Surface Traps in Colloidal Quantum Dot Solar Cells,
their Mitigation and Impact on Manufacturability

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ABSTRACT

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Colloidal quantum dots (CQDs) are potentially low-cost, solution-processable semiconductors which are endowed, through their nanoscale dimensions, with strong absorption, band gap tunability, high dielectric constants and enhanced stability. CQDs are contenders as a standalone PV technology as well as a potential back layer for augmenting established photovoltaic (PV) technologies, such as Si. However, owing to their small size (ca. few nanometers), CQDs are prone to surface trap states that inhibit charge transport and threaten their otherwise wonderful optoelectronic properties. Surface traps have also, indirectly, impeded scalable and industry-compatible fabrication of these solar cells, as all of the reports, to date, have relied on spin-coating with sophisticated and tedious ligand exchange schemes, some of which need to be performed in low humidity environments.

In this thesis, we posit that an in-depth understanding of the process-structure-property-performance relationship in CQDs can usher in fresh insights into the nature and origin of surface traps, lead to novel ways to mitigate them, and finally help achieve scalable fabrication. To this end, we probe the CQD surfaces and their interactions with process solvents, linkers, and ambient environment employing a suite of spectroscopic techniques. These fundamental insights help us develop facile chemical and physical protocols to mitigate surface traps such as solvent engineering, remote molecular doping, and oxygen doping, directly leading to better-performing solar cells. Our efforts finally culminate in
the realization of >10% efficient, air-stable CQD solar cells scalably fabricated in an ambient environment of high, uncontrolled R.H. (50-65%). As-prepared solar cells fabricated in high humidity ambient conditions are found to underperform, however, an oxygen-doping recipe is devised to mitigate the moisture-induced surface traps and recover device performances. Importantly, these solar cells are fabricated at coating speeds of >15 m min\(^{-1}\) with roll-to-roll compatible techniques such as blade and bar coating requiring 1/25\(^{th}\) the CQD material consumed by the standard spin-coated devices, overcoming the two major challenges of manufacturability and scalability faced by CQD PV.
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Chapter 1

Introduction

The rising global energy demands are running akin to a waning non-renewable resource supply. Besides, consumption of non-renewable resources is directly linked to greenhouse gas emissions ultimately leading to global warming. The critical situation asserts an urgent need for bringing renewable resources into the fray. There have been promising developments, of late, that establish hope of a successful switch to sustainable energy solutions. For example, last year Portugal achieved a major milestone with its national electricity consumption running continuously on renewable energy for a record 107 hours.\[14\] Solar power forms a crucial fraction of the renewable energy sector. PV technology involves absorption of solar photons and their subsequent conversion into electrical energy. 2016 was a new record-breaking year for PV with the global installed solar power breaching 300 GW, covering 1.8% of the total electricity generation.\[15\]

Solar cell technologies can be broadly categorized into three generations: first generation comprises of mono-crystalline silicon solar cells, second generation involves cells based on amorphous silicon, cadmium telluride (CdTe) and copper indium gallium diselenide (CIGS), and the third generation includes solution-processable thin film solar cells. Although, mono-crystalline silicon solar cells have been the key player in PV market, they have stringent requirements on the purity of silicon, the production of which is costly besides leading to greenhouse gas emissions. Also, since silicon is an indirect band gap semiconductor, large amounts of the material is needed for efficient absorption of sunlight, resulting in large and bulky PV modules limiting them to roof-top applications. These
demerits have together led to a long energy break-even time for silicon PV.\textsuperscript{16} The second generation PV employs thin films for light absorption compared to large silicon wafers of the first generation. However, the reliance on rare materials such as indium and tellurium, and the low charge mobility of amorphous silicon coupled with vacuum-deposition for the production process render this generation industrially uncompetitive with Si. Third generation PV aims to extend the benefits of the second generation with an aim of making the technology industrially viable. This PV category thrives on the cost-effective solution processability of the light absorbing material which can be cast on flexible substrates (paper, plastic, glass) via roll-to-roll printing techniques. This generation includes a widely-researched variety of PV technologies: \textit{dye-sensitized solar cells}, \textit{organic solar cells} (which include polymer- and small molecule-solar cells), \textit{CQD solar cells} and \textit{hybrid organic-inorganic perovskite solar cells}.\textsuperscript{17-19} Due to the direct band gaps of these materials, only a few hundred nanometers (nm) thick film is sufficient to maximize solar light absorption. Photon absorption leads to exciton (electron-hole pair) formation which can then be separated and the charges extracted employing electron- and hole-extracting contacts.

CQDs, a few nanometer-sized particles, are semiconductors at the nanoscale. These are chemically synthesized as colloids in organic solvents (for example, octane) employing proper organic surfactants that impart colloidal stability. Importantly, synthesizing CQDs with diameters below the Bohr exciton radius leads to confinement of the photo-generated exciton. Band structure (and, therefore, the band gap) of CQDs in this regime can be size-tuned, in accordance with the ‘quantum size effect’. CQDs, therefore, present the opportunity of band gap tunability. Since ca. 50\% of the solar spectrum falls in the near IR
which the silicon solar cells cannot efficiently absorb, band gap-tuned CQDs can be used as the bottom cells leading to enhancement of overall power conversion efficiencies (PCEs) of the silicon PV modules. Importantly, CQDs offer the unique prospect of multiple exciton generation (MEG) per each photon absorbed.\textsuperscript{[20-21]} MEG makes CQDs exceptional amongst all the other PV materials and, in theory, allows going past the single-junction Shockley-Queisser limit of ca. 33\% PCE.\textsuperscript{[22-23]} These virtues have put CQD solar cells on the roadmap to third generation PV and have fuelled intense research activity over the past decade.

Lead chalcogenide (lead sulfide, PbS and lead selenide, PbSe) CQDs have attracted the most attention for solar cell applications due largely to their large dielectric constants, which allow efficient delocalization of the photo-generated excitons resulting in high carrier mobilities.\textsuperscript{[24-25]} Another consequence is the small exciton binding energies due to efficient charge screening, leading to low energetic losses in these CQD solar cells during charge separation. Since CQDs employ a large surface-to-volume ratio, proper passivation of the surfaces becomes crucial. Emphasis has, therefore, been laid on efficient ligand passivation protocols. The impressive rise of CQD solar cells over the past decade has been underpinned by parallel breakthroughs in chemical passivation schemes and device engineering protocols. These have led to ca. 12\% certified PCEs.\textsuperscript{[26]}

Surfaces of the CQDs are infested by defect states which arise chiefly due to improper passivation, dangling bonds and interaction with the ambient environment, including moisture and oxygen. These defects behave as traps for photo-generated charge carriers in the CQD solids thereby limiting device performance. In fact, as we shall find during the
course of this thesis, surface traps have been essentially holding back scalable fabrication of CQD solar cells in ambient, uncontrolled humidity environments – a strict requirement for industrial compatibility.\cite{27}

The initial organic ligands used to impart colloidal stability to CQDs in organic solvents are long-chain, insulating fatty acids (usually, oleic acid, OA) resulting in poor charge transport through solids made from these CQDs. These solids can be made conductive via the so-called *solid-state ligand exchange* – wherein, the insulating ligands are replaced by shorter, conducting ligands (thiols, halides) by briefly dipping the OA-capped CQD (OA-CQD) solid in a solution of the shorter ligands. The exchange process brings the CQDs closer enhancing charge hopping rates besides ensuring that the CQD surfaces remain efficiently passivated. The resulting, ‘exchanged’ solid is then washed twice with a process solvent to remove any loosely bound, unexchanged OA and excess shorter ligands. This cycle is repeated around 10-12 times, in a layer-by-layer (LbL) process, to yield a ca. 300 nm thick film that can be used as the active layer in a solar cell.\cite{28} Although the solid-state exchange process tremendously enhances charge transport and leads to efficient suppression of surface traps, it relies on spin coating making the processing highly wasteful and incompatible with industrial scale-up. More recently, an alternate route to realizing ligand exchange has been developed that employs a solution phase to carry out the exchange process. The *solution-phase ligand exchange* or SolEx yields an exchanged CQD ink that helps realize single-step deposited active layers, moving away from the time- and materials-wasting LbL process.\cite{13,29-30} SolEx, therefore, presents itself as a more economic and industrially viable route to CQD PV scale-up.
As pointed above, ambient moisture is also a source of surface traps in CQD solids.\textsuperscript{[31]} This is the reason why almost all the CQD devices reported thus far have been entirely processed and fabricated in dry environments (low moisture). In order for CQD PV to make a strong case of industrial scale-up, ambient manufacturability in uncontrolled humidity environments must be achieved.

In this thesis, we investigate the surface structure-property-performance relationship in CQDs. We employ a suite of surface-sensitive characterization techniques such as photoemission spectroscopy and probe CQD surface traps. Our efforts lead to the demonstration of several trap suppression protocols such as: solvent engineering, remote molecular doping, and oxygen doping, resulting in better-performing solar cells. Our studies on surface traps finally lead us to a handle on the issue of moisture-attack. We effectively find a route to cure the moisture-induced surface traps, a finding that leads us to break the age-old compromise between ambient manufacturability, process scalability and high CQD solar cell performances.

The outline of this thesis is as follows. Chapter 2 \textit{reviews} the latest developments in the CQD PV field with special emphasis on two key areas that have been behind the rise of device performances in this field: ligand passivation schemes and solar cell architectures. We also discuss the two main challenges on the path to commercialization, namely, scalable fabrication and ambient manufacturability.

Chapter 3 deals with the \textit{methodology} employed in this thesis that helped glean important information regarding surface traps.
Chapter 4 discusses the *solvent engineering* protocol that enabled us to demonstrate a modified solid-state ligand exchange. This protocol allowed fabrication of CQD solar cells in as little as 3 LbL steps, compared to 10-12 LbL steps, significantly curbing materials and time wastage.

Chapter 5 develops a *remote molecular doping* approach for CQD solids. The doping recipe is a facile, single-step method that is compatible with device fabrication. Here, it is applied to the simple case of a p-n heterojunction solar cell. It is shown that the p-type CQD active layer is initially sub-optimally doped, owing to in-gap traps. P-doping the solid leads to trap suppression and hence device performance increase.

Chapter 6 extends the application gamut of the molecular doping approach to modern-day CQD solar cells that employ an n-i-p architecture. It is shown that p-doping of the p-type CQD hole-transporting layer (HTL) aids device performance by enhancing band bending across the device.

Chapter 7 presents an *oxygen doping* protocol that efficiently curbs the moisture-induced traps states in CQD solids. It is realized that solar cells manufactured under ultra-high humid ambients suffer from a sub-optimally doped CQD HTL owing to moisture-induced surface traps. A dry air storage effectively ‘oxygen-dopes’ the HTL leading to trap suppression and performance recovery of the devices. This also allows us to demonstrate scalable CQD solar cells using high-speed blade- and bar-coating.

Chapter 8 concludes the thesis and presents perspectives for future CQD PV research.
Chapter 2

Process-Surface Structure-Property-Performance Relationship in CQD PV: A Review

In this chapter, we cover the basics of CQDs in PV – from synthesis to their application as absorber layers in solar cells, with an emphasis on the crucial role played by their surfaces in determining their properties. Along the way, we shall follow the two major developments that have underpinned growth in CQD PV: the various ligand exchange approaches and solar cell architectures. We will highlight how improvements in ligand exchange protocols have resulted in curtailing surface traps and how developments in solar cell architecture have led to better charge extraction. In tandem, these developments have taken CQD solar cells from <1% to >12% PCE over the last 10 years. Finally, we discuss some of the key challenges associated to commercialization of CQD PV.

2.1 Colloidal Quantum Dots

CQDs are nanoscale semiconductors which can be mass-produced in a cost-effective, solution-processable manner. They have size-tunable optical absorption and sharp emission linewidths making them attractive for applications in thin-film PV, display, lasing, photodetector and transistor applications. This section covers the chemical synthesis of these exciting materials, reviews some key efforts pertaining to their surface passivation and gives a basic introduction to charge transport through solids made out of them.

2.1.1 Synthesis

The earliest studies on CQDs date back to the 1980s when Graetzel and Brus independently reported cadmium sulfide (CdS) CQD synthesis. This was followed by the
demonstration of monomer passivation of CQD surfaces. These CQDs were capped with phenyl ligands and were soluble in pyridine.\textsuperscript{[34]} Annealing in alkylphosphine oxide solvents was found to enhance the crystallinity of the CQD cores.\textsuperscript{[35]} These early efforts culminated in the birth of nanochemistry.

In 1993, Murray published a groundbreaking paper describing the synthesis of CdE (E = S, Se, Te) CQDs from organometallic precursors.\textsuperscript{[36]} This work provided a standard protocol to CQD synthesis and opened the door to application-based nanochemistry. The so-called ‘hot-injection’ method, relies on a rapid injection of organometallic precursors into a high boiling point surfactant maintained at an elevated temperature (Figure 2.1a, b). Hot-injection leads to a rapid nucleation followed by a slow growth of the CQDs. The idea behind rapid injection is to segregate the steps of nucleation and growth in order to avoid Ostwald ripening that is known to cause defocusing/polydispersity of the CQD size. This work built on the theoretical work published in 1950 on sulfur crystals by LaMer and Dinegar which can be linked to the thermodynamic foundations laid by Ostwald.\textsuperscript{[37-39]}

Building on the advantages associated with alkanephosphine oxide solvents demonstrated earlier, Murray employed the high boiling point solvent trioctylphosphine oxide (TOPO). The precursors dimethyl cadmium (CdMe\textsubscript{2}) and elemental selenium (Se) in trioctylphosphine (TOP) were rapidly injected into the solvent TOPO maintained at 300 °C. The injection led to the nucleation of CdSe CQDs accompanied by a temperature drop to 170 °C. The fall of temperature quenched any further nucleation and the remaining precursors in the solution led to a slow growth of the CdSe nuclei at an elevated but \textless 300°C temperature. Solution temperature was found to dictate the CQD size with higher temperatures leading to larger particles. Growth is retarded due to steric hindrance effects
of the TOPO molecules that attach to the Cd sites on the CQD surfaces via dative bonding. The slow growth, *per se*, mediated defects and annealed the CdSe cores leading to increased crystallinity. It was also observed that employing shorter alkanephosphine oxides, such as tributylphosphine oxide, as the coordinating solvent led to faster, uncontrolled growth at elevated temperatures. Addition of a non-solvent led to crashing and separation of the particles. This is usually followed by redispersing them into an organic solvent to yield a stable colloid.

The success of hot-injection method lies in the high size-monodispersity (5-10%) of the final product. This was effectively implemented for PbS CQD synthesis in 2003.\textsuperscript{[40]} Trimethylsilyl sulfide (TMS) in octadecene was injected into a vigorously stirring solution of lead oleate maintained at 150 °C. OA-PbS CQDs were precipitated by addition of a non-solvent and finally redispersed in an organic solvent such as chloroform or toluene. It is interesting to note that although, in general, OA binds via the carboxylic group, in some cases it can also coordinate via the double bond in its alkyl chain thereby rendering the particles soluble in polar solvents.\textsuperscript{[41]} This makes OA a highly versatile capping agent.
Figure 2.1. (a) Schematic representation of the hot-injection method.\textsuperscript{[42]} (b) The reaction proceeds with a nucleation burst followed by a slow growth.\textsuperscript{[43]} (c) Optical absorption spectra obtained at room temperature for CdSe CQDs in hexane with diameters ranging from 1.2 to 11.5 nm synthesized by the hot-injection method.\textsuperscript{[36]} (d) TEM images of PbTe and PbSe CQDs synthesized in various sizes.\textsuperscript{[44]} (i), (ii) 9.0 nm PbTe CQDs, (iii) 14.3 nm
cube-like PbTe CQDs, (iv) 15 nm cubic-sized PbSe CQDs, (v) as-synthesized PbSe CQDs with a wide size distribution, and (vi) PbSe cubes 27 nm in size. Size changes are associated with changes in morphology. However, since the hot-injection method relies on expensive and toxic organometallic precursors, there has been research motivation in utilizing more stable metal precursors as a cost-effective route.\[45-46\] This simplified, alternative non-hot-injection method allows for lower temperature synthesis of CQDs without compromising on the physical and chemical properties of the final product.\[47\] Flow reactor synthesis of PbS CQDs has recently been demonstrated with the advantage of being a large-scale synthesis.\[48\] The study reported a high quantum yield (QY) and monodispersity.\[48\]

2.1.2 Size-tunable band gaps
Lead chalcogenide CQDs have high dielectric constants which allow efficient screening of charge carriers resulting in efficient delocalization of carrier wavefunctions and hence high mobilities. High dielectric constants also result in large Bohr radii of photo-generated excitons in these materials (18 nm for PbS).\[49-51\] CQDs with diameters comparable to or smaller than the exciton radius harbor unique optical and electronic properties owing to quantum size confinement effects. Figure 2.2a shows the effect of size reduction on the 1\textsuperscript{st} exciton of PbSe CQDs. The band gap of these CQDs, and hence the absorption can be tuned simply by changing their size (Figure 2.2b, c). Thus, whereas bulk PbS exhibits a band gap of 0.37 eV, PbS CQDs of diameters ~3.5 nm show a gap of ~1.3 eV. Coupled with strong absorption, band gap tunability makes CQDs attractive for solar cell applications, as they allow for more efficient harvest of the solar spectrum compared to conventional solar modules which are limited by single band gap absorption (1.1 eV for Si).
Figure 2.2. Quantum size effect. (a) Schematic demonstrating increase in quantum confinement with decreasing size of PbSe CQDs.\cite{52} (b) Variation of the band gap of PbSe CQDs as a function of their size.\cite{52} (c) Absorbance spectra showing excitonic maxima of PbS CQDs with sizes ranging from 3 to 10 nm. Spectra are found to red-shift with increasing size.\cite{53}

