands include a carboxylic acid functional group, the NMR and FTIR results are not conclusive as to the origins of the COOH and COO- in the final films. Both oleic acid and MPA are highly soluble in methanol, therefore shifting the focus onto possible low-solubility complexes.
We turned to density functional theory (DFT) to investigate several potential complexes and how they would influence the density of states if incorporated into CQD films. Parts a-d of Figure 5-2 compare the predicted effect of MPA, deprotonated MPA, lead oleate, and a lead oleate-MPA complex on density of states. Oleic acid alone was not considered as it does not result in a luminescent long wavelength state in PbS CQD films. MPA, whether protonated or not, is not predicted to produce midgap states. The same applies to lead oleate. However, the introduction of lead oleate with a lead-bound MPA molecule near the dot surface is predicted to produce an electronic trap state in the bandgap localized on the molecular complex (Figure 5-2d). The origin of lead oleate on the surface of the film comes from the solid state exchange procedure itself. It has been shown to desorb in abundance from PbS CQD surfaces during solid state ligand exchange in addition to the oleic acid ligand alone. The blue shift that could be expected due to slight CQD shrinkage is not observed. We propose that, in highly coupled CQD films, this process competes with mild CQD aggregation that accounts for the net (though small) red shift. All DFT calculations were undertaken using charge-balanced PbS CQDs whose surfaces are therefore trap-free. It has been previously shown that unbalanced CQDs contain primarily shallow trap states on the surface distinct from the relatively deep traps localized off the surface and on the nearby complex for the case of the complex-associated traps of Figure 5-2.
Figure 5-2 Identification of oleate-based impurity. DFT wave function calculations of an MPA-terminated PbS CQDs (a), deprotonated MPA terminated PbS CQDs (b), and MPA terminated PbS CQD with (c) lead oleate or (d) a lead oleate–MPA complex near the CQD surface. The wave function within the CQD shifts entirely to the complex in (d) but remains in the core of the CQD in cases (a–c), indicating the presence of a midgap electronic state. The accompanying density of states calculations by DFT illustrate the emergence of a midgap state for the lead oleate–MPA complex case (indicated by dashed line). (e) Photoluminescence of lead oleate treated with methanol (black curve) and dilute MPA (green curve) rinses showing the ∼1550 nm luminescence of the lead oleate–MPA complex. (f) A sprayLD film with an excess of lead oleate added to the CQD solution illustrates the emergence of the long wavelength peak (1550 nm) as a lead oleate–MPA complex forms.

To gain experimental insight into the identity and energetics of possible electronic trap states associated with complexes, we investigated the origins of midgap luminescence observed in the more inconsistent spin-coated films. In light of the DFT results, we
synthesized Pb-oleate-MPA in bulk and studied the photoluminescence spectra of the resulting waxy solid, comparing it with that of pure lead oleate (Figure 5-2e). While pure lead oleate shows no measurable signal in the observed range, the Pb-oleate-MPA complex generates a sizeable signal near 1550 nm.

We sought to verify whether this low-energy luminescence would persist if the complex were incorporated into CQD films at realistically low concentrations. We added a small volume of excess lead oleate during the deposition of a spray-coated film (which consistently show no measurable light emissions signal beyond their 1150 nm band-edge luminescence before excess Pb oleate addition). The resultant film was analyzed by electroluminescence (Figure 5-2f) and was found to exhibit a strong 1550 nm luminescent feature. As seen in DFT, defects on the CQD surface are predicted to result in one charge carrier localized on the defect site and one delocalized over the QD. The overlap between these two carriers is small, and the defect appears dark in the predicted absorption spectrum, as well as weak predicted luminescence. Also from DFT, the defect due to the complex localizes both electrons and holes onto the complex, leading to a strong carrier overlap and thus a bright luminescent state. Both single-molecule (Figure 5-2d) and polymerized complexes were modeled and exhibited the same localized state on the molecule with similar midgap defects.

Thus, from a combination of DFT, the synthesis of the posited low-energy complex, its photoluminescence as a pure material, and its persistent luminescence when incorporated into CQD films, we had gathered a body of evidence that a Pb-oleate-MPA complex could lead to performance-limiting midgap electronic states.

We sought a chemical means of removing such a complex from CQD films to ensure reproducibility across all fabrication methods. We began by testing the solubility of the synthesized Pb-oleate-MPA complex in a variety of standard polar and non-polar solvents (Figure 5-3a-e: water, methanol, acetonitrile, octane and toluene, respectively). Unfortunately, the complex proved completely insoluble in each case. This further strengthened the supposition that, once generated during solid-state ligand-exchange, such a complex would likely remain incorporated into films and offer the potential to degrade performance as an impurity-based recombination centre.
Figure 5-3 Solubility of lead oleate–MPA complex in common solvents including (a) water, (b) methanol, (c) acetonitrile, (d) octane, and (e) toluene. Solubility of the same lead oleate–MPA complex in acids with decreasing pK\textsubscript{a} including (f) acetic acid, (g) lactic acid, (h) formic acid, and (i) pyruvic acid.

Considering that neither polar nor non-polar solvents appeared to affect the complex solubility, a deeper structural examination of the complex itself was required. While standard characterization techniques were precluded due to the complete insolubility of the complex and the complicating inclusion of heavy lead atoms, we obtained hints about structure by synthesizing related complexes. Mixing lead oleate with ethanedithiol (EDT), the other major bifunctional ligand commonly employed in PbS CQD films, led to the formation of a similar waxy solid (Figure 5-4).

Figure 5-4 Solubility of lead oleate-EDT complex (yellow in color) in a variety of solvents and acids of increasing pK\textsubscript{a}. The complex (similar in form to Figure 5-3 with EDT taking the place of the central MPA molecule) forms a floating clump in water. It remains insoluble in other common solvents and weak acids, including formic, pyruvic and oxalic acids. The solution is clear and colorless without any remaining precipitate in hydrochloric acid, indicating breakdown of the complex. The added strength of a Pb-S
bond (as opposed to a Pb-COO- bond in the MPA complex case) requires a stronger acid to dissociate the complex. For this reason, Pyruvic acid is insufficient to break the Pb oleate-EDT complex while it is sufficient to break the Pb oleate-MPA complex.

By contrast, mixing lead oleate with ligands with single lead-binding functional groups (thioglycerol, for example) did not produce any trace of a solid complex. These results suggest that the combination of lead oleate and a bifunctional molecule may create a complex of linked lead oleate moieties and an overall large, insoluble compound. Additionally, we posit that formation of impurity complexes in CQD solid formation may be relatively widespread wherever bifunctional ligands are employed.

A large molecular weight complex is consistent with the difficulty in dissolving it using the solvents of Figure 5-3a-e. We posited that it would be necessary to cleave the linkages at the MPA-bound lead centres, and that this could be accomplished by reprotonating the carboxylate MPA functional group. This could allow individual lead oleate-MPA moieties to dissolve in a common solvent such as methanol. Figure 5-3f-i show a suite of acids, pictured in order of decreasing pKa (acetic, lactic, formic and pyruvic, respectively), at roughly 0.7M in methanol. While the first three fail to fully dissolve the complex, pyruvic acid in methanol readily dissolves the entire added aliquot of the complex.