2.1.3 Ligand exchange strategies

The ligand molecules serve three crucial purposes: (i). slowing the growth leading to enhanced crystallinity; (ii). sterically stabilizing the cores thereby effectively avoiding aggregation; and (iii). passivating the surface of the CQDs.\cite{54} However, these long-chain surfactant molecules make the CQDs highly insulating. Therefore, in order to utilize the CQDs for the various applications they are attractive for, such as biosensing, light emission, optoelectronics, lasing, etc., these initial organic surfactants have to be exchanged with another set of molecules or atoms to appropriately tailor the properties of the CQDs.
Consequently, a post-synthesis ligand exchange is required to bring the CQDs closer with enhanced electronic coupling and allow thin films that can efficiently transport charges. Introduction of short conducting ligands between semiconducting CQDs was shown to increase the carrier mobility by several orders of magnitude.\textsuperscript{[55]} Talapin et al. reported high electron and hole field-effect mobilities (0.9 and 0.2 cm\(^2\)V\(^{-1}\)s\(^{-1}\) respectively) of initially poorly conducting films of PbSe NCs upon chemical treatment with hydrazine.\textsuperscript{[56]} The ligand exchange protocols employed can be broadly categorized into two types: solid-state ligand exchange and solution-phase ligand exchange.\textsuperscript{[57]}

**Solid-state ligand exchange:**
One of the first demonstrations of solid-state exchange dates back to 2003 by Guyot-Sionnest and involved TOPO-CdSe CQDs. The bulky organic ligands were replaced by dithiols and diamines enhancing charge transport.\textsuperscript{[58]} The successful demonstration of a solution-processed PbS CQD based solar cell by Sargent in 2005 spurred interest in the materials science community.\textsuperscript{[24]} It was realized that for charge transport to be efficient, uniformity of the active layers needed to be ensured. Spin-coating, a coating technique known to yield highly uniform layers, was implemented and accepted as the standard method for casting CQD absorber layers. Replacing bulky, organic ligands with shorter ones, however, involves significant volume loss and leads to unwanted cracks and pinholes in the film (Figure 2.3a, b)\textsuperscript{[59]}
Figure 2.3. Optical images of spin-coated (a) OA-PbSe CQD film and (b) the same film after EDT ligand exchange. Massive crack can be seen owing to the volume contraction upon exchange. (c) SEM image of an LbL film formed via dip-coating shows a smooth surface.\textsuperscript{[59]} (d) TEM images showing reduction in inter-dot distance when OA-PbSe CQD solids are dipped in solutions of shorter ligands (aniline and ethylenediamine).\textsuperscript{[60]} (e) Reduced inter-dot distance is suggestive of CQDs coming closer leading to enhanced coupling and therefore, a conductive solid.\textsuperscript{[52]}
A way around was suggested by Luther et al. in the form of LbL solid-state exchange, in which several layers of exchanged CQDs were deposited, one-after-the-other, leading to a crack-free, thick conductive solid (Figure 2.3c).\textsuperscript{[59]} Conductive PbSe NC thin films made by LbL dip coating and subsequent solid-state ligand exchange were obtained using 1,2-ethanedithiol (EDT) as the surface passivant, thereby effectively reducing the inter-dot distance and enhancing carrier transport.\textsuperscript{[59]} This important work demonstrated LbL as a general method for fabricating CQD solids for solar cell applications.

Figure 2.3d shows a series of TEM images wherein solid-state exchange was performed on an OA-PbSe CQD solid.\textsuperscript{[60]} The inter-dot distance decreased from 1.8 nm for OA ligands to 0.8 nm for aniline-capping. This further reduced to < 0.4 nm for the case of ethylenediamine ligands. Reduced inter-dot distance leads to enhanced electronic coupling between adjacent CQDs resulting in better charge transport, as illustrated in Figure 2.3e.
Figure 2.4. Solid-state ligand exchange. Schematic demonstrates the various steps involved in this exchange process. (I) The longer surfactant-capped CQDs (in this case, OA) are cast into a thin solid film. (II) The film is then dipped for a short duration in the solution of a shorter ligand (thiol, halide, amine, etc.). The treatment leads to replacement of the longer ligands with the shorter ones (shown here with green dots capping the CQD surfaces). (III) The exchanged thin film is rinsed with a process solvent to remove any traces of the clipped ligands. This process can be repeated several times to build the thickness of an electronically coupled CQD active layer for solar cell applications.

The solid-state ligand exchange process involves the repetitive deposition of the insulating ligand-capped CQD film via spin coating followed by dipping in the new, shorter ligand solution, as shown in Figure 2.4. The dipping step replaces the insulating ligand (for example, OA) with the shorter ligands. At the start of this PhD, thiols (3-mercaptopropionic acid, MPA), delivered in methanol (MeOH) solvent, were typically employed as the standard shorter ligand in CQD solar cells. This process is repeated several times, in an LbL fashion, until the desired film thickness is achieved.\textsuperscript{[59, 61]} The sudden volume contraction of the film accompanying ligand exchange is expected to lead to voids and cracks which might act as charge traps. The LbL buildup employed in CQD solar cells mediates this demerit by infiltrating the CQDs into the cracks leading to an overall uniform, smooth and dense film essential for strong light absorption and efficient charge transport.
**Solution-phase ligand exchange:**

SolEx involves the replacement of the initial surfactants with new conductive ligands in solution phase. A highly efficient exchange process has been demonstrated recently that involves replacing the long-chain insulating hydrocarbon ligands with inorganic molecular metal chalcogenides (MCC) yielding field-effect electron mobilities (FET) as high as 38 cm$^2$ V$^{-1}$ s$^{-1}$.[62-64] These demonstrations illustrate the remarkable capability of SolEx to passivate surface traps and electronically couple CQDs.

The first attempts at employing solution-phase exchange for PV applications goes back to 2005 when Gur *et al.* used pyridine molecules to replace the OA ligands on rod-shaped CdSe and CdTe CQDs. These exchanged CQDs were used as absorber layers of Schottky solar cells reaching 3.0% PCEs.[65] In the context of PbS CQDs, one of the first demonstrations of the solution-phase exchange came in the form of a 1.8% PCE Schottky solar cell that employed n-butylamine (BTA) ligand to replace the OA capping layer in solution phase.[66]

The previous attempts (noted above) employed more than one layer to achieve the desired absorber thickness. However, the virtue of SolEx lies in the possibility of a single-step deposited absorber layer that can do away with the menial LbL protocol. The first such attempt involved replacing the initial OA ligands with shorter, conducting thioglycerol (TG) molecules in solution phase (Figure 2.5a).[67] The exchanged CQDs were re-dispersed in a polar solvent, dimethyl sulfoxide (DMSO) and were drop-cast to make the absorber layer. Drop-casting was necessary since DMSO is a high boiling point solvent (189 °C) and therefore the film formation requires a longer time (ca. 5 hours). The CQDs, however, suffered from poor surface coverage leading to low PCEs (ca. 2%). Also, charge
transport was found to be limited by the morphological inhomogeneity of the film, including pinhole formation in the drop-cast film, which was reflected by the low fill factor (FF) of 35%. The procedure nonetheless opened routes towards achieving directly-deposited conductive active layers of PbS CQDs in a single-step, avoiding the rigor and materials wastage involved in the standard solid-state ligand exchange process.\cite{61,67}

**Figure 2.5.** Solution-phase ligand exchange. (a) OA-PbS CQDs in octane (left) are mixed in solution-phase with TG. The CQDs become soluble in a polar solvent such as DMSO following the exchange (right).\cite{67} (b) The latest SolEx recipes involve exchanging OA ligands with metal halides, pseudohalides, and hybrid perovskite. The resulting exchanged CQDs are re-dispersed in BTA solvent.\cite{13,29}

Recently, metal halides and hybrid perovskites have been explored as the shorter ligands in the latest brand of solution-exchanged CQD inks.\cite{13,29-30,68-72} Halide-, pseudohalide- and halometallate-capped CQD inks with excellent optical and electronic properties were obtained ushering in a new class of robust inks that could be deposited, in a single-step, as active layers for solar cells.\cite{30,69-70} In one such report, iodide-capped CdSe CQD films were found to have mobilities as high as 12 cm$^2$ V$^{-1}$s$^{-1}$ (**Figure 2.6**).\cite{69}
Figure 2.6. Halide-, pseudohalide- and halometallate-capped CQDs obtained via solution-exchange exhibiting excellent charge transport properties. The exchanged CQDs are soluble in N-methylformamide (NMF).[69] The first fruit from these robust, solution-exchanged CQD inks in the context of a PV device came in 2014 when Ning et al. demonstrated a solar cell featuring a single-step deposited CQD active layer.[71] The CQDs were capped with iodide ligands obtained via solution-exchange. The solar cell exhibited a PCE of ca. 6%, an encouraging device performance given that no solid-state LbL treatment was needed. The steps involved in the exchange process and film fabrication are shown in Figure 2.7a. A solution of methylammonium iodide (MAI) precursor in dimethylformamide (DMF) was mixed with an octane-based colloid of OA-PbS CQDs. Vigorous mixing of the two phases led to ligand exchange in the solution phase observed as a phase separation, similar to the scenario shown in Figure 2.5b. These exchanged CQDs were then separated, centrifuged and re-dispersed in BTA. The advantage of using the lower boiling point solvent BTA (77-79 °C), as compared to the previous attempt which employed DMSO, is that it enables a faster solidification of the CQD film, thereby allowing to move away from drop-casting. The BTA-based CQD ink is spin-coated to form a single-step deposited, uniform and
continuous active layer. The final film is mildly annealed to remove the organic methylammonium countercations, leaving behind a completely inorganic CQD solid.

This demonstration was followed by a report where the authors employed a mixture of MAI and lead iodide (PbI$_2$) as precursors in the solution-exchange step.$^{[29]}$ This resulted in replacement of the OA ligands and formation of methylammonium lead triiodide (MAPbI$_3$), a hybrid perovskite, on the surface of the CQDs, upon mild annealing (Figure 2.7b). These perovskite-shelled CQD solar cells exhibited high PCEs approaching 9%, which was remarkable for a single-step deposited device.

A novel precursor mixture was recently reported wherein the authors aimed to maximize the halide ligand coverage of the CQD surfaces (Figure 2.7c).$^{[13]}$ PbX$_2$ (X = I and Br) and ammonium acetate (AA) in DMF was used as the precursor solution. AA was found to facilitate the exchange process and was removed from the final CQD solid during precipitation. As a result of the high halide surface coverage, these CQD solids featured significantly suppressed band tails leading to massive gains in overall device performances, compared to all the previous SolEx-based CQD solar cells. With PCEs as high as 11.3%, this recipe, for the first time, also outperformed solid-state LbL-deposited CQD solar cells.
Figure 2.7. Latest SolEx approaches for PV absorbers. (a) Iodide-capped CQDs obtained using MAI as the precursor,\textsuperscript{[71]} (b) Perovskite-shelling of CQDs,\textsuperscript{[29]} and (c) PbX$_2$-CQDs employing ammonium acetate as a colloidal stabilizer.\textsuperscript{[13]} These latest solar cell breakthroughs suggest halide-ligands to be unique surface passivants. This aspect can be explained from a fundamental level, in view of recent insights gleaned from inelastic neutron scattering and \textit{ab initio} molecular dynamics simulations highlighting the role of CQD surfaces.\textsuperscript{[73]} Wood and co-workers have demonstrated that phonon modes on mechanically ‘soft’ CQD surfaces effectively couple with electronic transitions leading to carrier trapping. This study highlights the necessity of resorting to surface ligands that exhibit low vibrational modes, such as halides. Halide surface passivation results in ‘hard’ CQD surfaces, suppressing the electron-phonon coupling and leading to reduced carrier recombination.\textsuperscript{[74]}
**Atomic-ligand and Hybrid passivation:**
A few other surface passivation schemes that were met with immediate success a few years back are worth mentioning. Although all of these have now been outperformed by the novel, halide-based SolEx schemes (discussed above), it is important to briefly discuss them here. These schemes employed a combination of an initial solution-phase and a solid-state exchange, and at the time, led to high performing solar cells. These attempts (Figure 2.8) highlighted the importance of halide passivation and, therefore, guided the community towards the now-established halide-SolEx.

One of these schemes, the ‘atomic-ligand passivation’, employed an initial solution-phase step where the OA-PbS CQDs were first treated with a mixture of CdCl$_2$, tetradecylphosphonic acid (TDPA), and oleylamine (OLA). The resulting cadmium–tetradecylphosphonic acid (Cd–TDPA) complex passivated the surface dangling bonds that were, otherwise, left unsatisfied by the remaining OA ligands on the surface. The CQD solid obtained from this ink was then made to undergo a solid-state exchange with cetyltrimethylammonium bromide (CTAB) dissolved in MeOH. This second step ensured that the final solid was left with purely inorganic atomic passivants on the CQD surfaces, resulting in LbL-deposited devices with PCEs of ca. 6%, a CQD PV record at that time.

Another similar scheme developed n-type PbS CQDs by, first partially exchanging a few of the surface OA ligands with iodide atomic ligands. Tetrabutylammonium iodide (TBAI) precursor was employed. This was then followed by a solid-state exchange with TBAI solution in MeOH. This ‘sol-hal’ approach resulted in an n-type CQD solid which was exploited in a quantum junction CQD solar cell (p-n homojunction architecture; to be
discussed in detail later) with a PCE of 6.6%, besides the demonstration of a record electron FET mobility at the time (for a CQD solid with a band gap > 1.2 eV) of 0.24 cm²V⁻¹s⁻¹.

**Figure 2.8.** Schematics summarizing ligand exchange strategies that involved an initial solution-phase treatment followed by a solid-state exchange step. (a) Atomic ligand passivation scheme involving the removal of OA with Br atoms. Cetyltrimethylammonium bromide (CTAB) is used to carry the Br atoms to the surface. A solution-phase treatment of the OA-PbS CQDs with a mixture of CdCl₂, TDPA, and OLA aimed at passivating the surface dangling bonds precedes the solid-state exchange.¹¹ (b) The sol-hal approach involves an initial solution-phase halide passivation that removes some of the weakly bound OA and replaces them with halogen atoms. Iodine is delivered via TBAI salt dissolved in MeOH.⁷² This is followed by a TBAI-based solid-state exchange, resulting in an n-type CQD solid (c) Schematic explaining the concept of hybrid passivation. Solid-state exchange with organic ligands (MPA) leads to empty trenches on the CQD surface owing to steric interaction between the organic molecules (left). These un-passivated trenches can behave as carrier traps. An initial solution-phase treatment employing atomic passivants (for example, halides) can avoid this scenario (right).¹² (d) This strategy involves a solution-phase ligand exchange step in which chlorothiols and
CdCl$_2$ are introduced to the CQD surface. This is followed by the usual solid-state exchange with MPA.$^{[75]}$

In 2012, Ip and Thon showed that a ligand exchange strategy designed to deliver inorganic ligands in solution-phase and organic thiol molecules in solid-state can lead to maximum trap passivation and closest packing of the CQD solids.$^{[12]}$ This strategy, called the hybrid ligand exchange, translated into high performing solar cells with a certified PCE of 7%, a CQD PV record back then. The strategy involved supplying cadmium chloride (CdCl$_2$) to the as-synthesized OA-PbS CQDs in solution phase. Binding of the metal cations as well as the halide atoms to the surface atoms was confirmed spectroscopically. The halides and cations tied to the surface sites that are otherwise not easily accessible due to steric hindrance of the bulky OA molecules. These pre-treated CQDs were then subjected to a solid-state exchange with MPA, leading to efficiently coupled photovoltaic solids. The hybrid passivated CQD solids exhibited significantly suppressed trap states owing to enhanced surface passivation, as proved by ultra-violet and inverse photoemission spectroscopies that allow direct measurements of the band tail states.$^{[76]}$

Nonetheless, it is highly likely that the harsh and rough nature of the solid-state exchange step might leach-off some of the surface passivation imparted to the CQDs during the solution-exchange step, resulting in trap formation. To overcome this, a modification to the hybrid passivation scheme was developed with introduction of chlorothiols along with CdCl$_2$ in the solution-exchange step.$^{[75]}$ The strongly binding thiols remain attached to the CQD surface during the harsh solid-state exchange step resulting in better-than-ever surface passivation. This resulted in enhanced carrier diffusion lengths driven by a suppression of recombination centers leading to PCEs of 8.5%.
2.1.4 Ligands as remote dopants

Besides enhancing electronic coupling between CQDs, ligands can also be used to remotely tune the CQD carrier concentration by acting as remote dopants. Doping of the CQD solid allows for tailoring the film conductivity by changing the carrier concentration and is attractive for numerous applications, such as, photodetectors, solar cells and transistors. Significant effort has, therefore, focused on realizing doping of CQDs. Initial attempts which involved mixing of dopants with the CQD precursors in solution phase during synthesis were less successful. However, the striking observation, by Guyot-Sionnest and co-workers that sodium biphenyl leads to 1S-1P_intraband absorption in CdSe CQDs via remote charge-transfer opened doors to realizing successful doping schemes in CQDs. Significant increase in film conductivity was observed for CdSe CQDs when potassium was used as the dopant. Impressive enhancements in mobilities of PbSe CQD solids were found upon hydrazine treatment suggestive of charge transfer.

Substitutional doping, which requires the dopant to replace an atom from the CQD, forms the second important category of doping in CQDs. A charge–orbital balance picture has been suggested to predict the doping phenomenon in CQDs based on the overall stoichiometry. In this picture, the nature of doping (n- or p-type) can be determined simply by calculating the total number of excess electrons available to the PbS CQD. For the case of iodide ligands (Figure 2.9a (iii), (iv)), remote charge transfer results into an extra hole and, therefore, p-dopes the solid. Substitution of a sulfur atom with an iodide, on the other hand, results into an extra electron, thereby, n-doping the solid. Given the vast library of available ligands, the carrier...
concentration and doping of CQDs can be tuned over a large window, as shown in Figure 2.9b.

High carrier mobilities have been achieved for PbS CQDs capped with iodide ligands.\textsuperscript{[72, 91-93]} Employing iodide ligands, n-type PbS CQDs were realized leading to high efficiency quantum junction and inverted solar cells.\textsuperscript{[94-95]} Konstantatos group has demonstrated remote trap passivation by employing ZnO nanocrystals which were shown to remotely transfer electrons into the in-gap states of PbS CQDs leading to suppression of trap-assisted carrier recombination.\textsuperscript{[96]}

**Figure 2.9.** (a) Remote doping by the ligands can be explained from the alignment of energy levels at the interface of the CQD and the ligand. A molecule (potassium) with a shallow HOMO level (lying above the conduction band minima (CBM) of the CQD) will behave as a donor, leading to n-doping (i). On the other hand, a molecule (iodide) with HOMO deeper than the valence band maxima (VBM) of the CQD will result in p-doping (ii). (iii) and (iv) represent remote and substitutional doping scenarios by iodide ligands, respectively. The type of doping can be discerned simply by counting the total number of
excess electrons in the system for each case.\textsuperscript{[91]} (b) Effect of various ligand treatments on the doping density of PbS CQDs obtained from FET measurements.\textsuperscript{[91]}

It can be readily seen, from the above discussion, that the secondary function of ligands as remote and substitutional dopants has significantly helped CQD PV. Employing ligands for doping, nonetheless, involves modification of the CQD surfaces. To further enhance the doping level and carrier concentration of the CQD solids, a facile method is needed that is not limited by the lack of binding sites (surface coverage) on the ligand-passivated CQD surfaces. Electrochemical doping is an interesting avenue, however, it is not compatible with practical applications since it necessitates an externally applied bias.\textsuperscript{[97-98]} During this PhD, there were encouraging demonstrations of using molecules of cobaltocene, decamethylferrocene and decamethylferrocenium as remote dopants for EDT-PbSe and PbS CQD solids,\textsuperscript{[99-100]} however, the field lacked any demonstration of molecular remote doping directly leading to solar cell applications.

\textbf{2.1.5 Charge Transport in CQD Solids}

Ligand exchange effectively brings the CQDs in closer proximity leading to an increased overlap and coupling of the electron and hole wavefunctions. This results in enhanced charge transport in the CQD solid. However, this comes at the cost of an increased disorder in the film and also leads to a certain degree of CQD agglomeration. The exchange process destroys any signs of mesoscopic order that might have existed prior to the removal of the bulky ligands.\textsuperscript{[101]} Yet, the best performing CQD solar cells, to date, involve ligand exchanged CQD films having negligible signs of order and low mobilities ($10^{-2}$ to $10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$). The role of order and mobility in charge transport and hence the device performance has been a topic of debate. Also, despite the best efforts, band-like transport has largely not been observed with the carriers relying on hopping for transport suggesting
that the CQD films behave as semiconductors despite the enhanced overlap of carrier wavefunctions.\textsuperscript{102} Interplay of three energy terms dictates the nature of charge transport in a CQD film; these are: coupling energy ($\beta$), charging energy ($E_c$) and disorder-in-site energy ($\Delta\alpha$).\textsuperscript{103}

\textbf{Coupling energy ($\beta$):}
Coupling energy is related to the transmission probability between the electronic states of adjacent CQDs and therefore directly depends on the potential barrier and the inter-dot spacing. A high coupling energy enhances transport. It is related to the tunneling rate ($\Gamma$) between two neighboring orbitals, $\beta = h\Gamma$, h being the Planck’s constant. Approximately, $\Gamma = \exp(-2(2m^*\Delta E/h^2)^{1/2}\Delta x)$, where $m^*$ is the electron effective mass, $\Delta E$ and $\Delta x$ are the tunneling barrier height and inter-dot distance, respectively.\textsuperscript{102-103} $\Delta E$ and $\Delta x$ can be reduced via the choice of proper ligand thereby increasing the coupling energy. In accordance with the given relation for transmission rate, carrier mobility has been found to decrease exponentially with ligand length.\textsuperscript{57, 104-105} Furthermore, the strength of $\beta$ as compared to the thermal energy $k_B T$ at room temperature (T) gives rise to two charge transport regimes.\textsuperscript{54} $\beta \ll k_B T$ leads to a weak coupling between the CQDs with electron transport occurring via sequential tunneling between the neighboring CQDs. Strong coupling regime exists if $\beta \geq k_B T$. In this regime, strong overlap of individual wavefunctions leads to existence of delocalized states. Unfortunately, however, strong coupling regime exists only at very low temperatures and for solar cell related situations a PbS CQD solid exists as a weakly coupled system.
Charging Energy ($E_c$):
Charging energy is the energy required to transfer an electron from a CQD to another. This also involves the electron-electron repulsions. A lower charging energy is desired. The condition $\beta > E_c$ defines the Mott metal-insulator transition and wavefunction delocalization leads to metallic behavior. It should however be noted that strong electron-electron repulsions lead to a high value of $E_c$ in PbS CQD films.

Disorder-in-site energy ($\Delta \alpha$):
A significant source of the disorder-in-site energy is the finite polydispersity of the CQD systems. This leads to broadening of the orbital energies. Due to this, efficient electron transfer between CQDs via resonant tunneling becomes improbable and rather becomes phonon-assisted. Another reason behind the disorder-in-site energy is the lack of mesoscopic order. This leads to variable inter-dot spacing across the film. Further, a red-shift in the excitonic peak is observed following ligand exchange which is usually associated with an enhanced electronic coupling.\textsuperscript{[106-108]}. However, the energy scale of such an electronic coupling energy is not large enough to explain the magnitude of the red-shift. The excitonic shift has therefore been associated to agglomeration arising as a fallout of the exchange process.\textsuperscript{[102]} These sources make the disorder in the current CQD systems very high. A comparison of $\beta$ and $\Delta \alpha$ defines another metal-insulator transition; the Anderson localization. If $\beta < \Delta \alpha$, which is the case for CQD active layers, the film will suffer from low mobility and poor transport.
Figure 2.10. (a) A phase diagram demonstrating the various coupling regimes for a CQD system. Interestingly, the metal-insulator transitions can be observed only when the disorder is small. For very large disorder, the carrier wavefunctions become localized on individual CQDs independent of the coupling strength.\textsuperscript{[109]} (b) Theoretically obtained $V_{OC}$ is shown for a solar cell at room temperature assuming 100% absorption above the band gap. Exponentially decaying absorption tails of decay constants 0 meV, 30 meV and 50 meV (inset) are considered. $V_{OC}$ is found to drop significantly as a function of the decay constant.\textsuperscript{[102]}

It is clear from the above discussion that for the current CQD solids charge transport occurs via carrier-hopping. This leads to mobilities in the range of $10^{-2}$ to $10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$. It has been suggested that any further improvement in the mobilities will not benefit CQD solar cell performance as the transport is limited by recombination centers.\textsuperscript{[102]} In other words, increasing the carrier mobilities will result in increased recombinations. This explains why better surface passivation strategies in CQD PV have recently led to high performances even though the mobilities have been limited to $\sim 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$.

Disorder leads to tail states below the absorption edge,\textsuperscript{[102]} which are found to be highly detrimental to open-circuit voltage ($V_{OC}$) of the solar cells. As an example, an exponential tail with a decay constant of 50 meV has been theoretically suggested to lead to a $V_{OC}$ that is half the band-gap of the CQDs (Figure 2.10b). For the standard CQD solar cells, $V_{OC}$’s are, in fact, found to be around 50% of the band gap.\textsuperscript{[51, 110]}
2.2 Colloidal quantum dot solar cells

Thermalization of hot carriers to band edges accounts for 33% loss for a single-junction 1.1 eV band gap solar cell (Figure 2.11). Besides, the band gap sets a lower limit on the wavelengths that can be absorbed by the PV device. Subtracting the losses incurred due to extraction of charges leaves 33% of the available solar power that can be harnessed by the solar cell, a number also called the Shockley-Queisser (SQ) limit.[22] CQD solar cells, however, are capable of breaching the SQ limit thanks to their exotic properties. The MEG process has been established in CQDs.[21] Besides, it is possible to absorb the below-gap IR photons that are otherwise wasted, by engineering intermediate bands in CQDs.[111] These possibilities render CQD PV as one of the most promising thin film PV technologies and have been the guiding force behind the intense research in this area over the past decade.

**Figure 2.11.** Losses experienced by a 1.1 eV band gap solar cell. Considering these loss mechanisms, Shockley-Queisser (SQ) analysis puts the maximum achievable PCE by this device at 33%. [52]
Before discussing the various CQD solar cell architectures, we will briefly cover the fundamental concepts in PV.

2.2.1 Fundamental concepts

Figure 12a shows typical dark and light $J$-$V$ curves of a solar cell. Maximum power point (MPP) is the point on the $J$-$V$ curve ($V_{\text{max}}$, $J_{\text{max}}$) corresponding to maximum power output (grey shaded area). This determines the fill-factor (FF) of the solar cell. The short-circuit current, $J_{\text{SC}}$, is the maximum current density that can be obtained from the device. $V_{\text{OC}}$ is the maximum voltage that can be generated and corresponds to the difference between the quasi-Fermi levels, $F_n$ of electrons on the n-side, and $F_p$ of holes on the p-type side of the junction. The power conversion efficiency, PCE, of the solar cell for an incident light intensity $P_{\text{inc}}$ is given as:

$$PCE = \frac{V_{\text{max}} J_{\text{max}}}{P_{\text{inc}}} = \frac{V_{\text{OC}} J_{\text{SC}} FF}{P_{\text{inc}}}$$  \hspace{1cm} (1)

Figure 2.12. (a) Dark and light $J$-$V$ curves of a solar cell.$^{[112]}$ (b) A p-n junction showing photon absorption and subsequent generation of excitons.$^{[112]}$
Excitons (electron-hole pairs) are produced upon photon absorption. Unlike the case of organic solar cells, CQDs have a high free career density. This leads to formation of a depleted junction at the interface of the p-type CQD layer and the n-type metal oxide layer (Figure 2.12b). The excitons, exhibiting a small binding energy, are split by the in-built field and the carriers (electrons and holes) drift towards their respective extraction electrodes. Beyond the drift-driven regions on either side of the junction ($x_{p0}$ and $x_{n0}$), the carriers have to diffuse to reach the electrodes for subsequent extraction. Large diffusion lengths are therefore preferred in CQD solids. Since band-bending at the MPP is reduced (and therefore the drift-driven regions), this requirement for diffusion lengths becomes more important.

$$x_{p0} = \frac{W}{1 + N_A / N_D}, \quad x_{n0} = \frac{W}{1 + N_D / N_A}$$

(2)

As can be seen from these relations, a highly-doped n-region (large $N_D$) will maximize depletion of the p-region. This concept is employed in the depleted heterojunction architecture of CQD PV, as will be seen in the next section.
2.2.2 CQD PV efficiency chart

PbS CQD PV efficiencies have risen dramatically over the last decade taking this technology to the top echelons of third generation solar cells. The PCE growth is summarized in Figure 2.13, and can be categorized into three main eras: Schottky architecture era (brown), depleted heterojunction (DHJ) architecture era (blue) and n-i-p architecture era (red).

![PbS CQD PV efficiency chart](image)

*Figure 2.13. PCEs for CQD PV over the years.* The PCE growth can be ascribed, largely, to the introduction of three main solar cell architectures over time, Schottky (brown), DHJ (blue) and n-i-p (red). These device engineering breakthroughs have been further augmented along the way with robust surface passivation recipes. * represents an unpublished result.

In each of these eras, modifications to ligand exchange, interface modifications and control over doping type and amplitude have kept pushing the PCEs up.

2.2.3 Device architectures

Below we summarize the major CQD solar cell architectures.

*Schottky architecture:*
Schottky solar cells employ a fairly simple architecture with a thin CQD absorber layer sandwiched between the bottom (a low-work function metal) and top Ohmic-contact transparent (ITO) electrodes (Figure 2.14a). The CQD absorber forms a Schottky contact with the metal electrode which effectively separates excitons photo-generated in the absorber. However, since the junction is formed at the backside (far-end) and transport in CQDs is limited owing to small minority carrier diffusion lengths, thickness of the absorber and hence absorption are limited. The design intrinsically leads to ineffective collection of charges generated at the back end of the cell. A second disadvantage of this architecture is the Fermi level pinning limiting the $V_{OC}$ which cannot exceed half the CQD band gap value. Schottky architecture was, in fact, the first to be studied. The first demonstration employed solid-state ligand exchange with EDT ligands and led to PCEs of 1.8%. \cite{2} Improvement was demonstrated when a combination of SolEx and solid-state exchange was employed. \cite{10} Solid-state exchange with 1,4-benzenedithiol (BDT) has recently taken these cells to 5.2%, \cite{4} however, the interest in Schottky architecture has waned since the advent of the better-performing DHJ and n-i-p architectures. The growth of CQD PV employing the Schottky architecture is represented by the brown line in Figure 2.13.

**Depleted heterojunction (DHJ) architecture:**
One of the first demonstrations of the DHJ architecture employed PbSe CQDs in contact with a ZnO layer and resulted in 1.6% PCE.\cite{113} This architecture was quickly taken up by the PbS CQD community,\cite{6,8} and was an immediate success resulting, simultaneously, in high $J_{SC}$ and $V_{OC}$ and therefore high PCEs. These solar cells carry the obvious distinction of a p-n heterojunction between the p-type CQD and the n-type large band gap metal oxide layers (Figure 2.14b). Importantly, the depleted heterojunction is situated closer to the
transparent front contact, overcoming the charge extraction bottleneck associated with the Schottky architecture, leading to high FFs in excess of 55%. Since the excitons generated at the back end had to rely on diffusion for extraction, robust passivation schemes were developed to suppress traps and enhance diffusion lengths in the solids. Atomic-ligand and hybrid passivation strategies made impacts and led to record PCEs at that time. These strategies employed a pre-treatment of SolEx passivation of CQDs, followed by a solid-state exchange of the films, to ensure better overall surface passivation.

Since the DHJ architecture had to rely on diffusion-limited charge transport beyond the depleted CQD solid, it was argued that enhancing the depletion region would benefit charge extraction, similar to the effect of increasing carrier diffusion lengths. This led to the concept of the ‘donor-supply electrode’. The electron accepting metal oxide was placed in contact with a shallow work function front electrode. This effectively enhanced the electron density in the oxide layer via charge-transfer doping. The n-type oxide with an increased free carrier density pushed forward the depletion region in the CQD solid, resulting in better charge collection. The concept led to 8.5% PCE DHJ solar cells, a record at that time. These devices employed the hybrid passivated CQDs.

The hybrid passivation scheme, as mentioned earlier, involved a CdCl₂ surface treatment of the CQDs in the solution-phase, besides the usual solid-state treatment (usually with MPA) of the solid. It was found that replacing CdCl₂ with amines in the SolEx induced partial fusion of the CQDs leading to self-passivation of the surfaces. This modified hybrid passivation approach, effectively, reduced the overall CQD surface area leading to significantly reduced surface traps.
Figure 2.14. *CQD PV solar cell architectures.* The three major classes of device architectures are shown, (a) Schottky,\textsuperscript{115} (b) DHJ,\textsuperscript{115} (c) quantum homojunction,\textsuperscript{95} (d) graded doped,\textsuperscript{116} (e) nano-heterojunction,\textsuperscript{117} (f) bulk nano-heterojunction\textsuperscript{118}
These robust CQDs featured record-high diffusion lengths in excess of 200 nm allowing fabrication of 600 nm thick absorber layers resulting in $J_{SC}$ as high as 29.5 mA cm$^{-2}$. This strategy took the DHJ solar cells to 9.2%.