We therefore explored the addition of a low concentration of pyruvic acid to the methanol rinse step that is implemented immediately after the solid-state ligand exchange, with the goal of breaking up, dissolving, and washing away the embedded Pb-oleate-MPA complex. We explored a range of pyruvic acid concentrations from 0-0.8% v/v in methanol for this complex-rinse processing step. We investigated not only device performance but also electroluminescence spectra (Figure 5-5a, increasing pyruvic concentration top to bottom). The control devices exhibited a significant feature at 1500 nm. This feature disappeared when pyruvic acid was added to the methanol rinse. FTIR (Figure 5-5b) revealed that eliminating the complex shifted the carboxylate stretch from the bound signature (COO- dominated, 1500-1550 cm\(^{-1}\)) to the unbound (protonated carboxylate, 1600-1700 cm\(^{-1}\)). There was no significant change in the absorption spectra of the films with and without pyruvic acid treatment (Figure 5-6).
Figure 5-5 Impact of impurity removal. (a) Electroluminescence of CQD solar cell devices with treatments of (i) 0.0% pyruvic acid, (ii) 0.2% pyruvic acid, (iii) 0.4% pyruvic acid, (iv) 0.6% pyruvic acid, and (v) 0.8% pyruvic acid illustrating the removal of the luminescent midgap defect state caused by the lead oleate–MPA complex. At 0.8% pyruvic acid, only the band edge luminescence at 1150 nm remains. (b, top) FTIR transmission of control (untreated film) and pyruvic acid treated film showing the same reduction in relative contribution of a deprotonated carboxylate versus carboxylic acid observed in Figure 5-1b. (b, bottom) FTIR transmission of pure pyruvic acid and pure oleic acid highlight that the relative peaks are not dominated by free acid introduced within the film. The strong peak at 1700 cm$^{-1}$ for both acids is muted relative to the stronger carboxylate and carboxylic acid peaks found within the films. (c) Histograms of control (red) and pyruvic acid treated devices (blue) with accompanying Gaussian fits illustrating the much tighter distribution with a shifted center toward higher fill factor (left) and lower series resistance (right).
Figure 5-6 Film absorption comparison for MPA-capped PbS CQD films (Control) and films treated with pyruvic acid. There is no significant change in the observed absorption (beyond sample-to-sample variation) between control and pyruvic acid treated films.

We investigated the impact of the new complex-removal step on solar cell performance. Exploring the same range of pyruvic acid concentrations as previously outlined, we found that power conversion efficiency was maximized when films were treated using 0.2\% v/v pyruvic acid in methanol (Figure 5-7); beyond 0.8\% v/v treatment, device performance was significantly lower due to decreasing open-circuit voltage ($V_{OC}$) without any further corresponding fill factor (FF) gain.
Figure 5-7 Evolution of photovoltaic figures of merit with varying concentrations of pyruvic acid incorporated into methanol rinse step.

In the subsequently fabricated films, the series resistance (Rs) and the fill factor vary widely in the control devices (Figure 5-5c, red). We propose that uncontrolled variations in available lead oleate (due to synthesis variations, post-synthesis washing procedures, and solid-state exchange conditions) account for sample-to-sample variability. By contrast, removing the complex with pyruvic acid treatment (Figure 5-5c, blue) leads to consistently lower RS and higher FF, even using the same dot batches with their presumed variations in initial oleic acid/lead oleate concentrations. This trend holds true when compared with a large control sample set and many initial CQD batches (Figure 5-5c) as well as when considering only side-by-side controls (Figure 5-8).
Figure 5-8 Side-by-side device comparison. Histograms of control (red) and pyruvic acid treated devices (blue) for side-by-side fabricated devices with accompanying Gaussian fits illustrating the much tighter distribution with a shifted center towards higher fill factor (left) and lower series resistance (right). While several sets of experiments were compiled to produce this figure, only one control per set was fabricated, leading to 20 pyruvic acid-treated samples and 7 side-by-side controls.

For all histograms, each data point represents a device on a distinct substrate. The new treatment thus allows the fabrication of more consistently conductive films. Typical head-to-head photovoltaic performance with and without pyruvic acid treatment is shown in Figure 5-9, and full statistical figures of merit for devices in Figure 5-5c are given in Table 5-1. We propose that the complex, which includes high molecular weight fatty acid complexes, adds series resistance and hampers charge transport at maximum-power-point conditions.
Figure 5-9 Typical device performance for side-by-side control (red) and pyruvic acid treated (blue) devices, with current-voltage profile (solid lines) and output power density (dotted lines).

Table 5-1 Photovoltaic figures of merit for all samples counted in Figure 5-5c.
We did observe that it is possible to overtreat the films using higher pyruvic acid concentrations, thereby reducing performance. We offer the following explanation for the formation of electronic defects upon overly aggressively treatment with pyruvic acid. The MPA molecule likely exists in multiple configurations within the film:

1) Surface-bound to a CQD solely at the thiol end, with a dangling, protonated carboxylic acid group;

2) Bound in a bidentate fashion with both the thiol end and carboxylate end bound to Pb on the surface of a CQD;

3) Within the proposed complex wherein both the thiol and carboxylate ends are bound to lead oleate.

We propose that the desirably low concentrations of pyruvic acid were sufficient to reprotonate and cleave the complexes, leading to improved performance and consistency. Higher pyruvic acid concentrations may have brought protons to the surface-bound carboxylates of configuration 2, reprotonating the carboxylate and generating configuration 1. This reaction would leave behind a newly unpassivated surface site on the CQD: a trap.

This work identifies an inorganic-organic complex that is expected to form whenever Pb-oleate CQD synthesis precursor and crosslinking ligands such as MPA and EDT are introduced during CQD film formation. The use of a sufficiently strong acid to reprotonate and cleave the complex prior to its irreversible incorporation in the film leads to its substantial removal and an improvement in performance consistency. The new strategy led to significantly higher device reproducibility by ensuring that electronic transport through the film is dictated by the quantum dots themselves and not by uncontrolled levels of embedded insulating moieties. More broadly, the work suggests that further avenues should be explored that could circumvent complex formation in the first place. Ongoing work on solution-phase exchanges to final capping ligands offers promise in avoiding incorporating undesired impurities at the time of film formation.
Chapter 6 Achieving a Record Diffusion Length in CQD Solids

Research described in the preceding three chapters highlighted key components in the pursuit of long diffusion length colloidal quantum dot solids. Namely, it was shown that mobility (half of the contribution to efficient diffusion) can be improved by addressing dot-to-dot spacing in films and striving for maximal film density. It was shown that recombination lifetime (the remaining contribution to diffusion) must be improved by minimizing the concentration of trap states present in a film. This was accomplished by two distinct means: first by ensuring optimal surface passivation, to avoid trap states caused by unpassivated surface sites, and second by identifying and eliminating electronically active impurities intercalated between quantum dots (namely, oleate-based compounds). The following chapter is the culmination of all preceding findings; an alternative synthesis and film fabrication strategy is devised which takes into account all three aforementioned findings, leading to the longest diffusion length measured in CQD solids to date and significant improvements in photovoltaic device efficiency.