An interesting modification of the DHJ architecture aimed at enhancing charge extraction from the absorber by employing nanostructured electron acceptors. The idea is similar to the scheme well-known in organic PV, and was called the depleted bulk-heterojunction (DBH) and aims to break the photon absorption-carrier extraction compromise in the DHJ solar cells (Figure 2.14b). Usually, nanopillars, nanowires or larger nanoparticles of the electron acceptor are employed into which CQDs are deposited.[119-121] This allows deposition of thicker PV solids and lends a three-dimensional spatial extent to the p-n junction, compromising for the short diffusion lengths of minority carriers in these solids. These have been interesting demonstrations, however, the PCEs have so far remained well below the best achievable by DHJ solar cells.

**Quantum homojunction:**
The slight offset between the bands of the electron acceptor and the CQD solid in the DHJs leads to an unfavorable ‘kink’ at the interfacial band structure, which either hurts the $V_{OC}$ or the $J_{SC}$, depending on its direction. This necessitates the concept of a homojunction which can guarantee a smooth band bending at the interface. This need fuelled the demonstration of the first quantum homojunction CQD solar cell.[95] It had an added advantage of photon absorption by both the n- and p-sides of the junction, thereby enhancing light harvest. The architecture is shown in Figure 2.14c and employs a thick n-type CQD solid atop a thin p-type CQD layer. A highest performing device of 5.4% PCE
was achieved. Importantly, this was one of the first demonstrations of a PV device employing n-type CQDs.

The n-type solids employed in this architecture had low doping. Increasing the doping of these layers can lead to a higher $V_{OC}$, however, will decrease the depletion region width. To solve this, a graded doping approach was developed (Figure 2.14d). A highly n-doped CQD solid was placed atop the n-type CQD layer aiding carrier extraction and also the overall $V_{OC}$. This adjustment led to a 7.4% PCE quantum junction solar cell.

**Nano-heterojunction:**
A device architecture very similar to the quantum junction, but employing two different categories of CQDs was reported with promising results. Importantly, this design employed non-toxic Bi$_2$S$_3$ CQDs as the n-type solid in contact with the p-type PbS CQDs. Figure 2.14e shows the schematic of the architecture. Red spheres represent PbS CQDs while blue spheres denote Bi$_2$S$_3$ CQDs. It was found that these devices benefited when the two types of CQDs were mixed together to yield the ‘bulk nano-heterjunction’. Impressive PCEs approaching 5% were demonstrated (Figure 2.14f).

**N-i-p architecture:**
In 2014, another important innovation in the young history of CQD PV with far-reaching consequences was demonstrated. Researchers noticed that it was possible to affect energy level shifts in the CQD band structures by varying the surface ligands (Figure 2.15a). Whereas halide ligands were found to push the band structures deep (large electron affinities), thiols would render the CQD band structures shallow (small electron affinities). It was suggested that the overall changes to the band structures were due to a combination of the CQD-ligand interface dipole and the interface dipole moment of the ligand.
Figure 2.15. The n-i-p architecture thrives on the concept of ligand engineering of CQD band structures. Photoemission spectroscopy was employed to track the changes to the vacuum level for a variety of ligands. Employing this information, suitably chosen ligands were employed to form the n-i-p architecture.[3]

This information led to the development of a novel device architecture wherein a thin film of EDT-PbS CQDs with a shallow CBM was placed atop the absorber layer (Figure 2.15b, c).[3] This additional layer prohibited backflow of photo-generated electrons into the hole-collecting electrode while aiding hole-extraction, thereby behaving as a HTL. It is important to mention that TBAI-PbS CQD solids were earlier used as absorbers, however, employing an EDT-PbS CQD HTL helped increase the PCEs significantly, besides enhancing air stability.
This new device architecture has opened routes to further improvements and catalyzed the steep growth in CQD PV over the past couple of years, as Figure 2.13 suggests. Soon after this demonstration, a CQD absorber exchanged with a combination of SolEx and solid-state exchange with halide ligands (iodide) led to 10.2% PCEs, benefiting from enhanced passivation.\cite{123} This was followed by a vacuum level modulation of the electron transporter by self-assembled monolayers resulting in a high $V_{OC}$ of 0.66 V with PCEs reaching 10.7%.\cite{9} Modification of the electron transporter with EDT has also been recently reported.\cite{124}

Recently, SolEx has been utilized to yield single-step deposited CQD absorbers, taking the CQD PV technology a step closer to scalable fabrication. These solar cells have also employed a top EDT-PbS CQD HTL in an n-i-p configuration. Hybrid perovskites and lead halide ligands have been used to cap the CQD surfaces in solution-phase resulting in highly efficient CQD inks which have led to the realization of 11.3% PCE solar cells.\cite{13, 29-30} Importantly, these solar cells do not require LbL build-up of the absorber layer. A modification of this recipe has, of late, further increased the PCEs to a record-high of 12.5% (unpublished results). To achieve this, a PbI$_2$-amine coordinating matrix was engineered that effectively enhanced the carrier diffusion length, besides suppressing surface traps. This allowed effectively extracting charges from thicker active layers, leading to a $J_{SC}$ as high as 32 mA cm$^{-2}$.

The n-i-p architecture has also been found to benefit tandem solar cells fabricated from CQDs.\cite{125} Two subcells of equally-sized CQDs featuring TBAI-CQDs as the absorber and EDT-CQDs as the HTL were connected via an ultrathin Au layer which acted as the
inorganic recombination layer. The overall device performance of the tandem device approached 9.0% which is almost twice the previous best all-CQD tandem solar cell.[126]

2.3 Surface trap mitigation and process scalability

Introduction of the hot-injection method made possible the synthesis of a variety of CQDs. Successful demonstration of PbS CQD synthesis paved the way for them to be used as absorber layers in solar cells. Over the years, CQD PV has advanced driven by parallel developments in surface passivation and device architectures leading to efficient surface trap suppression and improved extraction of photo-generated charges. It is evident that smart management of surface traps holds the key to achieving scalability of the device fabrication process.

At the time this PhD began, the LbL protocol was the mainstay of CQD PV fabrication. Although the LbL scheme helped realize uniform, pinhole-free and conductive PV solids, it involved overwhelming materials and time wastage and was, therefore, incompatible with industrial scale-up. Developing an efficient, alternate ligand exchange scheme involved a deeper understanding of how the exchange process modified the surface structure and properties of the CQDs. This understanding could then be used to modify the exchange process to achieve higher device performances and scalability. It was, therefore, important to study the process-structure-property-performance relationship of CQDs in the context of the solid-state ligand exchange. Such a study was expected to give insights into the exchange process and could help develop routes to an alternate, more efficient way of carrying out ligand exchange.
Device performances stand to benefit from improved charge transport. One way to achieve this goal is to realize controlled net doping in CQD solids. Doping of CQDs can be used to suppress traps and tune the carrier concentration. However, at the time of this PhD, there was no demonstration of a doping protocol compatible with solar cell fabrication. It would, therefore, be to good effect to achieve controlled net doping by devising a procedure that was compatible with device fabrication.

As this PhD has progressed, solution-phase ligand exchange has been effectively optimized, leading to realization of single-step deposited CQD absorbers. These absorbers, nonetheless, still involve spin-coating and achieving process-scalability is a challenge. Another major challenge in CQD PV is the manufacturability and operation of the solar cells in high humidity ambient environments. Moisture is known to be deleterious to CQD solar cell and, as such, the majority of reports, to date, have involved fabrication either under controlled humidity or in the winter season where ambient humidities are expected to be low. Fabrication of a robust, scalable CQD PV technology in a humid lab environment such as KAUST, where relative humidity (RH) remains in the range of 50-65% round-the-year, will be a litmus test for this technology. Success of these studies will rely on developing efficient ways of mitigating the humidity-induced CQD surface damage.
Chapter 3
Methodology

In this chapter, the general experimental methodology employed in this thesis is presented. This covers the surface characterization using photoemission spectroscopy (PES), ex-situ and in-situ materials and process characterizations, solar cell fabrication protocols and subsequent testing and characterization. Also included in this chapter are the chemical synthesis protocols and theoretical simulation methodologies that were carried out at partner laboratories (Prof. Sargent’s group at University of Toronto, Prof. Marder’s group at Georgia Institute of Technology) as part of collaborations.

3.1 Photoemission Spectroscopy (PES)

PES, as the name suggests, works on the principle of photoemission or the photoelectric effect, and is, therefore, a ‘photon-in-electron-out’ technique. The measurements were carried out in an ultra-high vacuum (UHV) chamber housed in the OEPV Lab, pictured in Figure 3.1. The UHV system maintains an ultra-high vacuum (~10^{-9}-10^{-10} mbar) with the help of a suite of turbo-molecular, ion and titanium sublimation pumps. Photons with a fixed kinetic energy (KE) are produced and employed to excite the valence band/shallow core/deep core electrons of the sample to be studied, transferred to the UHV chamber. Depending upon the KE of the incident photons, PES can either be X-ray PES (XPS) or ultraviolet PES (UPS). Details of the XPS and UPS measurements reported in this thesis are elaborately mentioned in this section.

PES sample preparation was carried out by spin-coating the CQD absorbers on non-patterned indium tin oxide (ITO) substrates (1.0 x 1.0 cm²), which were cleaned shortly
before deposition by a brief ultrasonication/rinsing with isopropanol (IPA) followed by a 2-3 min UV-ozone plasma treatment. The samples were soldered to the base of the sample plates using tantalum foils to ensure proper grounding of the samples during measurements and to avoid undue charging effects, which can easily lead to misinterpretation of the PES data. Importantly, it was made sure that the thickness of the CQD solids always remained \( \leq 100 \) nm (2-3 LbL cycles of solid-state ligand exchange or a high-speed (6000 rpm) spin-coating of the SolEx CQD inks) to avoid charging effects. The samples were immediately transferred into the UHV via a fast-entry load-lock.
3.1.1 XPS

XPS measurements were carried out in UHV chamber (Omicron NanoTechnology, Taunusstein, Germany) equipped with a SPHERA U7 hemispherical energy analyzer. X-ray photons were generated 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. For all the measurements reported in this dissertation, the survey spectra for all the measurements were acquired at a pass energy of 40 eV, while the high resolution core level peaks for the various elements were obtained at a pass energy of 20 eV. The photoelectrons were
collected by the SPHERA U7 hemispherical energy analyzer with a 7 channel MCD detector, in Constant Analyzer Energy (CAE) mode. Wherever possible, the spectra were referenced to the C1s core level peak with its sp² (C–C) component neutralized at 284.8 eV.

The XPS spectra were analyzed using the CasaXPS software (Casa Software Ltd.). All the peaks were fitted with a GL(30) lineshape which employs a 70% Gaussian and 30% Lorentzian shape, subtracted with a Shirley background. Most of the Pb 4f and S 2p doublets fitted in this work employ an FWHM of 0.9-1.0 eV and 0.8-1.0 eV, respectively.

3.1.2 UPS
UPS measurements were carried out under UHV base pressures of < 8 × 10⁻⁹ mbar with the pressure in the He-line in the range of 7-9 x 10⁻² mbar. The photon linewidth was ca. 250 eV and the minimum spot size ca. 1 mm. He I photons (21.2 eV) were used to acquire the spectra at normal emission (photoelectron take-off angle of 90° with respect to the substrate plane). Spectra reported in this work have been measured at a pass energy of 2 eV, by applying a bias of -10 V at a resolution of 0.1 eV. The application of a negative bias during UPS measurements (especially the measurement of the secondary electrons (SEs) for work-function estimation) is important as it differentiates the secondary electrons from the sample from those of the analyzer. Also, it is crucial to measure the UPS spectra of a biased sample at normal emission, as has been reported earlier.

Some of the PES data reported here (Chapter 4) has been measured at the VLS-PGM beamline of the Canadian Light Source (CLS) having a Scienta SES100 hemispherical energy analyzer and an energy resolution of 0.05 eV. The data was obtained at normal
emission and room temperature. Synchrotron-based PES has the obvious advantage over the fixed-photon energy UPS in that a range of incident photon KEs with high flux is available. This allows for better resolution, especially, of the energy states near the Fermi level, i.e. the region of interest (for example, defect states).\textsuperscript{[128]} The spectra were measured at an incident photon KE of 100 eV.

3.2 \textit{Ex-situ} materials characterization

3.2.1 \textbf{Fourier transform infra-red spectroscopy (FTIR)}

FTIR measurements were performed on a Nicolet 6700 infrared spectrometer coupled with a Nicolet Continuum Microscope (Thermo Electron Corporation, UK). The spectrometer has a KBr beam splitter and an EverGlo IR source. The microscope has a mercury cadmium telluride (MCT-A) detector refrigerated with liquid nitrogen and a 15X Reflachromat Objective (0.58 N.A.). Reflection mode was used for collecting the FTIR spectra that were recorded with the nominal resolution of 4 cm\textsuperscript{-1} over the range 600 cm\textsuperscript{-1} – 4000 cm\textsuperscript{-1}. 100 nm Au coated FTOs were used as substrates.

3.2.2 \textbf{Variable-angle spectroscopic ellipsometry (VASE)}

Spectroscopic ellipsometry probes the optical properties of thin films by measuring the change in polarization of light, as it interacts with the films. The measurements are carried out by recording the angles, $\psi$ and $\Delta$, which are related to the ratio of reflectivities associated with the p- and s-polarized lights, $R_P$ and $R_S$, respectively, as shown in equation (1):

$$\frac{R_P}{R_S} = \tan(\psi) \exp(i\Delta)$$

(1)
Measurement of $\psi$ and $\Delta$ directly leads to information on $n$ and $k$, the refractive index and extinction coefficient of the film.

An M-2000XI, J. A. Woollam Co., Inc. ellipsometer (400 – 1700 nm) was used to study the variation in film thickness and optical properties of the CQD films coated on thermally oxidized Si substrates. The spectra were obtained at incidence angles in the range 45°-75° with respect to substrate normal, with discrete increments of 5°. The film properties were modelled assuming a B-Spline dispersion relation in the absorption region using the EASE and WVASE32 software packages from J. A. Woollam Co., Inc.

### 3.2.3 Infrared VASE (IR-VASE)

IR-VASE has been specifically used in Chapter 4. A J.A. Woollam Co., Inc. IR-VASE ellipsometer (500 cm$^{-1}$ – 5000 cm$^{-1}$) was used. The IR-VASE uses a Fourier-transform based infrared spectrometer combined with a variable angle ellipsometer incorporating a rotating compensator technology for accurate Psi and Delta measurements. The spectra were obtained at an incidence angle of 75°. The resulting elliptical beam spot has dimensions 3.9cm x 0.7cm. 100 nm Au coated soda lime glass slides were used as substrates.

### 3.2.4 Absorption measurements

Absorption measurements were carried out using an Agilent Cary 5000 UV-Vis-NIR instrument equipped with PMT (UV-Vis) and PbS (NIR) detectors. The samples were positioned using the solid sample holder accessory. Spectra were collected between 400 nm and 1200 nm using a spectral bandwidth of 2 nm and a scan rate of 600 nm/min. All
measurements were made in double beam mode, using reduced slit height and baseline correction.

**3.2.5 Photoluminescence (PL) measurements**

PL measurements (Chapter 5) were carried out on a confocal micro-Raman system (Horiba Jobin Yvon Aramis), using a 785 nm laser as the excitation source. A 100× objective lens with a numerical aperture (N.A.) of 0.90 was used to focus the laser beam and collect scattered light. The exposure time was ca. 90 s for all spectra (3 scans, ca. 30s per scan). CQD films were spin coated on bare soda-lime glass cleaned via ultrasonication sequentially in acetone, isopropanol and ethanol. 2 layers of CQDs were deposited leading to very smooth and shiny films of total thickness ~60 nm.

PL measurements reported in Chapter 6 were carried out using a Horiba Fluorolog system. Light from a monochromatized xenon lamp was used as the photoexcitation source. Photoluminescence was collected by a single grating spectrometer and measured with a photo-multiplier tube detector.

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

GISAXS measurements were 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. CQD films were spin-coated on Si with a thermal oxide.

Since the GISAXS technique exploits total external reflection of the X-rays, it is crucial to have an incidence angle similar to the critical angle of the CQD film (~0.17°). This limits
the beam penetration to a top few nanometers of the film and allows for probing the surface in detail without influence from the substrate below. In any case, the incidence angle must not be higher than the substrate’s critical angle (0.23°), as doing so leads to background scattering from the substrate resulting in a low signal-to-noise ratio.

3.2.7 Surface morphology characterization

*Atomic force microscopy (AFM)*: An Agilent 5400 instrument in tapping mode was used to obtain AFM images.

*Scanning electron microscopy (SEM)*: High Resolution SEM images were acquired using an FEI Nova Nano630 scanning electron microscope equipped with a field emission electron source and through-lens electron detectors at an electron beam voltage of 5 kV.

3.2.8 Kelvin-probe (KP) measurements

A KP Technology KP020 system was used to obtain the surface potential of the samples. A gold polished plate was used as a standard reference. Measurements were taken at ambient conditions with an off-null configuration.

3.2.9 Impedance spectroscopy (IS)

The impedance measurements were carried out on an Autolab system. During the measurements, AC voltage signals with amplitude of 10 mV were applied in the frequency range from 0.1 Hz to 1 MHz with no external DC voltage (zero bias) applied to the solar cells. During the impedance measurements, the solar cells were kept in dark at room temperature. In order to reduce noise and to increase reproducibility, the solar cells were kept in an electrically shielded aluminum box.
3.2.10 Secondary ion mass spectrometry (SIMS)
SIMS experiments were performed on a Dynamic SIMS instrument from Hiden analytical company (Warrington-UK) operated under ultra-high vacuum conditions, typically $10^{-9}$ Torr. The Dynamic SIMS is equipped with a gas source allowing for both argon or oxygen ion beams to be employed. However, in order to reduce the fragmentation effect leading to the formation of small hydrocarbon fragments, the inert Ar$^+$ beam was chosen to conduct the measurements. In addition, the effect of the incoming oxygen on the sputtered organic material is also avoided.

Throughout the sputtering process, the selected ions ascribed C, F, Si, S, I, Mo and Pb were sequentially collected using a Hiden MAXIM (MAXIMum sensitivity) spectrometer equipped with a quadrupole analyser. Ions were collected from the sample by a shaped extraction field and energy filtered using a parallel plate system, with the energy resolution matched to that of the quadrupole analyser. After passing through a triple filter system, detected ions were measured using a pulse counting detector having a 4 keV post acceleration potential to increase further the detection efficiency at high masses.

Prior to acquiring mass spectra and depth profiling curves, the experimental conditions including the primary ion type, energy and current of the sputtering beam were first optimized. The raster of the sputtered area is estimated to be $500 \times 500 \, \mu m^2$. In order to avoid the edge effect during depth profiling experiments, it is necessary to acquire data from a small area located in the middle of the eroded region. Using an adequate electronic gating, the acquisition area from which the depth profiling data were extracted was approximately $50 \times 50 \, \mu m^2$. The conversion of the sputtering time to sputtering depth scale...
was carried out by measuring the depth of the crater generated at the end of the depth profiling experiment using a stylus profiler from Veeco.

3.2.11 Transient absorption (TA)
TA measurements were done using femtosecond pulses produced from a Light Conversion Pharos regeneratively amplified Yb:KGW laser at a repetition rate of 5 kHz. The 440 nm pump signal was produced from a portion of the 1030 nm probe light with a Light Conversion Orpheus optical parametric amplifier. A Helios Ultrafast optical bench received the pump and probe beams where the probe light generated a near-IR continuum with a crystal from Ultrafast. The probe signal was optically delayed to introduce time delay. Alternating pump pulses were blocked with a chopper. A charge-coupled device measured the transmitted probe after being collected and dispersed with a grating spectrometer. A pump pulse intensity of 6 µJ/cm² was used in all measurements and the samples were translated during measurement.

3.2.12 Time-resolved photoluminescence (TRPL)
TRPL measurements (chapter 6) were conducted by applying an optical parametric oscillator (OPO) from Radiantis pumped by a Spectra Physics Maitai oscillator. The desired output of 650 nm from the OPO was routed through the pulse picker (Pulse Select from A.P.E) and focused to pump the CQD samples. The associated PL signal is then collected and focused through optical lenses to the slit entrance of the spectrograph and carried to the Infrared streak camera (Hamamatsu), and finally the detected signal is analyzed and optimized on a computer. All measurements were performed at room temperature.
3.2.13 Cross-sectional electron microscopy

*Cross-Sectional TEM:* Cross-sectional TEM sample preparation was done using focused ion beam (FIB, FEI Helios 400s) with the lift-out method. The lamella was prepared by Ga ion milling with beam conditions 30kV and 9nA. It was then transferred to copper TEM grid using the nanomanipulator (Omniprobe). The lamella was thinned down to a thickness of 50 nm and cleaned with ion beam conditions 2kV and 4.7 pA. HRTEM (FEI, Titan Super Twin) analysis was done at 300kV.

*Cross-Sectional SEM:* A field emission scanning electron microscope (FESEM, FEI Quanta 600FEG) was used to acquire cross-section SEM images.

3.3 *In-situ* materials deposition and process characterization

In this section, we discuss the detailed methodology of the in-situ probes used in this thesis.

In the context of the current work, these probes allow for discerning interactions of the CQDs with the process solvents and ligands, and evolution of CQD solid formation.

3.3.1 Quartz-crystal microbalance with dissipation monitoring (QCM-D)

QCM-D is an important tool to track mass changes on rigid surfaces in real time. The changes to the resonance frequency of an oscillating quartz crystal are followed to track the mass changes on its surface, via the Sauerbrey equation:

\[
\Delta m = -(C \cdot \Delta f)/n
\]  

(2)

where, \( \Delta m \) (ng.cm\(^{-2}\)) is the areal mass change corresponding to the frequency change \( \Delta f \) (Hz) of the \( n^{th} \) overtone. \( C \) (17.7 ng.cm\(^{-2}.\text{Hz}^{-1}\)) is the vibrational constant.
The Sauerbrey equation can be applied if three conditions are followed: (i) the deposited/desorbed mass is comparable to the sensor’s mass, (ii) it is rigid and vibrates along with the sensor, and (iii) it is evenly distributed on the sensor’s surface.

QCM-D also offers the advantage of measuring the energy dissipation, which gives an idea of the weakening, or not, of the frequency as it travels through the attached mass. The dissipation (D) is defined as:

\[ D = \frac{E_{\text{lost}}}{2\pi E_{\text{stored}}} \]  

(3)

where, \( E_{\text{stored}} \) is the total energy stored in the oscillator in one cycle, and \( E_{\text{lost}} \) is the energy lost. The driving voltage is occasionally turned off to monitor the energy dissipation, a procedure that can be repeated 200 times per second, giving QCM-D a high sensitivity. Rigid films strongly tethered to the sensor surface offer a loss-less path to the travelling frequency leading to minimal energy loss and hence low D. Similarly, softer films result in a high value of D.

Importantly, QCM-D can be used to track film formation and modification in the solution-phase in real-time. In the context of the CQDs, this means that phenomenon such as ligand exchange and solvent interactions can be probed \textit{in-situ}. This is illustrated in Figure 3.2a, where an OA-PbS CQD film bearing sensor surface is shown to be in the environment of a non-interacting solvent (red). Since the solvent does not interact with the CQDs, the OA ligands remain intact on the CQD surface and no mass-loss is detected. However, switching to a different, contrasting solvent (blue) leads to negative changes in frequency. This is interpreted as a mass-loss, arising from a loss of OA ligands into the liquid phase above. Changes happening to the liquid phase atop the sensor surface are not detected by the
QCM-D since the evanescent frequency wave travelling through the deposited film perishes exponentially at the surface:liquid boundary.

Figure 3.2b illustrates the idea of dissipation monitoring. OA ligands attached to the CQD surfaces are expected to render the coupled mass relatively ‘softer’ owing to their vibrational modes. The film, therefore, impedes the propagating frequency, leading to energy loss and hence a high D. A loss of OA ligands to the liquid phase (blue solvent) leads to reduction in the energy dissipation resulting in a low value of D. These concepts will be used later in Chapter 4 where we shall study these solvent and ligand interactions with the CQD surfaces in detail.

For the deposition of CQD solids, the AT-cut quartz crystals (5 MHz resonance frequency) were cleaned by ultra-sonication sequentially in acetone, iso-propanol and ethanol followed by a 10 minute UV-Ozone treatment. Thin films of OA-PbS CQDs were fabricated by spin-coating 50 µL of the ink for 10 seconds at 2500 rpm on SiO₂ coated quartz crystal sensors. Coated quartz sensors were loaded into a QCM-D open module (E4 model, QSense, Biolin Scientific) maintained at 25°C. Drop-casting measurements were carried out by dropping 150 uL of the process solvents and ligand exchange solutions on the surface of the coated sensors.
Figure 3.2. Illustration of the working principle of a QCM-D. (a) Loss of OA surface ligands leads to a negative change in frequency which is interpreted as a mass loss. (b) Loss of OA ligands leads to decreased energy dissipation in the film, suggesting a ‘harder’ or more rigid film.
3.3.2 In-situ UV-Vis absorption measurements
The absorption measurements were performed using a F20-UVX spectrometer with a tungsten halogen light source (Filmetrics, Inc.) with a repetition rate of 10 Hz and an integration time of 0.1s for each spectrum during spinning and/or annealing. The absorption spectra were calculated from transmission spectra using the equation (4):

\[ A_\lambda = -\log_{10}(T) \]  

(4)

where \( A_\lambda \) is the absorbance at a certain wavelength, \( \lambda \), and \( T \) is the calibrated transmitted radiation.

3.3.3 In-situ spectroscopic ellipsometry
In situ spectroscopic ellipsometry (SE; M-2000XI, J. A. Woollam Co., Inc) measurements were performed to monitor the thinning of the CQD solution during spin-coating, subsequent thin film formation and evolution during the annealing process. For these reflection-mode measurements, CQD films coated on thermally oxidized Si substrates (single crystal silicon wafer (100) with a 300 nm-thick thermal oxide). The spectra were obtained at an incidence angle 70° with respect to the substrate normal. The film properties were modelled assuming a B-Spline dispersion relation in the absorption region using the EASE and WVASE32 software packages from J. A. Woollam Co., Inc.

3.3.4 Thermo-gravimetric analysis (TGA)
TGA was conducted using a TGA 5500 apparatus. The samples were heated at a rate of 10 °C/min up to 80 °C. CQD solids were first deposited on glass substrates by spin-coating. The solids were then scraped-off and the powder was contained in alumina crucibles for the TGA measurements.
3.4 Device fabrication, testing and characterization

Here, we discuss the details of solar cell fabrication, testing conditions and subsequent characterization. P-n heterojunction (Chapter 4, 5) and n-i-p architectures (Chapter 6, 7) will be covered.

3.4.1 Device fabrication

p-n heterojunction solar cells: ITO/FTO substrates were cleaned following standard procedure (15 minutes of ultra-sonication each in Triton/DI water solution, DI water, Acetone and Isopropanol). The substrates were exposed to UV-ozone for 5 minutes before deposition of TiO$_2$ nanoparticle (NP) films which acted as the electron-transport layers (ETLs). OA-PbS CQDs were then deposited on these ETL-coated ITO/FTO glass substrate using the LbL scheme. First, 50 µL of 50 mg mL$^{-1}$ OA-PbS CQDs in octane were spin-coated under ambient condition at 2500 rpm (to obtain the 3 LbL absorbers in Chapter 4, a concentration of 100 mg mL$^{-1}$ was used with a spinning speed of 750 rpm). This was followed by soaking in MPA in MeOH (v/v) for 3 seconds (or 60 seconds for the 3 LbL absorbers). The layer was then rinsed twice with MeOH to remove the exchanged OA ligands. The process resulted in a layer with the thickness of approximately 30 nm. The process was repeated 10-12 times until the desired thickness was achieved.

To obtain molybdenum tris(1-(trifluoroacetyl)-2-(trifluoromethyl)ethane-1,2-dithiolene) or Mo(tfd-COCF$_3$)$_3$-doped solar cells, the assembly soaked in Mo(tfd-COCF$_3$)$_3$-containing ACN solution, for a certain time (few minutes). The excess solution was then removed by spinning and the film was twice flushed with ACN to remove excess dopant.
The top electrode was finally deposited using thermal evaporation, which comprised of 40 nm MoO$_3$ (0.2 Ås$^{-1}$) and 120 nm gold (1 Ås$^{-1}$) at a pressure of 1×10$^{-6}$ mbar.

*n-i-p solar cells:* For this architecture, ZnO NPs were used to form the ETL atop cleaned ITO glass substrates as per published protocol.$^{[3]}$

Synthesis of perovskite-shelled PbS CQDs was carried out according to the reported protocol.$^{[29]}$ Equal amounts of MAI and PbI$_2$ precursors (0.3 mol.L$^{-1}$) were mixed in 5 mL of DMF solvent at room temperature. Once a clear solution was obtained, ca. 5 ml of OA-PbS CQDs (10 mg mL$^{-1}$) were added and the vial was vortexed for 5 min. This resulted in solution-phase ligand exchange CQDs which were washed twice with octane (5 mL) to remove the residual OA ligands, separated from the vial, precipitated with toluene solvent (2.5 mL) and centrifuged at 6000 rpm for a couple of minutes. The precipitate thus obtained was dried under vacuum for 1 hour. This was then redispersed in BTA yielding a stable ink of desired concentration.

Synthesis of metal halide ligand capped PbS CQDs followed a recent report.$^{[130]}$ A clear solution of the precursors (0.1 M PbI$_2$, 0.02 M PbBr$_2$, 0.04 M ammonium acetate) was first made in 5 ml DMF solvent. 5 ml of OA-PbS CQDs (10 mg mL$^{-1}$) were then added to the vial and vortexed for 5 min. The resulting solution-phase ligand exchanged CQDs were washed thrice with octane. These were then precipitated with toluene and separated by centrifugation (6000 rpm, 2 min) and left under vacuum for drying for 1 hour. The powder was then redispersed in BTA to obtain a stable ink of desired concentration.

The active layer was directly deposited by spin-coating 40μL of the solution-phase exchanged CQD ink (160 uL solution in butylanline solvent) at 6000 rpm. The MAPbI$_3$-
PbS CQD layer was annealed at 70 °C in a nitrogen glove box. No post-annealing was required for the PbX₂-PbS CQD layer. The resulting single-step deposited absorber layers were found to be of high quality; thick, dark brown and shiny without any pinholes. This was followed by deposition of two layers of EDT-PbS CQDs via solid-state ligand exchange, in an LbL fashion. The thin EDT-PbS CQD solid acts as an HTL.

To obtain Mo(tfd-COF₃)₃-doped ETLs, the overall assembly was soaked in the dopant solution of a particular concentration for ~30 seconds. This was followed by an ACN wash to remove any excess dopant. 120 nm gold was finally deposited via thermal evaporation as the top electrode (0.5 Å/s).

3.4.2 Device testing

J-V curves were measured using a Keithley 2400 source-meter at ambient temperature, with the device held in a constantly purged nitrogen environment. 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⁻²). The source intensity was measured with a Melles-Griot broadband power meter through a circular 0.049 cm² aperture. The same aperture was used in the J–V measurement; the aperture is slightly smaller than the top electrode to avoid overestimating the photocurrent. The entire photon fluence passing through the aperture was counted as incident on the device for all current analyses. The spectral mismatch of the system was characterized using a calibrated reference solar cell (Newport). The total AM 1.5 spectral mismatch—taking into account the simulator spectrum and the spectral responsivities of the test cell, reference cell, and broadband power meter—was re-measured periodically and found to be ≈4.4%. This multiplicative factor, M = 0.956, was applied to the current density values of
the $J$-$V$ curve to most closely resemble true AM 1.5 performance. The uncertainty of the current–voltage measurements was estimated to be 7%.

We have also fabricated devices with active areas of 0.1 and 0.5 cm$^2$.

### 3.4.3 External quantum efficiency (EQE) measurements
EQE spectral traces were taken by illuminating the cells with a 400W Xe lamp passed through a monochromator and appropriate cutoff filters. The monochromator output power was calibrated with Newport 818-UV and Newport 838-IR photodetectors. The light beam was chopped at a 220 Hz frequency and focused in the pixel alongside 1 sun intensity light bias from a solar-simulator. The photoresponse of the cell was recorded through a Lakeshore preamplifier connected to Stanford Research 830 lock-in amplifier at short-circuit conditions (virtual-null).

### 3.5 Band structure simulations and device modeling

#### 3.5.1 Density functional theory (DFT) simulations
These simulations are specific to Chapter 5. Simulations were performed using CP2K software utilizing a mixed planewaves and molecular orbitals basis.$^{131}$ Goedecker–Teter–Hutter pseudopotentials were employed with a 300 Ry grid cutoff. The metal-organic dopant molecule was simulated using the B3LYP exchange-correlation functional as it is known to better reproduce the band gaps and electron affinities. A 3 nm PbS CQD was modeled in a (40 Å)$^3$ unit cell using a less computationally expensive PBE functional to confirm the charge transfer from the CQD to the dopant.
3.5.2 Device modeling
Optoelectronic simulations were performed with SCAPS.\textsuperscript{[132]} The solar cell structure was modeled based on an n-i-p structure. The p-layer represents the modified EDT, the i-layer represents the perovskite-shelled CQDs and the n-layer consists of ZnO. The acceptor doping concentration of the EDT layer was varied and analyzed for its impact on the various photovoltaic performance metrics. The perovskite-shelled CQD solid consists of a parabolic grading combination of the parameters listed herein. The CQD band-edge for a given exciton peak was calculated from the absorption edge of the exciton peak.