Section 6.1 includes content from: G.H. Carey, L. Levina, R. Comin, O. Voznyy, E.H. Sargent, Record Charge Carrier Diffusion Length in Colloidal Quantum Dot Solids via Mutual Dot-To-Dot Surface Passivation, Advanced Materials, advance online publication, 2015. Figures are reprinted with permission, copyright 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. I was involved in all facets of this research, with assistance on CQD synthesis (L. Levina), XPS measurements (O. Voznyy) and PL lifetime studies (R. Comin).

6.1 Improving CQD Solid Diffusion Length Via Dot-to-Dot Passivation

A key advantage of CQDs resides in the quantum confinement effect wherein the bandgap and optoelectronic properties can be tailored simply by adjusting the size of nanoparticle used. This flexibility brings with it a challenge compared to the case of typical bulk polycrystalline semiconductors. The CQD diameter (in, for example, PbS and PbSe) to achieve a ~ 1.0-1.3 eV bandgap is in the range of 3-4 nm. As a result, a large proportion
of atoms making up the quantum dot are surface atoms that require careful termination in light of the crucial influence of nanocrystal surfaces on passivation and confinement.\textsuperscript{100,101} Much of the work in this field has focused on passivating maximally these surface sites using ligands. Indeed, innovative strategies including both molecular\textsuperscript{23,66,73,102,103} and atomic\textsuperscript{55,65,104} ligands have recently led to considerable advances in in-gap trap state density and consequently solar cell performance. While considerable progress has been made, quantum dot surface passivation remains a significant limiter of film optoelectronic properties and device performance.\textsuperscript{105}

Recent reports of partially-fused quantum dot systems\textsuperscript{106,107} hint at a possible new passivation strategy. Rather than passivate every surface site using extraneous chemical additives, we would seek to combine chemical passivation with partial fusing of certain surfaces presented by adjacent quantum dots. Our strategy (depicted in Figure 6-1a) would unite dot-to-dot surface-coupled self-passivation (to reduce the overall surface-to-volume ratio within the quantum dot solid) with strong chemical passivation of the remaining surface sites. We show herein that reducing the available surface area while strongly passivating remaining sites led to a very low density of electronic traps. We further show that, at the same time as excellent electronic transport was achieved, impressively long-lived excited-state lifetimes were simultaneously observed. The combination of excellent transport and reduced trapping led to the longest reported diffusion lengths observed in a colloidal quantum dot solid.
**Figure 6-1 Partial quantum dot fusing.** a) Schematic of a typical collection of colloidal quantum dots after ligand exchange when initially capped with oleic acid and chloride (left) or a short primary amine and chloride (right). Amine-capped dots allow partial fusing, reducing total available surface sites in a film. b) Transmission electron microscope image showing partial quantum dot fusing occurring—the insets show prominent instances of two or more dots fusing. Scale bars indicate 20 nm in the overview and 5 nm in the two inset images.

The aforementioned recent reports, in which quantum dots were partially connected, did not incorporate the most effective passivation strategies. Indeed, this was not an option, for the surface fusing was based on harsh processing conditions that stripped off all passivating ligands.

We therefore devised a new process that could allow partial facet fusing to be combined with excellent chemical surface passivation. It is based on a combination of a strongly bound atomic ligand, which serves to provide efficient passivation, and a more labile organic ligand, used only to ensure steric colloidal stabilization. Amine treatments have recently been deployed to create well-packed, connected, and highly conductive arrays of quantum dots. We therefore developed a synthesis method designed to produce
PbS quantum dots capped with amine ligands instead of oleic acid. The synthesis design was informed by recent reports of highly passivated, amine-stabilized CdSe quantum dots. The synthesis is described in full in Appendix A; as shown in Figure 6-2, CQDs are initially synthesized with oleic acid capping ligands, which are immediately replaced with chloride atomic ligands and tributylphosphine (PBu₃). Chloride ligands are added to the surface to stoichiometrically balance the charge of the displaced, negatively charged oleate; these ions bind both at former oleate binding sites, and at less sterically accessible locations, with tributylphosphine weakly binding remaining surface sites to retain stability. A mixture of n-hexylamine and n-octylamine is then used to replace the PBu₃, balancing the need for ligands long enough to stabilize the nanocrystals in a standard organic solution, yet short enough to enable partial fusing during film formation.

![Chemical reaction diagram](image)

**Figure 6-2 Synthesis of PbS-RNH₂-Cl colloidal quantum dots.**

The ligand exchange was tracked via Fourier transform infrared spectroscopy (FTIR); Figure 6-3 characterizes one representative dot batch at each stage of the exchange. In contrast with the previously reported exchange using CdSe CQDs, oleate is evident at all stages of the PbS CQD exchange until the final amine replacement step.
Figure 6-3 FTIR spectra throughout exchange - oleic acid features (specifically the C=C peak at 3050 and COOH around 1750 cm$^{-1}$) remain until the final, amine exchange step.

X-ray photoelectron spectroscopy (XPS) measurements were performed on pristine, dropcast films of the amine-exchanged PbS CQDs (Figure 6-4), showing the presence of chloride ligands (Figure 6-4a), and the full elimination of PBu$_3$ and oleate (Figure 6-4b and c). We hypothesize that the PBu$_3$ and Me$_3$Si-Cl exchange steps partially replace oleic acid on the surface, providing initial surface chloride ligands and facilitating the final, full amine exchange required for subsequent facet fusing.
**Figure 6-4 XPS characterization** showing mutually-passivated CQDs before MPA exchange, indicating a) the presence of chloride ligands, b) the absence of phosphine from PbBu₃, and c) the absence of oleate ligands, characterized by the absent carboxylate signal. d) Films of control PbS CQDs show minimal difference in surface chloride whether exchanged with MPA or an MPA/CdCl₂ mixture.

Using HRTEM, we investigated whether any quantum dot fusing occurred in the resultant films following film deposition and ligand exchange using 3-mercaptopropionic acid (MPA). Figure 6-1b shows HRTEM images that, even at the very low concentrations required to generate a sub-monolayer of quantum dots, evidence partially fused dot clusters. The insets in Figure 6-1b show specific instances of two or more dots that have fused, and alignment in diffraction fringes is evident among multiple adjacent quantum dots. Such alignment (oriented attachment) is a prerequisite for fusion to produce mutual passivation.

Further evidence of partial surface fusing was observed in full ligand-exchanged films. Films were fabricated using a layer-by-layer spin-coating approach; each layer of amine-capped PbS quantum dots was place-exchanged by treating with a solution of MPA mixed with a low concentration (0.2 mM) of CdCl₂. The goal of the inorganic metal halide salt was to retain and indeed improve halide passivation. Comparing absorption in solution
to film absorption after ligand exchange (Figure 6-5a), we note two evident features. First, significant broadening has occurred, with a larger long-wavelength contribution after exchange, consistent with fusing within the film. Second, despite evidence of fusing, the excitonic feature is still relatively strong, indicating that the exchange process has not eliminated the quantum confinement effect from the resulting film.

![Absorbance vs Wavelength](image)

**Figure 6-5 Mutually-passivated film characterization.** a) Absorbance (normalized to exciton peak) of amine-capped PbS quantum dots in solution (blue) and in film after ligand exchange with 3-mercaptopropionic acid and CdCl₂ (black). b) X-ray photoelectron spectra examining sulfur and chlorine characteristics in films of oleic acid (red) or amine (black) capped quantum dots exchanged with 3-mercaptopropionic acid and CdCl₂. The arrows in the sulfur spectrum indicate the positions of lead-bound sulfur and ligand sulfur.

XPS measurements provide further support for fusing, as well as evidence of improved overall passivation. Control quantum dots (oleic acid/CdCl₂ passivated PbS) were compared with mutually passivated quantum dots (amine/chloride passivated PbS). Each film was treated with MPA and CdCl₂ as described above, to maintain an equivalent number of chloride passivation steps; this is not expected to significantly impact the surface chemistry of control dots compared with a typical, MPA-only exchange. Figure 6-
4d provides evidence from XPS measurements that the addition of CdCl$_2$ to the ligand exchange step does not impact the amount of chloride in a control dot film. Comparing mutually-passivated to control CQD films, it is observed that the thiol contribution to the sulfur 2p signal (left-hand contribution to sulfur signal in Figure 6-5b) is significantly reduced, consistent with reduced available surface area. By contrast, the chloride 2p signal is unchanged between the two treatment types, since atomic (chloride) ligands are less impacted by the steric limitation of fused dot surfaces.

We interpret these stoichiometry data as promising with respect to the prospects for improved passivation. Fewer surface sites are available in the fused-surface case, since these surfaces are already occupied. Thus, having an equivalent density of chloride atoms in the film suggests a larger number of passivating halide anions per surface atom of the quantum dots, i.e. it points to the possibility of increased passivation density of the exposed facets.

We now turn to studies of minority carrier diffusion length (L$_D$), a key parameter most urgently in need of major progress in the field of CQD photovoltaics. We have shown recently that extending diffusion length will rely principally on reducing the density of deep electronic traps in CQD solids, while improving dot-to-dot transport will also offer advantage in the best present-day films. We employed transient photoluminescence (PL) measurements to determine carrier diffusion lengths, for these methods have been extensively practiced in organic$^{110}$ and perovskite$^{111,112}$ semiconductors in very compelling recent reports. We would thereby directly compare control vs. fused-and-passivated CQD films, and also benchmark our results to analogous reports in other materials systems.

The PL-based derivation of diffusion length relies on evaluating variation in the PL lifetime for pristine films (of known thickness) with and without a photoexcited-state-quenching interface. The dynamics and times scales of photogenerated carriers are subsequently interpreted within a 1D diffusion model in order to estimate the carrier lifetime and diffusion length.

CQD solids were formed via spin-coating on glass and were ligand-exchanged with MPA (control) or a mixture of MPA and CdCl$_2$ (mutually-passivated), as described above.
Unquenched films were prepared on bare glass, with film thicknesses of roughly 250 nm to ensure adequate PL signal and accurate carrier lifetime measurements. As shown in Figure 6-6, single layer films exhibited an abnormally fast decay time, potentially attributable to cracks and voids, whereas thicker films exhibited minimal thickness dependence on decay time due to the infilling of cracks by subsequently deposited layers.

![Photoluminescence lifetime measurements](image)

**Figure 6-6 Photoluminescence lifetime measurements** of MPA/CdCl₂ exchanged mutually-passivated PbS quantum dot films of various thicknesses deposited on bare glass. The single layer film (olive) exhibits a significantly faster decay profile than thicker films indicating quenching by cracks and defects.

Quenched films were prepared by spin-coating an electron-accepting layer of phenyl-C₆₁-butyric acid methyl ester (PCBM) on titanium dioxide, then depositing a two quantum dot layers (50 +/- 5 nm and 75 +/- 5 nm for the control and mutually-passivated films, respectively). The thickness was chosen to fall below expected diffusion length in each case in order to ensure a sizeable quenching effect. In all cases, the pulsed excitation source (633 nm) was incident on the CQD film side. Steady-state photoluminescence measurements (Figure 6-7) were used to determine the emission wavelength of interest for subsequent decay measurements (1110 nm for control dots, 1225 nm for mutually-passivated dots).
Time-resolved PL decay measurements are shown in Figure 6-8, along with two-component exponential fits to each data set, representing a fast exciton dissociation time constant and a slower transport-assisted recombination lifetime. The fast, but not resolution-limited, exponential component was accurately determined by fitting data measured on a smaller time window (Figure 6-9). The carrier lifetimes for each case are reported and compared in Table 6-1; even before evaluating the results within the framework of the diffusion model, one readily observes that the mutual-passivation method leads to a doubling of carrier lifetime compared to the control. At the same time it produces a significantly shorter quenching lifetime, suggesting the sought-after improved transport.

**Figure 6-7 Steady-state PL spectra** for control and mutually-passivated films.
Figure 6-8 Photoluminescence lifetime measurements of MPA-exchanged films of a) control PbS quantum dots and b) mutually passivated PbS quantum dots. The red points represent data for thick (>200 nm) films on glass, while the orange points represent thin films (50 and 75 nm, respectively) on a quenching layer of PCBM/titanium dioxide.
Figure 6-9 **Short time range PL decay** data for a) control and b) mutually-passivated films. Grey area represents the instrumental response function (IRF) with a HWHM of 80 ps, and fits are calculated as a convolution of the IRF and the biexponential decay. The fast component corresponds to exciton dissociation, is not affected by the substrate-assisted quenching and depends solely on mobility.

<table>
<thead>
<tr>
<th></th>
<th>Unquenched Lifetime [ns]</th>
<th>Quenched Lifetime [ns]</th>
<th>Diffusion Length [nm]</th>
<th>Mobility [cm² V⁻¹ s⁻¹]</th>
<th>Exciton Dissociation Rate [ns⁻¹]</th>
</tr>
</thead>
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<tr>
<td>Control</td>
<td>148 +/- 4</td>
<td>24 +/- 3</td>
<td>70 +/- 10</td>
<td>1 x 10⁻²</td>
<td>2.0 +/- 0.1</td>
</tr>
<tr>
<td>Mutually-passivated</td>
<td>268 +/- 5</td>
<td>11 +/- 1</td>
<td>230 +/- 20</td>
<td>8 x 10⁻²</td>
<td>3.7 +/- 0.1</td>
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Full details on the diffusion model applied to the PL decay results can be found in previous reports; in brief, the dynamics are modeled using a one-dimensional diffusion equation (equation 6.1):

\[
\frac{\partial n(x,t)}{\partial t} = D \frac{\partial^2 n(x,t)}{\partial x^2} - k(t)n(x,t) \tag{6.1}
\]

where D is the diffusion coefficient, and k represents the unquenched PL decay rate. Equation 6.1 is solved for the time- and depth-dependent carrier concentration by assuming
appropriate boundary conditions, i.e. that all carriers at the quantum dot/PCBM interface are quenched, leading to the condition \( n(L, t) = 0 \), where L is the film thickness, and that the carrier population outside the film is zero, i.e. \( n(x, t) = 0 \), for \( x < 0 \). Additionally, the initial excitation distribution can be written as \( n(x, 0) = n_0 \exp(-\alpha x) \), where \( \alpha \) is the absorption coefficient at the excitation wavelength. Absorption coefficients for each film were extracted from Figure 6-10.