3.6 Chemical synthesis protocols
3.6.1 CQD synthesis
For all the device results reported in this thesis, the OA-PbS CQDs were synthesized using a variation on a literature method,\textsuperscript{[40]} employing previously reported SolEx halide treatments following reported recipes,\textsuperscript{[12, 116]}

3.6.2 Dopant synthesis
Nickel bis(1,2-bis(trifluoromethyl)ethane-1,2-dithiolene), Ni(tfd)\textsubscript{2};\textsuperscript{[133]} Molybdenum tris(1-phenyl-2-benzoyl-1,2-dithiolene), Mo(PhBz-dt)\textsubscript{3};\textsuperscript{[134]} Ruthenium (pentamethycyclopentadienyl)(mesitylene) dimer, (RuCp*mes)\textsubscript{2};\textsuperscript{[135]} and Mo(tfd-COCF\textsubscript{3})\textsubscript{3}\textsuperscript{[136]} were prepared according to the literature.
Chapter 4

On the Nature of the Solid-State Ligand Exchange: Implications for CQD Solar Cell Manufacturability and Performance

4.1 Introduction

In Chapter 2, we highlighted the importance of the solid-state ligand exchange in CQD PV, and also the fact that it is a highly wasteful and tedious protocol. While, on the one hand, the process has helped realize CQD solids with remarkably enhanced charge transport, on the other, its wasteful nature has rendered the technology industrially incompatible and unscalable. The state-of-affairs makes it incumbent to understand the nature of this exchange process and transform the knowledge into the first attempts towards a more scalable and facile route to performing ligand exchange.

We choose to focus our studies on the MPA ligand, the shorter thiol molecule that has been known to the CQD PV community as an excellent replacement to the insulating OA surfactants in the solid-state. We realize that there is a lack of an in-depth knowledge as to how many MPA ligands need to be optimally supplied to the OA-PbS CQD films to achieve the most efficient, electronically coupled solid. The OA-PbS CQD films are usually soaked in an MPA solution for 3-5 s, resulting in the exchange, with the majority of reports employing a solution of 1-10% v/v MPA in MeOH solvent (MPA/MeOH) without any report, to the best of our knowledge, using any other concentration and solvent.[6-7,12,126] We take the view that these optimized conditions have been arrived at by ‘trial-and-error’ and a fundamental understanding of how the MPA ligands and the standard process solvent, MeOH, interact with the OA-PbS CQD surface is missing. To
fill in this gap, we have carried out the following study. A part of these findings was published in *Adv. Mater.*, back in 2014.[137]

The first part of this chapter deals with the interaction of the MPA linker with OA-PbS CQDs. We perform ligand exchange on OA-PbS CQD films with a variety of MPA concentrations (referred to [MPA] here onwards), and identify two contrasting regimes – *higher concentrations* lead to effective ligand exchange resulting in an optimized CQD surface ligand coverage, inter-dot spacing, film density and absorption and, consequently, higher solar cell performance; while *lower concentrations* result in ineffective exchange and hence poorly performing solar cells. This study demonstrates that an optimized solid-state ligand exchange process embodies optimization of the various physical and chemical attributes of the CQD solids and provides a definitive answer as to why higher ligand concentrations have thus far been found to yield the best CQD solar cells.

The second part focusses on the effect of the process solvent environment on the optoelectronic properties of the CQD solids. We find that the standard process solvent, MeOH, in fact, interacts strongly and erodes the CQD surfaces during an extended exposure, a finding that helps explain why most solid-state exchange reports have resorted to a brief (3-5 s) MPA/MeOH exchange. Since a brief exposure can only soak and efficiently exchange a thin CQD solid, this recipe has always required an LbL build-up of the absorber layer requiring around 10-12 steps. Based on our findings, we explain that so many steps are needed because extensive exposure to MeOH leaches surface halides. We introduce a modified solid-state ligand exchange process that eventually allows us to fabricate solar cells of similar thickness and ligand exchange quality in 3 LbL steps, in the
process reducing by half the materials wastage and cutting the fabrication time by three, without compromising on device performance.

4.2 Linker-CQD interactions

4.2.1 Solvent- and linker-dominated regimes
Ligand exchange is expected to drastically change various physical and chemical properties of the CQD film at the micro- and nanoscales.\textsuperscript{61, 138} OA-PbS CQD thin films (ca. 80 nm) were treated with a series of [MPA] in MeOH. The treatment was limited to 3-5 s in accordance with the standard active layer fabrication protocol. In order to track the efficacy of ligand exchange, we probed the film thickness, refractive index and absorption using VASE and inter-dot spacing was studied using GISAXS. Results are shown in Figure 4.1.
Figure 4.1. Solvent- vs. linker-dominated regimes: CQD films capped with OA were ligand exchanged with a series of [MPA] in MeOH solvent. The various film properties, (a) thickness, (b) refractive index, (c) inter-dot spacing and (d) excitonic absorption were found to follow a similar trend. Blue lines are drawn as a guide to the eye. Lower concentrations are not found to affect the films considerably leaving the final films similar to the unexchanged control (the data points in black circles). The film properties show drastic change in the concentration range of $10^{-4}$ to $10^{-2}$ (blue shaded regions), whereafter the changes are found to relatively saturate. Green hue: linker-dominated regime, red hue: solvent-dominated regime, white hue: transition regime.

Lower concentrations do not have any noticeable effect on the film thickness (Figure 4.1a) where the thicknesses resemble the untreated baseline. As [MPA] is increased, a sudden transition is observed above $10^{-4}$ %. The film thickness is found to reduce to ca. 50% of
the initial thickness for $10^{-2}$ %. Films treated with higher [MPA] do not show any further thickness decrease. The OA-PbS CQD film is expected to show thickness reduction upon ligand exchange as the bulkier OA ligands are replaced by the shorter MPA molecules. We find the film density to follow a similar trend. The refractive index ($n_{1200}$) measured at 1200 nm increases significantly for [MPA] $\geq 10^{-2}$ % indicating film densification, as shown in Figure 4.1b. We also find that the excitonic peak, $\lambda_{\text{peak}}$, red-shifts upon ligand exchange. The ligand exchange-induced red-shift in CQD films is well-known and has been previously ascribed to a combination of enhanced electronic coupling between the CQDs and the increased film disorder. The $\lambda_{\text{peak}}$ red-peak shift, therefore, is another important indicator to efficient ligand exchange. We find that the red-shifts increase and saturate for MPA $\geq 10^{-2}$ % (Figure 4.1d). We were also interested in studying the effect of [MPA] on inter-dot spacing, $d$. Ligand exchange is known to bring CQDs closer to each other leading to better coupling and enhanced delocalization of charge carrier wavefunctions. Figure 4.1c shows a similar variation of $d$ as a function of [MPA]. Weaker [MPA] conditions are ineffective in bringing the CQDs closer while higher [MPA] ($\geq 10^{-2}$ %) lead to a closely packed CQD solid with an average $d$-spacing of ca. 3.5 nm.

The above trends reveal an important insight into the nature of solid-state ligand exchange. The lower [MPA] regime is dominated by the solvent, MeOH, and is incapable of exchanging the OA ligands while the higher [MPA] regime is dominated by MPA and leads to efficient ligand exchange. The various film properties are found to saturate for these concentrations. The intermediate concentrations, $10^{-4} \leq [\text{MPA}] \leq 10^{-2}$, represent a transition regime.
Figure 4.2. Tuning surface ligand coverage: High resolution S 2p core level peaks as found from XPS. The baseline film (a) shows a doublet as expected, arising from the S atoms in the CQD. S 2p peaks for the ligand exchanged films (b)-(d) show a new component arising from S atoms of MPA ligands bonded to Pb, $S_{MPA}$ (red shaded doublets). Pb:S ratio is expected to decrease after ligand exchange.

<table>
<thead>
<tr>
<th>[MPA]</th>
<th>Pb</th>
<th>S</th>
<th>C</th>
<th>Cd</th>
<th>Cl</th>
<th>O</th>
<th>Pb/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>11.2</td>
<td>6.1</td>
<td>74.6</td>
<td>0.4</td>
<td>2.0</td>
<td>5.7</td>
<td>1.84±0.06</td>
</tr>
<tr>
<td>1</td>
<td>21.2</td>
<td>18.6</td>
<td>42.5</td>
<td>1.2</td>
<td>4.1</td>
<td>12.0</td>
<td>1.14±0.01</td>
</tr>
<tr>
<td>5</td>
<td>20.2</td>
<td>17.9</td>
<td>46.0</td>
<td>1.0</td>
<td>4.7</td>
<td>10.2</td>
<td>1.13±0.01</td>
</tr>
<tr>
<td>10</td>
<td>23.6</td>
<td>19.8</td>
<td>35.5</td>
<td>1.3</td>
<td>4.7</td>
<td>12.7</td>
<td>1.19±0.01</td>
</tr>
</tbody>
</table>
Having studied the effect of [MPA] on the various physical and chemical properties of the OA-PbS CQD films, we were interested in understanding these changes on a more fundamental level. We therefore employed X-ray photoelectron spectroscopy (XPS) to track the changes to the surface chemistry of the CQD solid exchanged with various [MPA]. Figure 4.2(a)-(d) show S 2p core level peaks for the OA-PbS CQDs and those exchanged with [MPA] usually employed for CQD absorber fabrication. The untreated OA-PbS CQD solid shows a two-component structure corresponding to the S from PbS. Upon ligand exchange, S from MPA (denoted as $S_{\text{MPA}}$) chemically binds to the CQD surface and the S 2p peak shows a complex structure which can be de-convoluted into two doublet peaks – one belonging to S from the PbS CQD ($S_{\text{QD}}$) and the other to $S_{\text{MPA}}$ (the latter are shown as red-shaded components). The relative atomic concentrations for the various elements in the solids are summarized in Table 4.1. The $S_{\text{MPA}}$ components are found to increase relative to $S_{\text{QD}}$ as [MPA] increases. Expectedly, S:Pb ratio increases with [MPA].

The linker-CQD interaction was studied in detail using the QCM-D technique. QCM-D measures the mass loading on the surface of an AT-cut quartz sensor (cut 35°25’ to the z-axis) in terms of a shift in its resonance frequency. 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 exchange. A negative change in the resonance frequency of the loaded crystal represents a mass loss. Importantly, for these measurements we switched to another solubilizing
solvent, acetonitrile (ACN). We shall find out in the second part of this chapter that ACN does not interact with the CQD surface. Since, here we are more interested in studying the linker-CQD interactions, we want to limit the interaction of the solvent with the CQDs. Results are shown in Figure 4.3a.

Figure 4.3. (a) Frequency changes of a QCM-D crystal loaded with a OA-PbS CQD solid and exchanged with various [MPA]. The frequency changes relate to mass changes on the CQD surface. (b) Since the mass change represents exchange of OA with MPA, we are able to convert this information into ligand exchanged per CQD as a function of [MPA]. Solvent- and linker-dominated regimes are obvious. Green hue: linker-dominated regime, red hue: solvent-dominated regime, white hue: transition regime. This crucial information allowed us to convert the net mass changes ($\Delta m$) into $N$, the total number of ligands exchanged per unit area, for each [MPA], using equation (1).

$$\Delta m = N \cdot (M_{\text{MPA}} - M_{\text{OA}})$$

(1)

Here, $\Delta m$ is the mass-change detected by QCM-D, $M_{\text{MPA}}$ is the molecular weight of MPA, $M_{\text{OA}}$ is the molecular weight of OA, and $N$ is the total number of ligands exchanged per unit area. It was assumed that ACN does not lead to any mass change (we shall verify this assumption in the next part of this chapter). Next, considering random packing of CQDs in the solid, and using inter-dot spacing (Figure 4.1c), we were able to track the number
of ligands exchanged per CQD (Figure 4.3b). We again find that the trend can be roughly split into solvent- and linker-dominated regimes.

### 4.2.2 Solid-state ligand exchange model

**Schematic 4.1** summarizes the model of solid-state ligand exchange that we propose on the basis of the above findings employing various spectroscopic and analytical probes.

![Schematic 4.1](image)

**Schematic 4.1.** Schematic representation of the solid-state ligand exchange model as discerned from the findings reported above. Solvent- and linker-dominated regimes are separated by a transition regime residing in intermediate values of [MPA]. Green hue: linker-dominated regime, red hue: solvent-dominated regime, white hue: transition regime. Ligand exchanges employing lower concentrations of the linker ([MPA] < 10^{-4}) belong to the solvent-dominated regime and are incapable of successfully replacing the OA ligands.

As the [MPA] is increased, a transition regime is observed where the CQD solid appears to undergo a sudden phase transition-like change in properties (10^{-2} < [MPA] < 10^{-4}). Above [MPA] > 10^{-2}, in the linker-dominated regime, the properties saturate and the CQD solid is found to be nearly fully-exchanged. It appears that a certain number of MPA ligands is necessary to be delivered to the CQD surface in order to bring about a sudden, complete exchange of the solid (as shown in Figure 4.3b), whereby a sudden change and saturation in properties is observed.
4.2.3 Implications for CQD PV
As a proof of concept, we were interested in knowing the implications of our solid-state ligand exchange model on CQD solar cells. To this end, we made solar cells employing PbS CQDs as the absorber layer. In Figure 4.4 we demonstrate that the solar cells do indeed follow the [MPA] trend as discussed above. This is expected since the various physical and chemical attributes of the CQD absorber layer peak for the linker-dominated higher [MPA] regime. In general, our device performances were low since they were fabricated in a high RH lab environment in summers (we shall finally tackle and overcome this intrinsic ambient manufacturability challenge with CQD PV in Chapter 7).
We were not able to fabricate working devices with $10^{-4} \% < [\text{MPA}] > 1\%$ as these concentrations led to drastically poor film morphologies resulting in either delamination or significant pinhole formation. The device parameters are summarized in Table 4.2. It is evident that performances undergo a sudden transition below $10^{-2}\%$ [MPA], suggesting a transition point. Improper and incomplete ligand exchange below this point results poor charge generation ($J_{\text{SC}}$) and extraction (FF). This also raises the series resistance of the devices ($R_s$).

**Figure 4.4.** (a) $J$-$V$ curves of CQD solar cells fabricated by employing various [MPA] in the solid-state exchange. (b), (c) various device parameters as a function of the [MPA].
Table 4.2. Device parameters for solar cells fabricated in various [MPA] regimes.

<table>
<thead>
<tr>
<th>[MPA], %</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>$R_S$ (Ω·cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>13.99</td>
<td>0.57</td>
<td>63.1</td>
<td>5.1</td>
<td>5.1</td>
</tr>
<tr>
<td>$10^{-1}$</td>
<td>14.99</td>
<td>0.50</td>
<td>56.4</td>
<td>4.2</td>
<td>6.4</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>14.19</td>
<td>0.49</td>
<td>55.2</td>
<td>3.9</td>
<td>8.1</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>6.82</td>
<td>0.48</td>
<td>26.8</td>
<td>0.9</td>
<td>71.8</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>4.64</td>
<td>0.45</td>
<td>38.9</td>
<td>0.8</td>
<td>55.4</td>
</tr>
</tbody>
</table>

This variation of the device parameters with [MPA] is consistent and readily explainable from our model of the solid-state ligand exchange.

4.3 Solvent-CQD interactions

This part of the chapter extends our investigation of the solid-state exchange process by focusing on the solvent-CQD interactions. The motivation behind this study is explained as follows. One possible way of achieving process scalability, while utilizing the merits of the solid-state exchange process, is to be able to fabricate the absorber in fewer steps than the standard protocol (10-12 cycles of LbL). Doing so will require increasing the thickness of each individual layer (by increasing the CQD ink’s concentration and reducing the spin-coating speed) so as to achieve the same overall thickness as the standard LbL process. However, this will, in turn, require a longer ligand exchange to be performed so that the MPA/MeOH solution soaks the entirety of each individual thicker OA-PbS CQD layer, compared to the standard 3-5 s exchange in the current 10-12 LbL protocol. This modified exchange process entails an extended exposure of the process solvent, MeOH, with the CQD surfaces, necessitating an elaborate study into nature of these interactions.
4.3.1 MPA/MeOH extended ligand exchange

We started by employing the longer ligand exchange strategy to fabricate solar cells that featured a 3 LbL process, with each individual layer being 100 nm in thickness. The results are shown in Figure 4.5 and illustrate the scalability issue with CQD PV.

[Figure 4.5. J-V curves for a standard processed device - a solid-state exchange using MPA/MeOH treated for 3 s per 30nm layer (black) and reduced material devices, treated for 3 s per 100nm layer (blue) and for 60s per 100nm layer (red). A standard device with ~7% power conversion efficiency (PCE) was made, employing a 300 nm absorber fabricated in 10 LbL cycles: 80 nm/30 nm (pristine/exchanged) individual layers including a 3 s ligand exchange. We then fabricated a similar device with a reduced number of steps (3 instead of 10), effectively building up the absorbing layer in ~250 nm/100 nm steps, but without extending the ligand exchange duration. We observe a significant performance loss (see Table 4.3 for device parameters), likely due to incomplete ligand exchange within the thicker CQD films, as evidenced by low J_{SC}. Next, we fabricate a 3 LbL device employing an extended ligand exchange. To our surprise, the]
devices perform even worse (~3.7% PCE), due in large part to a reduction in $V_{OC}$, 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 CQD films thicker than 250 nm/100 nm (pristine/exchanged) without compromising on film morphology.