**Figure 6-10 Absorption per unit length** measurements comparing control and mutually-passivated films.

As previously reported, this model can be simplified to a plot of diffusion length in units of film thickness against the ratio between quenched and unquenched PL lifetimes (Figure 6-11).
Figure 6-11 1D diffusion model plotting diffusion length ($L_D$) in multiples of film thickness (d) versus ratio of quenched ($\tau_{PL}$) to unquenched ($\tau_0$) carrier lifetime. The left point corresponds to a mutually-passivated film with diffusion length 230 +/- 20 nm, while the right point corresponds to a control film with diffusion length 70 +/- 10 nm.

Plotting the two observed lifetime ratios on this curve leads to an estimated diffusion length of 70 +/- 10 nm for the control, and of 230 +/- 20 nm for the mutually-passivated films. From the relation $L_D = \sqrt{D\tau}$ as well as Einstein’s relation (equation 6.2), the effective electron mobility can also be estimated for each film. Diffusion length and mobility are reported together with carrier lifetime measurements and estimated exciton dissociation rates in Table 6-1.

$$D = \frac{\mu k_B T}{q}$$

(6.2)

The three-fold improvement in diffusion length compared to control films represents the highest reported diffusion length to date in colloidal quantum dot solids. This measured value is comparable to diffusion lengths in those perovskite films typically utilized in mesoporous electrodes, though shorter than the longest $L_D$ values reported and employed in planar perovskite architectures.
A compelling example application of a significantly longer diffusion length is the realization of a photovoltaic device that can exploit a notably thicker light-absorbing layer, enabling a higher current density and maintaining fill factor. For control films, it has been previously reported that the optimal film thickness is typically in the range of 300 nm, beyond which any minimal gains in current density are more than offset by a loss in fill factor. By contrast, devices prepared using the mutual-passivation method were found to have an optimal thickness of 600 nm. Electrical characterization of a hero device is shown in Figure 6-12a; fill factor for the thick device is comparable to that of standard-thickness control devices (58% fill factor), while the additional 300 nm of absorptive material allows the generation of just below 30 mA cm\(^{-2}\) in current density (confirmed by external quantum efficiency measurements, Figure 6-12b). While open-circuit voltage is somewhat lower than control devices (likely explained by the red-shift due to fusing observed in Figure 6-12b), the power conversion efficiency is 9.2%. 
Figure 6-12 Record device performance. a) Current (black) and power (blue) density versus applied bias measurements for a high diffusion length film (thickness 600 nm), with maximum power point power conversion efficiency of 9.2%. b) External quantum efficiency measurements for thickness-optimized control films (red circles, calculated current 21.6 mA cm$^{-2}$) and mutually passivated films (black circles, calculated current 29.5 mA cm$^{-2}$). Total spectral current generation density for a hypothetical 100% EQE device is shown (upper solid curve); additional spectral current density gained by the mutually passivated devices compared with control is shown by the lower solid curve.

The dot-to-dot mutual surface passivation approach, when combined with the best available methods in quantum dot chemical passivation, leads to the formation of films with diffusion lengths fully three times longer than previously-reported quantum dot solids. Applying this materials processing approach to photovoltaic devices allows for thicker optimized films, with significant increases in photocurrent and negligible fill factor loss. Additionally, the approach offers a robust platform for interesting future applications; low trap density and long diffusion length are desirable qualities when constructing high-performance current-matched tandem photovoltaic devices, either fully CQD-based or as efficient IR conversion in conjunction with crystalline semiconductor cells.
Chapter 7  Conclusions and Perspectives

7.1  Conclusions

Progress in the field of colloidal quantum dot photovoltaics has been hampered, in part, by very limited diffusion lengths in films. This has, in turn, limited the active material layer thickness, a tradeoff which sacrifices light absorption to preserve reasonable electrical carrier transport. This thesis has identified three key factors which limit diffusion length in CQD solids, addressed each factor individually, and used the knowledge gained from these research approaches to create a long diffusion length CQD solid and a highly efficient photovoltaic device.

The first limiting factor, carrier mobility, was discovered to be closely connected with quantum dot packing in films. Methods were explored to increase the packing density of CQD solids, by introducing variations to both the solution phase and the ligand exchange process. The second limiting factor, quantum dot surface passivation, could be significantly improved by using a complementary pair of ligands, particularly a significant surface concentration of halide anions. Given this finding, the ligand exchange process was examined in detail, with variations on processing conditions and solvent environment implemented to reduce the impact of this process on surface halide anions. Finally, a significant active, recombination-inducing impurity was discovered in quantum dot films. It was found to be a compound including lead oleate, a byproduct of the ligand exchange of oleic acid capped lead sulfide quantum dots. A reasonable chemical process was developed to minimize the presence of this compound in CQD solids.

The culmination of these findings was presented in Chapter 6, with the development of the mutually-passivated colloidal quantum dot solid. This process elegantly addresses each of the limiting factors mentioned above. By initially depositing films of CQDs capped with hexyl- and octylamine, rather than a much longer capping ligand, the initial dot-to-dot spacing was greatly reduced, minimizing the volume reduction upon ligand exchange. After the ligand exchange, dot spacing was reduced to the point of necking between quantum dots, without losing quantum confinement. Overall, this boosted the carrier mobility in these films compared to a standard control.
Passivation, a central theme of the preceding chapter, was creatively addressed by changing the frame of reference used to think about how surfaces are capped; rather than expecting to chemically passivate every surface site, by creating partially fused layers of quantum dots, a significant portion of the available surface was removed from consideration. Applying knowledge gained in Chapter 4, the remaining surfaces were strongly passivated with a mixture of halide and bifunctional organic molecules. In addition to improving mobility and passivation, this approach avoids the key impurity consideration introduced in Chapter 5 – by eliminating all oleic acid from the quantum dot solution prior to film formation, there is no chance of forming the electronically active intercalated compound observed in typical PbS CQD solids.

The combination of these considerations led to the longest reported diffusion length to date in colloidal quantum dot solids, fully three times longer than previous reports. This enabled a doubling in the active layer thickness for subsequent photovoltaic devices, leading to a sizeable increase in generated photocurrent, without the drop in fill factor typically observed in over-thick low diffusion length devices. At the time of writing, devices generated using this process hold the highest published efficiency for CQD solar devices, at 9.2% power conversion efficiency.

7.2 Perspectives

Continued progress in the field (Figure 7-1) will rely on progress in three key areas. The first strives to synthesize a population of improved quantum dots, and to produce well-packed, well-passivated quantum dot films from them; fulfilling this prescription will rely on expertise in materials science and materials chemistry. While large strides have been made in recent years to improve quantum dot surface passivation, orders of magnitude remain between the defect density levels observed in bulk semiconductors and the best quantum dot solids to date. Studies of novel passivation strategies, including new or hybrid ligand systems, surface engineering, core/shell strategies, and self-healing surfaces, will reduce trap states, improve carrier transport and reduce the extent of energy level pinning. A second route to improved electronic transport in quantum dot films will rely on densifying nanocrystal films through improved packing and, ideally, ordering. Such films will eliminate diversity in path length and thus tortuosity in charge transport through the
device. Improvements in this area will be driven by engineering actively order-generating quantum dot surfaces, and by careful work to achieve a higher degree of film purity, with extraneous chemical species eliminated from the quantum dot film.

Figure 7-1 Pathways forward for CQD photovoltaics.

The second pillar of research focuses on constructing the most efficient device architecture using a given material. Advances in this area have led to the most recent record CQD solar cell efficiencies, and will continue to have vital influence over progress in the field as a whole. Studies must focus on optimizing both light and photocurrent management, the goal being full capture of all incident energy, and the high-yield conveyance of the resultant photogenerated charge to an external circuit. This will rely on careful engineering of the band structure of the quantum film in concert with that of selective top and bottom electrodes. Significant studies have been performed on the electron-transporting component (transparent conductive metal oxides, typically), yet as the optoelectronic quality of the quantum dot solid improves, even greater enhancements will be required in both the electron- and hole-accepting layers to ensure optimal performance. Studies are already beginning to examine the role of the electron-accepting oxide, and the variations between titanium dioxide and zinc oxide, both in performance and light-soaking requirements; minimal thorough research has been carried out on the top interface to date, examining the impact of material choice and deposition conditions. Research will need to adjust existing systems or apply novel material solutions (various oxides, organic films, etc), while intensely studying the interfaces between the quantum
dot film and electrodes to eliminate any potential losses. Photonic enhancements will be required to further increase absorption in a given thickness of light-absorbing material.

Finally, as single-junction quantum dot solar cells advance and improve, a renewed focus will be placed on multiple junction integration, with the goal of creating high-efficiency devices through improved spectral utilization and minimal loss associated with photocarrier thermalization. Tandem and triple-junction all-CQD solar cells will exploit control over quantum dot size to maximize spectral capture efficiency and boost device voltage. It may be particularly attractive to combine CQDs, distinctive among solution-processed materials in their infrared harvesting capability, with established solar technologies such as crystalline silicon, or with novel large-gap solar technologies such as lead halide perovskites.

The past few years have seen a deepening in understanding – through a combination of experimental and computational studies – of how quantum dots and ligands, through their composition and binding, lead to rationally-described transport, trapping, and consequent device performance. Continued progress in the fundamental physical chemistry and device physics of CQD devices will be a key driver of ongoing progress in this fast-moving, highly relevant field.
References


Appendix A – Experimental Details

Common to all sections

Quantum dot synthesis

PbS quantum dots were synthesized according to a previously published method.\textsuperscript{113}

Preparation of metal halide precursors

Cadmium chloride (Sigma-Aldrich, 99.98\%) or lead chloride (Alfa Aesar, 99.999\%) and TDPA (Alfa Aesar, 98\%) were dissolved in oleylamine (technical grade, Acros, 80\%) by pumping for 16 h at 100 °C. The solution was then kept at 80 °C to avoid solidification. In a typical procedure, precursor with a 13.6:1 Cd:TDPA molar ratio was made by dissolving 0.30 g (1.64 mmol) of CdCl\textsubscript{2} and 0.033 g (0.12 mmol) of TDPA in 5 ml of oleylamine.

Metal halide treatment

For metal halide treatment, 1.0 ml metal halide precursor was introduced into the reaction flask after sulphur source injection during the slow cooling process. A 6:1 Pb:Cd molar ratio was maintained during the synthesis. When the reaction temperature reached 30–35 °C, the nanocrystals were isolated by the addition of 60 ml of acetone then centrifugation. The nanocrystals were then purified by dispersion in toluene and reprecipitation with acetone/methanol (1:1 volume ratio), then re-dissolved in anhydrous toluene. The solution was washed with methanol two or three more times before final dispersal in octane (50 mg ml\textsuperscript{-1}).

AM1.5 photovoltaic performance characterization

Current–voltage data were measured using a Keithley 2400 source meter. The solar spectrum at AM1.5 was simulated to within class A specifications (less than 25\% spectral mismatch) with a xenon lamp and filters (ScienceTech; measured intensity of 100 mW cm\textsuperscript{-2}). The source intensity was measured with a Melles-Griot broadband power meter through a circular 0.049 cm\textsuperscript{2} aperture at the position of the sample and confirmed with a
calibrated reference solar cell (Newport). The accuracy of the current–voltage measurements was estimated to be ±7%.

**External quantum efficiency (EQE) measurements**

The EQE spectrum was obtained by passing the output of a 400 W xenon lamp through a monochromator and using appropriate order-sorting filters. The collimated output of the monochromator was measured through a 1 mm aperture with calibrated Newport 818-UV and Newport 818-IR power meters as required. The beam was optically chopped and co-focused on the pixel with a solar simulator at 1-sun intensity. The measurement bandwidth was ~40 nm and the intensity varied with the spectrum of the xenon lamp. The current response was measured with a Stanford Research Systems lock-in amplifier operating in current mode where a virtual null at the input approximates short-circuit conditions. The accuracy of the EQE measurements was estimated to be ±8%.

**X-ray photoelectron spectroscopy**

The surface elements and chemical states of the PbS CQD films were analyzed using X-ray photoelectron spectroscopy (XPS) (PHI-5500). A monochromated Al K radiation source (1486.7 eV) was used to excite photoelectrons in an ultrahigh vacuum atmosphere at ≈10^{-9} Torr. The binding energy scale was calibrated using the Au 4f 7/2 peak at 83.98 eV and the Cu 2p 3/2 peak of sputter-cleaned Cu at 932.67 eV.

**Fourier transform infrared spectroscopy**

FTIR was performed on a Bruker Tensor spectrometer in transmission mode. Analysis of CQD films was performed by fabricating films as outlined above on glass substrates, manually scraping material off the substrate and mixing the resultant powder with KBr powder in roughly a 1:100 w/w ratio. The mixture was compressed into a thin pellet using a PIKE Technologies pellet press. Measurements for solutions were carried out by depositing and spreading a small volume of each compound on a KBr disk and immediately measuring. A background subtraction against air was carried out for the entire data set.
Sections 3.1 and 4.1

Film fabrication

PbS CQD films were deposited using a layer-by-layer spin-coating process under an ambient atmosphere. For each layer, the CQD solution (50 mg mL$^{-1}$ in octane) was deposited on the ZnO/TiO$_2$ substrate and spin-cast at 2,500 r.p.m. In the hybrid and organic approaches, solid-state ligand exchange was performed by flooding the surface with 1% v/v MPA in methanol for 3 s before spin-coating dry at 2,500 r.p.m. Two washes with methanol were used to remove unbound ligands. Each device consisted of 8–12 layers. Top electrodes were deposited using an Angstrom Engineering Åmod deposition system in an Innovative Technology glovebox. The contacts typically consisted of 10 nm thermally evaporated molybdenum trioxide deposited at a rate of 0.2 Å s$^{-1}$, followed by electron-beam deposition of 50 nm of gold deposited at 0.4 Å s$^{-1}$, and finally 120 nm of thermally evaporated silver deposited at 1.0 Å s$^{-1}$.