**Table 4.3.** Device parameters for CQD absorbers processed according to three different recipes. A solid-state exchange using MPA/MeOH, 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>
<tr>
<th></th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH – 3s/30nm</td>
<td>-0.580</td>
<td>21.5</td>
<td>56.7</td>
<td><strong>7.07</strong></td>
</tr>
<tr>
<td>MeOH – 3s/100nm</td>
<td>-0.572</td>
<td>16.4</td>
<td>52.8</td>
<td><strong>4.99</strong></td>
</tr>
<tr>
<td>MeOH – 60s/100nm</td>
<td>-0.409</td>
<td>18.1</td>
<td>49.6</td>
<td><strong>3.67</strong></td>
</tr>
</tbody>
</table>

### 4.3.2 Probing solvent-CQD interactions

Taking the view that an extended solvent-CQD interaction during the ligand exchange step may be the culprit behind the device performance degradation, we carry out an in-depth investigation into the effect of solvent environment on CQD solar cell manufacturability and performance. Our evaluation reveals indeed that MeOH, the ligand exchange solvent, chemically damages the CQDs 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 ACN, which leaves the CQDs physically and chemically intact even after extended exposure. Using ACN, we successfully demonstrate a CQD solar cell employing an active layer fabricated in only 3 steps without any compromise on performance. At the time of publication of this work,[137] these 3 LbL solar cells employing the extended MPA/ACN ligand exchange were the most efficient PbS CQD PV devices when normalized to the absorber material required.
The carboxylic hydrogen atom plays a key role in the solubility of OA.\cite{144} 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. On the other hand, 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-CQD interactions. A key difference in the solvent-CQD interactions is illustrated in Figures 4.6a and 4.6b, where we have compared FTIR transmittance spectra of a pristine CQD film with that of a CQD film exposed to MeOH and ACN for 10 minutes. The spectra reveal significant loss of OA from the CQD surface upon extended interaction with MeOH. Atomic ratio of OA to lead (Pb) for the pristine and solvent treated films, as measured from XPS, are shown in the insets of Figures 4.6a, and 4.6b. 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 4.6. Probing solvent-CQD interactions. FTIR spectra showing the C-H stretching vibration for CQD thin films before and after exposure to (a) MeOH and (b) ACN for a duration of 10 minutes, indicating significant loss of OA from CQD surface upon extended MeOH exposure, whereas minimal change is detected following exposure to ACN. Insets in figures (a) and (b) show the Carbon to Lead atomic ratio highlighting the effect of
MeOH and ACN exposures, respectively. (c) QCM-D measurements of mass change upon exposure of pristine CQDs 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 CQD films after their exposure to MeOH and ACN for 100s, revealing the MeOH-treated CQDs 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 CQDs dissolved in octane as determined from QCM-D measurements, revealing the CQDs are rendered insoluble by exposure to MeOH for nearly 90 seconds. (g) In-situ mass loss from (c) is converted into OA-ligand loss per CQD.

The solvent-CQD interaction was also probed using the QCM-D technique, which should be sensitive to OA removal as well as to the loss or not of CQDs when solvent-treated CQDs are exposed to octane, a good solvent for CQDs. QCM-D reveals significant mass loss upon dropping MeOH onto a CQD-coated QCM-D crystal, indicating exponential decay of mass (Figure 4.6c). The mass loss detected by QCM-D suggests the detachment of OA from the CQD 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 s of MeOH exposure, whereas no noticeable change is detected in case of ACN-treated CQD films. Following a 100 s exposure to MeOH or ACN, octane was dropped upon the surface of the N2-dried CQD film. The ACN-treated CQDs dissolved nearly completely (Figure 4.6d) in a matter of seconds, whereas the MeOH-treated CQDs remained immobilized on the surface. IR-VASE measurements were performed in reflection mode on CQD films to probe the extent of OA loss with solvent exposure time. Employing the simple formalism developed in Section 4.2.1 above, we are able to convert the in-situ mass loss from Figure 4.6c into number of OA ligands loss per CQD (see Figure 4.6g). The following equation is used:

\[ \Delta m = N.M_{OA}, \]
where, \( \Delta m \) is the mass-change detected by QCM-D, \( M_{OA} \) is the molecular weight of OA and \( N \) represents the number of OA ligands lost per unit area.

![Figure 4.7](image)

**Figure 4.7.** IR-VASE measurements comparing the effects of MeOH and ACN on the C-H stretch of OA-PbS CQD films.

The IR signature of the C-H stretching vibrations in OA at 2852 cm\(^{-1}\) and 2922 cm\(^{-1}\) were followed over successive solvent treatments to track the evolution of OA content.\(^{[11]}\) Results are shown in **Figure 4.7.** Over a period of 10 minutes, MeOH removes approximately 80% of the OA whereas ACN shows only a 10% decrease (Figure 4.6e). IR-VASE measurements reveal the time-evolution of OA content in the CQD films and indicate that 40% overall loss of OA is required to render the CQD film entirely insoluble in octane. During this period, the MeOH-treated film collapses to \(~60\%\) of its initial thickness accompanied by densification, as suggested by significant increase of the refractive index as per UV-Vis-NIR VASE measurements. When treated for shorter times, MeOH is believed to remove OA predominantly from CQDs near the top surface of the film, which renders parts of the film insoluble in octane with the OA-rich CQDs still
breaking through the crust and dissolving in octane, as suggested by TEM, SEM and AFM images (see Figure 4.8).

Figure 4.8. 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 2 minute Octane wash to remove all but insoluble material.

The optical properties of the CQD films reveal a blue-shift of the quantum confinement peak at ~950 nm upon MeOH exposure, as shown in Figure 4.9a. With time, as MeOH removes OA, the dots come closer thereby reducing the inter-dot spacing from ~4.6 nm in pristine films to ~4.4 nm after 10 minutes of MeOH exposure, as demonstrated by GISAXS measurements (see Figure 4.9b).
In addition to the loss of OA, XPS measurements reveal a significant loss of the halide (Cl) from the surface of the CQDs when exposed to MeOH for 600 s. By contrast, the ACN-treated film shows almost no change in terms of OA fraction, solubility, thickness, optical properties, inter-dot spacing, or halide content.

The halide atoms on the surface of CQDs are crucial for assuring effective atomic passivation and mitigating the sub-gap trap state density, which strongly influences carrier recombination in CQD solar cells. Thus, we speculate that loss of halide atoms when exposing CQDs to MeOH may be the main reason for the degradation of PV 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 (see Figure 4.14). This is probably because ligand exchange is completed on a sub-second timescale for the low CQD film thicknesses.
involved in the 10 LbL process, irrespective of the solvent choice (Figure 4.10), and thus state-of-the-art device fabrication recipes do not require extensive exposure to MeOH.

Figure 4.10. Mass change during ligand exchange process as a function of treatment time for (a) ACN and (b) MeOH.

4.3.3 MeOH-induced halide-loss

Turning our attention to the loss of halide during ligand exchange, we have used XPS to look at the differences in the elemental composition of ligand-exchanged films using MeOH and ACN-based treatments for extended durations (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 (Figure 4.11a). Also shown in Figure 4.11a 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 4.11. X-ray and ultraviolet photoelectron spectroscopies were used to study the solvent-CQD 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 ~0.2 eV is observed for the MeOH-treated film as compared to the ACN-treated film. (c) Schematic illustrates the model of solvent-CQD interaction and compares the effects of MeOH and ACN.

We combine the XPS study detailed above with UPS in order to study the valence bands of the extended ligand-exchanged CQD films (Figure 4.11b). Enhanced near-Fermi level DOS in PbS CQDs have been suggested to behave as charge carrier traps which are detrimental to device performance.\cite{110, 119} Synchrotron-based UPS can be effectively used to study the near-Fermi level carrier trap states in PbS CQD based solar cells.\cite{145} 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 ~0.2 eV shift of the valence band edge towards the Fermi level as shown in Figure 4.11b by the black, dashed lines. We suspect this to be the reason for the reduction of the $V_{OC}$ for the MeOH-based 3 LbL device (see Table 4.3).

### 4.3.4 MPA/ACN extended ligand exchange

We now seek to demonstrate that ACN can be used to perform effective ligand exchange for longer duration on the thicker films required to fabricate the absorbing layer 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 (ex-situ) to measure the thickness and optical properties of thin (~80 nm) and thick (~180 nm) OA-PbS CQD films by exchanging them for a range of times (see Figure 4.12). VASE analysis of even thicker films (~250 nm) was complicated by virtue of thin film uniformity and roughness issues, thus we have limited our comparison to films of nearly ~180 nm, which after ligand exchange shrink down to ~75 nm.
Figure 4.12. VASE data showing a comparison of (a) thickness variation and (b) refractive index for extended ligand exchange times on thin (~80 nm) and thick (~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 to the sub-second timescale required for ligand exchange in the standard thickness films. The ligand exchange kinetics appears to be independent of the solvent used.

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 substantial decrease in the inter-dot spacing and an expected red-shift in the peak absorption as shown in Figure 4.13.\textsuperscript{[107-108]}

Figure 4.13. (a) Effect of extended ligand exchange on inter-dot spacing of the thin films (~80 nm) using ACN and MeOH as the solvents determined using GISAXS. The dots are found come closer immediately following the exchange, irrespective of the solvent employed for exchange. The MeOH-based exchange however is found to give a slightly smaller inter-dot spacing. (b) Absorption peak shows a red-shift as a result of the enhanced electronic coupling following ligand exchange. For thin films the peak saturates within a second of the exchange process, whereas the thicker films require ~20 s for saturation.

Interestingly, MeOH-based ligand exchange leads to smaller inter-dot spacing than ACN-based ligand exchange. Third, the thicker films show a slowed ligand exchange nearing completion after ~20 s, a duration nearly 6-7 times greater to fully exchange a film only 2.3 times thicker.
Figure 4.14. Three layer devices processed using 60s ligand exchange in MeOH or ACN solvent environments are compared. For comparison, we have included a 10 layer device using 3 s ligand exchange in ACN.

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 ~60 s is sufficient to complete the ligand exchange of CQD films with a exchanged/pristine thickness of ~100 nm/~250 nm. The device performance shown in Figure 4.14 validates this hypothesis. The ACN-based 3 LbL device (black) employing 60 s exchange shows much better performance than the MeOH-based 3 LbL device (red) and closely approaches performance observed in a standard MeOH- and ACN-based 10 LbL devices shown in Figures 4.5 and 4.14, alongside significant process simplification and consuming ~40% less CQD solution than the latter (discussed in the next section). The good performance of ACN-based devices is despite the fact that inter-dot spacing is larger than when MeOH-based ligand exchange is used (Figure 4.13a). 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 CQD film, resulting in a slightly larger inter-dot spacing. This, however, does not appear to harm device characteristics.

Table 4.4. Champion device characteristics for CQD thin films processed according to two different recipes. A solid state exchange using MPA in MeOH versus ACN, for 60s treatments per 100 nm layer for a total of 3 layers.

<table>
<thead>
<tr>
<th></th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH – 60s/100nm</td>
<td>-0.409</td>
<td>18.1</td>
<td>49.6</td>
<td>3.67</td>
</tr>
<tr>
<td>ACN – 60s/100nm</td>
<td>-0.622</td>
<td>21.7</td>
<td>51.4</td>
<td>6.81</td>
</tr>
<tr>
<td>ACN – 3s/30 nm</td>
<td>-0.611</td>
<td>21.2</td>
<td>48.3</td>
<td>6.32</td>
</tr>
</tbody>
</table>

4.3.5 Materials-savings

The modified ligand exchange recipe involving ACN as the carrier solvent leads to 3 LbL-deposited CQD solar cells with PCEs at par with the standard 10 LbL devices. However, this comes with an added advantage, making these findings a step towards industrially-compatible fabrication – these modified devices consume ~40% less CQD ink compared to the standard 10 LbL solar cells (Figure 4.15), and significantly less time, typically requiring one third of the processing time. The methodology for arriving at this number and the related calculations are elaborated in this section.
Figure 4.15. Quantity of CQDs 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\(^2\) 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.

I. CQD net mass consumed:

Quantity of CQDs used per device was calculated considering that for casting each layer of the LbL buildup on a 2x2 cm\(^2\) FTO substrate, 50 ul of the CQD solution is used.

**Standard 10 LbL device:**

CQD solution used = 10x50 ul (= 0.5 ml); 50 mg/ml.

Quantity of CQDs = 25 mg of CQDs.

**3 LbL device:**

CQD solution used = 3x50 ul (= 0.15 ml); 100 mg/ml.
Quantity of CQDs = 15 mg of CQDs.

**II. Fraction of CQD solution consumed per layer:**

Fraction of CQDs from a solution drop that ends up forming a single layer is calculated using the following formula:

\[
\text{Fraction of CQDs} = \frac{\text{Mass of CQDs in a layer (before exchange)}}{\text{Mass of CQDs in the solution dropped to spin-cast a layer}}
\]

**Mass of CQDs in the solution dropped to cast a layer:**

Volume of solution dropped per layer = 50 ul.

This gives a CQD mass of **2.5 mg** for the 50 mg/ml concentration and **5 mg** for 100 mg/ml concentration, per layer.

**Mass of CQDs in a layer (before exchange):**

To measure film density, Octane redispersal experiments were performed on 50 mg/ml CQD thin film coated QCM-D sensors. Density was measured to be 2.42 g/cm\(^3\). We take the same for 100 mg/ml dots.

Dimensions of the substrate = 2x2 cm\(^2\).

Pristine film thickness per single layer = 80 nm (or 250 nm for 100 mg/ml).

Therefore, Volume of the single-layer solid film (before exchange) = 320 x 10\(^{-7}\) cm\(^3\) (for 50 mg/ml) and 1000 x 10\(^{-7}\) cm\(^3\) (for 100 mg/ml).

So,

Mass of CQDs in a single layer = 320 x 10\(^{-7}\) x 2.42 = 774.4 x 10\(^{-7}\) g = 77.44 \(\mu\)g. (FOR 50 mg/ml film)
Mass of CQDs in a single layer = \(1000 \times 10^{-7} \times 2.42 = 2420 \times 10^{-7} \) g = 242 \(\mu\)g. (FOR 100 mg/ml film).

So, the fraction can now be obtained plugging in these values into the equation:

\[
\text{Fraction (50 mg/ml case)} = \frac{77.4 \mu g}{2.5 \times 10^3 \mu g} = 3.1 \times 10^{-2}
\]

Similarly,

\[
\text{Fraction (100 mg/ml case)} = \frac{242 \mu g}{5.0 \times 10^3 \mu g} = 4.84 \times 10^{-2}
\]

Consumption efficiency = \(\frac{(4.84 - 3.10) \times 10^{-2}}{3.10 \times 10^{-2}}\) x 100 \%

\~ 56 \%

The 3 LbL architecture therefore makes use of ~56 \% of the CQDs solution per layer that otherwise gets wasted in the 10 LbL strategy.

### 4.4 Conclusions

In summary, we have provided a fundamental and holistic understanding of the nature of solid-state ligand exchange process in the context of state-of-the-art PbS CQD solar cell fabrication methods at the time this thesis research started. Interactions of the ligand and process solvents with the CQDs have been thoroughly probed employing a suite of spectroscopies.

First, we have demonstrated that the exchange process is dominated by two contrasting linker concentration regimes. The exchange is complete only for higher linker concentrations when the CQD absorber reaches a certain final thickness, inter-dot spacing,
density and surface ligand coverage, leading to better performing solar cells. As the concentration is reduced, the absorber layer properties undergo a ‘step-like’ transition, with lower concentrations leading to unexchanged films. These findings explain as to why all the previous CQD solar cell reports have relied on higher ligand concentrations for effective solid-state exchange.

Second, we have studied the process solvent-CQD interactions and gleaned information on the role of solvent environment on CQD solar cell manufacturability and performance. 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. Understanding of solvent interactions with CQD films has led to the development of more efficient processing conditions based on use of ACN which allow us to achieve state-of-the-art performance using only three steps for active layer deposition. This work enhances the opportunity to fabricate solar cells in a more scalable manner, though significant work remains to be done in this regard.
Chapter 5

Remote Molecular Doping of CQD Absorbers in p-n Heterojunction Solar Cells

5.1 Introduction

There has been a significant interest in tuning the carrier concentration of CQD solids by remote doping. Electrochemical and solution-phase doping schemes have been attempted to tune the electrical conductivity over several orders of magnitude. However, there exist to date no examples of straightforward single-step, solution-processed doping that translates directly into solar cell efficiency enhancement. Remote doping is a versatile strategy that does not interfere with CQD surface chemistry, inter-dot spacing, and film order at the nanoscale. It is free from steric hindrance and can complement existing solution and solid-state ligand-exchange schemes. The observation of remote electron transfer in CdSe CQDs opened the door to realizing successful doping schemes in CQDs without resorting to chemical modification of CQD surfaces.\cite{77} Recently, remote passivation of in-gap trap states was demonstrated by introducing ZnO nanocrystals into the CQD solid, leading to suppression of trap-assisted carrier recombination.\cite{96}

In this chapter, we take the view that a single-step, post-deposition remote doping protocol that can treat CQD solids could be a robust and highly desirable platform for enabling the controlled net doping and trap passivation of CQD solids for a wide gamut of applications. We demonstrate that soluble molecular dopants with carefully selected energetics and sufficiently small size infiltrate and dope PbS CQD solids. The remote doping is achieved in a single step without altering the deposition and exchange protocols of the CQD solid,
making this a highly versatile scheme. We consider a variety of doping scenarios by employing a library of metal-organic complexes with different energetics (electron affinity, EA and ionization energy, IE). Deep EA complexes (oxidants) are found to shift the Fermi level of the CQD solids towards the valence band edge, as evidenced by UPS, indicating p-doping. Reductants with low effective IEs result in n-doping of the solids; however, the shift of the Fermi level for this case is minor. Employing UPS, we find that the lower concentrations lead to efficient electron removal/addition, while higher concentrations also result in significant surface-dipole formation. The facile procedure involves soaking the CQD solid into the dopant solution. The benefits of this solid-state remote doping scheme are demonstrated in the context of depleted p-n heterojunction CQD solar cells, where p-doping of the CQD absorber layer effectively removes mid-gap electrons and suppresses traps. This renders the absorber layer substantially intrinsic and leads to a ca. 25% enhancement in PCE over the reference case. Our demonstration proves facile and scalable control of carrier concentration and in-gap trap states in CQD solids. Given the vast number of available organic and metal-organic dopants, it opens new and facile routes to tuning the properties of CQD solids for photovoltaics, optoelectronics and other applications.