Grazing-incidence small angle X-ray scattering (GISAXS)

GISAXS measurements were performed on Beamline 7.3.3 of the Advanced Light source (ALS) at Lawrence Berkeley National Laboratory. Monochromatic light was used with a wavelength of 1.23984 Å (10 keV). The Pilatus 1M detector, a CMOS hybrid-pixel CCD camera with a pixel size of 172 µm × 172 µm and a total of 981 × 1,043 pixels with a 20-bit dynamical range per pixel, was used to record the scattering patterns. Typical readout time per image was <3.6 ms. The images were dark-current-corrected, distortion-corrected and flat-field-corrected by the acquisition software. Using a silver behenate powder standard, the sample-to-detector distance was determined to be 1,350.74 or 1,356.84 mm. The angle of incidence of the X-ray beam was varied between 0.02 and 0.15°. Typical exposure times ranged from 20 to 300 s. We plotted azimuthally integrated intensity profiles and used Gaussian fitting plus an exponential background to determine the location of the scattering rings at q ≈ 0.2 Å$^{-1}$. 
Time-of-flight

This method\textsuperscript{114} was used to measure hole carrier mobility. TOF experiments were carried out on samples with a geometry identical to that of the photovoltaic device, with the exception that the total nanocrystal layer in this case was thicker (>500 nm). The samples were excited using a diode-pumped passively Q-switched solid-state laser operating at 355 nm with 1 ns pulses at a 200 Hz repetition rate. The light was incident on the sample from the transparent FTO side. The devices were biased using a Keithley 228 voltage/current source, and a digital Tektronix TDS5104 oscilloscope was used to measure the current transient output across a 50 Ω load.

Section 3.2

Synthesis of 3MNXP

In a 100 mL oven-dried Schlenk flask, 3-mercaptopropionic acid (1 mL, 11.5 mmol) and a primary amine (11.5 mmol) were dissolved in ~30 mL of dichloromethane (DCM). The flask was cooled in an ice-bath, followed by the addition of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) (2 g, 13 mmol) and 4-dimethylaminopyridine (DMAP) (0.28g, 2.3 mmol). The mixture was stirred for 30 mins, the ice bath was removed, and the mixture was stirred for a further 12 h. The mixture was then washed three times with a saturated aqueous solution of citric acid, dehydrated using sodium sulfate, and filtered. The dichloromethane solvent was removed by rotary evaporation followed by 12 h vacuum pumping using a Schlenk line.

Film fabrication

CQD films were prepared on TiO\textsubscript{2} electrodes (50 nm of TiO\textsubscript{2} sputtered on fluorine-doped tin oxide (FTO)-coated glass) using layer-by-layer spin-coating deposition under ambient conditions, depositing a 50 mg mL\textsuperscript{-1} solution of quantum dots in toluene at 2500 rpm. Each layer was treated with 1% lactic acid in methanol (v/v) for 10 seconds, and rinsed with pure methanol, spinning at 2500 rpm after the rinse. Top electrodes were deposited by thermal and electron beam evaporation and consisted of 40 nm of MoO\textsubscript{3}, 50 nm of gold,
and 150 nm of silver, deposited at a rate of 0.2 (thermal MoO$_3$), 0.4 (electron beam Au), and 1 (thermal Ag) Å/s, at a pressure of $<1 \times 10^{-6}$ mbar.

**Section 4.2**

**Device fabrication**

CQD films were prepared on TiO$_2$ electrodes (50 nm of TiO$_2$ sputtered on fluorine-doped tin oxide (FTO)-coated glass) by multilayer spin-coating of a 100 mg mL$^{-1}$ solution of quantum dots in octane under ambient conditions. The layer thickness was adjusted by depositing at either 750 or 2500 rpm. Each layer was treated with 1% 3-mercaptopropionic acid in either methanol or acetonitrile (v/v), and then rinsed twice with either methanol or acetonitrile while spinning at 2500 rpm. The resultant layer thickness, post-treatment, was 100 or 30 nm for deposition rates of 750 or 2500 rpm, respectively. Top electrodes were deposited by thermal and electron beam evaporation, and consisted of 40 nm of MoO$_3$, 50 nm of gold and 80 nm of silver. These were deposited at a rate of 0.2 (thermal MoO$_3$), 0.4 (electron beam Au) and 1 Å/s (thermal Ag), at a pressure of $<1 \times 10^{-6}$ mbar.

**QCM-D measurements**

Thin films of CQDs were fabricated by spin-coating 100 μL of CQDs for 15 s at 2500 rpm on SiO$_2$-coated quartz crystal sensors, thermally oxidized Si wafers and Au-coated glass substrates. The AT-cut quartz crystals (5 MHz resonance frequency) and the Si wafers with 100 nm oxide layer on top were cleaned by ultrasonication separately in acetone, isopropyl alcohol and ethanol followed by a 10 min UV–ozone treatment. Film-coated quartz sensors were loaded into a QCM open module (E4 model, QSense, Biolin Scientific) maintained at 25 °C. Drop-casting measurements were carried out by dropping 150 μL of the process solvents and ligand-exchange solutions on the surface of the coated sensors.

**VASE analysis**

A J.A. Woollam Co., Inc. IR-VASE ellipsometer (500–5000 cm$^{-1}$) was used to study the fraction of the OA remaining in the thin films upon various solvent and ligand-exchange treatments. The IR-VASE uses a Fourier transform based infrared spectrometer combined
with a variable angle ellipsometer incorporating a rotating compensator technology for accurate Ψ and Δ measurements. The spectra were obtained at an incidence angle of 75°. The resulting elliptical beam spot had dimensions 3.9 cm × 0.7 cm. 100 nm Au-coated soda-lime glass slides were used as substrates.

GISAXS

Ex situ GISAXS analysis was carried out at the D-line at the Cornell High Energy Synchrotron Source (CHESS) (Cornell University). A beam with a wavelength of 1.23 Å was obtained from a wide bandpass (1.47%) double-bounce multilayer monochromator. The angle of incidence was varied discretely from 0.15° to 0.50° with respect to the substrate plane.

Photoelectron spectroscopy measurements

XPS studies were carried out in a UHV Omicron chamber equipped with a SPHERA U7 hemispherical energy analyzer, using X-ray photons with an incident kinetic energy of 1486.6 eV from a monochromated Al Kα X-ray source with a total energy resolution of 0.1 eV. The studies were carried out at room temperature. The PES spectra were obtained from the VLS-PGM beamline at the Canadian Light Source, Inc., having a Scienta SES100 hemispherical energy analyzer and an energy resolution of 0.05 eV. The spectra were obtained at normal emission and room temperature.

Section 5.1

Lead oleate–X synthesis

Lead oleate was prepared by mixing lead oxide with oleic acid at elevated temperature (100 °C for 8 h). Lead oleate was then warmed with a heat gun to ensure full liquid state before being mixed with equal parts of a 10% solution of a bifunctional short ligand (3-mercaptopropionic acid or ethanedithiol) in methanol. The solution was mixed vigorously and centrifuged to separate the resulting precipitate, which was then dried under vacuum for 30 min to remove excess solvent.

Device fabrication
CQD films were prepared on TiO$_2$ electrodes (50 nm of TiO$_2$ sputtered on fluorine-doped tin oxide (FTO)-coated glass) using layer-by-layer spin-coating deposition under ambient conditions, depositing a 50 mg mL$^{-1}$ solution of quantum dots in octane at 2500 rpm to obtain layers of roughly 30 nm thickness. Each layer was treated with 1% 3-mercaptopropionic acid in methanol (v/v) and rinsed with either pure methanol (control devices) or a solution of pyruvic acid in methanol (from 0.2 to 1.5% v/v), followed by a final pure methanol rinse and spinning at 2500 rpm after each rinse. Top electrodes were deposited by thermal and electron beam evaporation and consisted of 40 nm of MoO$_3$, 50 nm of gold, and 150 nm of silver, deposited at a rate of 0.2 (thermal MoO$_3$), 0.4 (electron beam Au), and 1 (thermal Ag) Å/s, at a pressure of <1 × 10$^{-6}$ mbar.

**Electroluminescence measurements**

Electroluminescence measurements were carried out by connecting a Keithley 2410 source meter to our devices and applying a range of forward bias voltages while reading the resultant current. The luminescence was collected through a set of lenses focused on an optical fiber and connected to an Ocean Optics NIR-512 spectrophotometer. Photoluminescence measurements cofocused the input to the same signal collection optics with a 630 nm wavelength continuous wave laser.

**Solid-state NMR**

All solid-state NMR experiments were performed on an Agilent DD2 700 MHz spectrometer with a 1.6 mm T2 NB HX Balun probe. Magic angle spinning experiments were conducted while spinning the sample at 25 kHz to ensure that there were no spinning sidebands in the region of interest. 1H chemical shifts were referenced to trimethyl silane ($\delta_{\text{iso}} = 0$ ppm) using adamantane as a secondary reference (1H: 1.85 ppm for the high-frequency resonance). For NMR analysis, the curves were fit by a superposition of Gaussians with peak centers corresponding to constituent ligands (MPA $\approx$ 0–2 ppm), residual methanol ($\sim$3 ppm) and water ($\sim$5 ppm) and by a residual synthesis precursor, tetradecyl phosphonic acid ($\sim$12 ppm). The additional $\sim$8 ppm peak was assigned to a protonated carboxylic acid.
Density functional theory calculations

Calculations were carried out using the Quickstep module of the CP2K program suite utilizing a dual basis of localized Gaussians and plane waves. The plane wave cutoff was 300 Ry, appropriate for the Goedecker–Teter–Hutter pseudopotentials that we employed, and the localized basis set of double-\(\zeta\) plus polarization (DZVP) quality optimized to reduce the basis set superposition errors. Calculations were performed using the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional. Simulations were performed with nonperiodic boundary conditions in a 50 × 50 × 50 Å\(^3\) unit cell for 2.5 nm quantum dot sizes. The quantum dot was carved out of bulk PbS. All singly bonded atoms were discarded, resulting in a faceted cuboctahedron shape. A mixture of Cl and thiol ligands was used to passivate all dangling bonds on (111) and (110) facets, with the (100) facets left unpassivated. Care was taken to select the stoichiometry that preserves the charge neutrality of the dot, necessary to position the Fermi level in the midgap. For all calculations, a single CQD was modeled with appropriate additions (MPA, deprotonated MPA, lead oleate as well as the monomer and dimer of the lead oleate–MPA complex). The lead oleate and complexes were not bound to the surface of the CQD but placed near the surface (approximately 3–5 Å). The distance was sufficient to observe no overlap between the electronic wave function of the states on the complex and those on the CQD itself.

Section 6.1

Amine exchange

PbS CQD for mutual passivation studies were synthesized using a slight variant of the aforementioned method: after the growth of oleic acid-capped CQD of desired size, tributylphosphine was injected during the reaction cooling process, with injection at 80 °C and 20 min reaction time. Trimethylchlorosilane was injected at 50 °C, with a 30 min reaction time. After the reaction vessel cooled to 30 °C, the quantum dot solution aggregated; the supernatant was removed and the reaction vessel was refluxed with argon. Subsequently, n-hexylamine was injected (stirring 80 min) followed by n-octylamine for an additional 80 min stirring. Following full reaction, the CQD solution was precipitated
with methyl acetate, dried for 16 h under mild vacuum, and redispersed at roughly 100 mg mL$^{-1}$ in octane. All reagents were purchased from Sigma Aldrich.

**Film fabrication**

CQD films were prepared on glass (for spectroscopy and PL studies) or TiO$_2$ electrodes (for photovoltaic devices; 50 nm of TiO$_2$ sputtered on fluorine-doped tin oxide (FTO)-coated glass) using layer-by-layer spin-coating deposition under ambient conditions. Control films were deposited from a 50 mg mL$^{-1}$ solution of quantum dots in octane at 2500 rpm to obtain layers of roughly 25 nm thickness, while amine-capped CQD were deposited from a 100 mg mL$^{-1}$ solution in octane, spun at 2500 rpm to generate roughly 35 nm thick layers. Each layer was treated with 1% 3-mercaptopropionic acid (MPA) in methanol (v/v); for mutually-passivated films, the MPA solution included 0.2 mM CdCl$_2$.

All films prepared for XPS measurements (control and mutually-passivated) were exchanged with an MPA/CdCl$_2$ solution to maintain a consistent number of Cl-passivation steps. All films were rinsed with pure methanol after ligand exchange, spinning at 2500 rpm after each rinse. For photovoltaic devices, top electrodes were deposited by thermal and electron beam evaporation, and consisted of 40 nm of MoO$_3$, 50 nm of gold, and 150 nm of silver, deposited at a rate of 0.2 (thermal MoO$_3$), 0.4 (electron beam Au), and 1 (thermal Ag) Å s$^{-1}$, at a pressure of $<1 \times 10^{-6}$ mbar.

**Transient photoluminescence**

Transient PL measurements were performed in reflection geometry (at an incidence angle of 30° from the sample surface to avoid spurious reflections of the incident light) using a 633 nm laser diode as a pulsed excitation source (with a temporal profile of $\approx$0.13 ns), in combination with a double-grating spectrometer. The time traces were acquired using a time-correlated single-photon-counting (TCSPC) near-infrared detector (air-cooled photomultiplier tube). The time window was set according to the measured timescale in order to ensure a complete decay of the photogenerated carriers between consecutive excitation pulses.
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