Findings presented in this chapter were published in ACS Energy Lett. in 2016.\cite{146}

5.2 General remote molecular doping platform for CQD solids

We begin by presenting the various doping scenarios examined in the study and the associated changes to the CQD band structures (Figure 5.1). We chose three metal-organic complexes having deep EA (p-dopants) and an organometallic dimer with shallow effective IE (n-dopant), with respect to the CQD energetics. Schematics represent the energetics of
the molecules and the CQD solids and the chemical structures of the various molecules involved. The doping procedure involved briefly soaking the CQD layer in a solution of dopant and ACN. ACN was chosen as the solvent based on previous results which suggest that ACN, being aprotic and a high-dipole-moment solvent, is benign to the ligands on the CQD surface, as indicated in the previous chapter.[137, 147] The standard protic solvent, MeOH introduces in-gap trap states over prolonged exposure of CQDs by leaching off the surface chloride atomic ligand. The molecule represented in Figure 5.1a, molybdenum tris(1-(trifluoroacetyl)-2-(trifluoromethyl)ethane-1,2-dithiolene) (Mo(tfd-COCF₃)₃,[136, 148] is a more soluble variant of molybdenum tris(1,2-bis(trifluoromethyl)ethane-1,2-dithiolene), Mo(tfd)₃, which has been successfully used to dope the hole transporting material (HTM) N,N'-di-[(1-naphthyl)-N,N'-diphenyl]-1,1'-biphenyl-4,4' diamine, (α-NPD), via co-evaporation in ultra-high vacuum.[149] The high EA (estimated to be >5.6 eV) makes it an oxidizing agent and, therefore, the conductivity enhancement was attributed to compensation of trap states and contribution of free carriers by hole-injection from the dopant. Nickel bis(1,2-bis(trifluoromethyl)ethane-1,2-dithiolene), Ni(tfd)₂, (Figure 5.1b), has a reduction potential of +0.33 V vs. FeCp₂⁺/0;[150] although its solid-state EA has not been directly measured, comparison of its electrochemistry with that of Mo(tfd)₃ suggests an EA of ca. 5.6 eV,[151] sufficiently oxidizing that it acts as p-dopant, accepting electrons from the valence band of CQDs (Figure 5.1a). Molybdenum tris(1-phenyl-2-benzoyl-1,2-dithiolene), Mo(PhBz-dt)₃, on the other hand, is much less oxidizing (−0.38 eV, which comparing to Mo(tfd)₃ corresponds to an EA of ca. 4.9 eV) and should, therefore, act as a weaker p-dopant (Figure 5.1c). Ruthenium (pentamethylcyclopentadienyl)(mesitylene) dimer, (RuCp*mes)₂ is a strong n-dopant (Figure 5.1d) with effective potential for the
monomer cation/neutral dimer redox couple of ca. –2.0 V vs. FeCp$_2$$^{+/-0}$\cite{135} roughly corresponding to an effective solid-state IE of < 3.0 eV.\cite{152}
Figure 5.1. General molecular doping platform for CQD solids. The doping scenarios examined in this study are demonstrated. The estimated EA (red) and effective IE (blue) molecular levels are shown corresponding to each dopant relative to the energetics of the CQD. (a) Mo(tfd-COClF)_{3} and (b) Ni(tfd)_{2} are expected to behave as strong p-dopants due to their deep EA, compared to the band
structure of CQDs. (c) Mo(PhBz-dt)$_3$, with a shallower EA, behaves as a weak p-dopant. (d) (RuCp*mes)$_2$ is a strong n-dopant having a low effective IEs. These expectations are largely verified by UPS measurements which show relevant changes to the band structures. The weak p-dopant shows a negligible shift to the Fermi level, while the strong dopants generally cause major shifts to the Fermi level. Importantly, these Fermi level changes are associated with corresponding shifts to the Pb 4f core levels, as evidenced by XPS. Significant changes to the vacuum level (dipole formation) are observed when the CQD solids are treated with high concentrations of the dopants (1 mg mL$^{-1}$).
We sought to probe band structure changes that might give experimental evidence of electron transfer. We used UPS, a direct probe electronic band structure – the density of states below the Fermi level (E_F) of a material – widely used to study the effects of changes to nanomaterial surfaces on their band structures.\textsuperscript{[76, 137, 153-154]} The challenges associated with UPS measurements on larger size CQDs (small band gap), have been recently highlighted and linked to the extremely low density of states (DOS) at the VBM.\textsuperscript{[155]} However, the CQDs considered in our work have a larger band edge as they are small-size particles; hence the UPS results are expected to be reliable, commensurate with the findings of the report.\textsuperscript{[155]}

Direct evidence of an electron transfer in doped MoS\textsubscript{2} films has recently been reported by Tarasov \textit{et al.} where a shift in the E\textsubscript{F} was observed and ascribed to transfer of electrons/holes.\textsuperscript{[156]} This shift corresponded to a similar shift in the Mo core level peak measured by XPS. CQD films obtained via spin coating were treated with various concentrations of the dopant solution to track changes to the band structure. Corresponding to the schematics in Figure 5.1 are the band structures of the doped CQDs as measured by UPS. Each set shows \textit{three} scenarios: undoped CQD baselines, CQDs doped with low concentration dopant solution and CQDs doped with high concentration dopant solution.

The effect of doping on the band structures can be broadly categorized into two regimes: \textit{smaller doping concentrations} lead to changes of the Fermi level, which moves towards the valence band for p-doped films and towards the conduction band for n-doped films, \textit{while higher doping concentrations} also result in changes to the vacuum level. A more detailed discussion of these two doping regimes will be done later.
Figure 5.2. Pb 4f core levels for the strong (Ni(tfd)$_2$) and weak (Mo(PhBz-dt)$_3$) p-doped CQD solids, as measured by XPS. Ni(tfd)$_2$ leads to a significant shift of the core level by ~0.3 eV whereas no apparent peak shift is observed for Mo(PhBz-dt)$_3$. These shifts correspond to the corresponding shifts in the Fermi level observed from UPS. The red component of the peak corresponds to the Pb bonded to S atoms in the CQD. The dashed blue component is the Pb bonded to the MPA ligand while the solid blue component is the tiny amount of Pb-O.

The observation of Pb 4f core level shifts from XPS corresponds to the electron transfer as a result of doping, as shown in Figure 5.2.\cite{156} We did not observe any new chemical components in the Pb or S core level peaks of the doped CQDs that might give an indication that of a chemical interaction of the dopants with the CQDs, confirming this to be remote doping.

5.3 P-doping the MPA-PbS CQD absorber

The fact that we observe effective p-doping of the CQD solids is of interest for solar cells in which the CQD solid is employed as the absorber layer. These absorber layers, which form a heterojunction with an n-type metal oxide (for example, titanium dioxide) have been recently suggested to be slightly n-type.\cite{122} We, therefore, took the view that a mild, post-
synthesis p-doping step should make the absorber layer more intrinsic leading to enhancement of $V_{OC}$ without compromising the depletion width, eventually enhancing the solar cell performance.

![Molecular orbital energies for the isolate dopant molecule calculated by DFT.](image)

**Figure 5.3.** Molecular orbital energies for the isolated dopant molecule calculated by DFT.

Encouraged by the successful deployment of Mo(tfd)$_3$ as a strong p-dopant for α-NPD, we chose the non-symmetrical Mo(tfd-COCF$_3$)$_3$, (ca. 0.11 V more oxidizing than Mo(tfd)$_3$ in solution$^{[148]}$) discussed in brief earlier (Figure 5.1a). The enhanced solubility of Mo(tfd-COCF$_3$)$_3$ makes it compatible with solution processing and, therefore, better suited for scalable manufacturing of CQD solids and devices thereof. We carried out a more in-depth study of the the scenario of CQD solid p-doped with Mo(tfd-COCF$_3$)$_3$. The orbital energies for isolated Mo(tfd-COCF$_3$)$_3$ were calculated using DFT and are shown in **Figure 5.3.**
Figure 5.4. (a) DFT simulations yield a picture qualitatively similar to that estimated from experiment, in which the molecule’s LUMO (depicted by the black arrow) occurs at similar energy to that VBM of the CQDs, opening the possibility of the depopulation of the mid-gap or VB electrons, depending upon the dopant concentration, via remote doping. Photoemission spectroscopy data for PbS CQD films treated with solutions of varying dopant concentrations. (b) VBM (blue) and Fermi levels (black) were acquired using UPS while the CBM (red) were estimated by adding the optical band gap (1.3 eV) to the VB energy. This is justified in the current case since the exciton binding energy (BE) for PbS CQDs is low (~0.09 eV). For low doping concentrations, the Fermi level is found to shift moderately towards the VB indicating mid-gap electron transfer. Higher doping concentrations however lead to valence electron transfer and surface dipole formation causing significant lowering of the vacuum level and Fermi level relative to vacuum. The energies of the dipoles formed (ED) are extracted from these results and shown in (c). The Pb 4f core level peak, obtained from high resolution XPS is shown in (d) for the MPA baseline and the maximum doping cases. The red component of the peak corresponds to the Pb bonded to S atoms in the CQD. The dashed blue component is the Pb bonded to the MPA ligand while the solid blue component is the tiny amount of Pb-O. The peak shows
a ca. 0.2 eV shift to lower binding energy for the maximum doping concentration which is commensurate with the Fermi level shift observed for that concentration due to electron transfer ($\Delta E_{VB}$ in (c)).

DFT simulation of the energetics at the interface of this system supports the possibility of remote charge transfer. The results are shown in Figure 5.4a. Hybrid ligand-exchanged CQDs (involving a solid-state exchange with MPA ligand, preceded by a halide-SolEx$^{[12]}$ were considered for these calculations. The DOS corresponding to Mo belong to the dopant. The results show a close proximity of the dopant’s LUMO with the VBM of the CQDs. This suggests the possibility that the dopant can extract mid-gap or valence electrons from the CQDs via electron transfer.

In Figure 5.4b we show the electronic band structures of the CQD solids for the various doping scenarios, experimentally determined by a combination of UPS and optical absorption. The band structures remain almost unchanged for lower doping concentrations, while significant changes are observed for higher concentrations. The UPS spectra are shown in Figure 5.5 and show the secondary-electron cutoffs (Figure 5.5a) and the valence band onsets (Figure 5.5b).
The total change in the work function of a doped CQD film (compared to the undoped, MPA baseline), denoted $\Delta \phi$, comprises the Fermi level shift with respect to the VBM owing to remote electron transfer ($\Delta E_{VB}$) and the shift in the vacuum level due to dipole formation on the CQD surface ($E_D$). This allows us to determine the energies $E_D$ for the various doping scenarios (Figure 5.4c). We find that as the doping concentration increases, the surface dipole strengthens. This can be expected since for 1.0 mg mL$^{-1}$ doping concentration, each CQD is surrounded by ca. 12 dopant molecules, as found from XPS atomic quantification. This drops to ca. 0.3 dopants per CQD for $10^{-2}$ mg mL$^{-1}$ dopant concentration, which agrees with the negligible value of $E_D$ for this case (Figure 5.4c).

To arrive at this conclusion, we have combined the XPS atomic quantification and insights from previously published DFT results on PbS CQDs,$^{[12]}$ as discussed here.
Table 5.1. Relative atomic concentration of Pb, S, C and F as found from high-resolution XPS. F/Pb ratio is found to increase with the doping concentration. Accordingly, the number of dopant molecules per CQD, $\chi$, also increases.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pb</th>
<th>S</th>
<th>C</th>
<th>F</th>
<th>F/Pb</th>
<th>$\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPA baseline</td>
<td>32.8</td>
<td>29.2</td>
<td>38.0</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.0 mgmL$^{-1}$</td>
<td>27.9</td>
<td>24.4</td>
<td>35.2</td>
<td>12.5</td>
<td>0.45</td>
<td>12</td>
</tr>
<tr>
<td>0.1 mgmL$^{-1}$</td>
<td>30.4</td>
<td>28.8</td>
<td>33.6</td>
<td>7.1</td>
<td>0.23</td>
<td>6</td>
</tr>
<tr>
<td>0.01 mgmL$^{-1}$</td>
<td>33.2</td>
<td>30.8</td>
<td>35.2</td>
<td>0.4</td>
<td>0.01</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 5.1 shows the relative atomic concentrations of the various elements in the control and doped CQD films (hybrid ligand exchanged). $\chi$ represents the number of dopant molecules per CQD and has been approximated, for the various doping concentrations, as follows. Each CQD has been considered to be containing ~500 Pb atoms in accordance with published DFT data. The dopant molecule contains 18 F atoms. Since F/Pb can be measured from XPS, it is possible to find, $\chi = (F/Pb)/(18/500)$.

We propose that the interface-dipole effects originate at the surface of each CQD as a result of dopant penetration through the nanoscale voids in the CQD solid, rather than being localized at the surface of the CQD film; we do not observe any accumulation of the dopants on the film surface, as evidenced from SIMS, even for the largest concentrations (Figure 5.6).
**Figure 5.6.** SIMS depth profiles for the CQD films doped with (a) 0.1 mg mL\(^{-1}\) and (b) 1.0 mg mL\(^{-1}\) dopant solutions\(^{[157]}\). The films were deposited on SiO\(_2\) wafers. The fluorine signal (green) is found to be enhanced for the 1.0 mg mL\(^{-1}\) treated film, (b). Importantly, dopant molecules (represented by fluorine) are found to penetrate through the films and no surface accumulation is observed. A single layer in the LbL deposition recipe for CQDs yields a ca. 30 – 40 nm layer. Films for these measurements were restricted to a single layer since deposition of more than a layer was found to yield highly inhomogenous films incompatible with the requirement for SIMS measurements.

The large \(\Delta \phi\) values for this regime also involve a significant \(\Delta E_{VB}\) hinting towards removal of valence electrons. For smaller concentrations, changes in \(\phi\) are largely associated with changes to \(E_F\) from mid-gap electron transfer (**Table 5.2**); in this regime a significant shift in \(E_F\) relative to \(E_{VBM}\) requires fewer dopants than when the Fermi level approaches the band edge and so the resultant interface dipole is relatively small. We also observe a ca. 0.2 eV shift of the Pb 4f core level peak (for 1.0 mg mL\(^{-1}\) doping concentration) towards a
lower binding energy compared to an undoped CQD solid, which can be ascribed to the downward shift of the Fermi level associated with p-doping (Figure 5.4d).[156] Core level shifts were observed for other concentrations as well and agreed with the accompanying Fermi level shifts.

**Table 5.2.** Change in work function, $\Delta \phi$, and the change in Fermi level with respect to the VBM, $\Delta E_{VB}$ are used to calculate the induced dipole, $E_D$, for the various doping scenarios using the equation, $\Delta \phi = \Delta E_{VB} + E_D$. The changes are measured with respect to the MPA baseline.

<table>
<thead>
<tr>
<th>Dopant concentration (mg/mL$^{-1}$)</th>
<th>$\phi$ (eV)</th>
<th>$\Delta \phi$ (eV)</th>
<th>$E_{VB}$ (eV)</th>
<th>$\Delta E_{VB}$ (eV)</th>
<th>$E_D$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-5}$</td>
<td>4.24</td>
<td>0.07</td>
<td>0.75</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>4.28</td>
<td>0.11</td>
<td>0.71</td>
<td>0.08</td>
<td>0.03</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>4.31</td>
<td>0.14</td>
<td>0.70</td>
<td>0.09</td>
<td>0.05</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>4.40</td>
<td>0.23</td>
<td>0.61</td>
<td>0.18</td>
<td>0.05</td>
</tr>
<tr>
<td>0.1</td>
<td>5.14</td>
<td>0.97</td>
<td>0.51</td>
<td>0.28</td>
<td>0.69</td>
</tr>
<tr>
<td>1.0</td>
<td>5.40</td>
<td>1.23</td>
<td>0.50</td>
<td>0.29</td>
<td>0.94</td>
</tr>
</tbody>
</table>

While photoelectron spectroscopies are near-surface measurements, we have confirmed the dopant infiltrates the bulk of the CQD solid by SIMS measurements (Figure 5.6). Despite this infiltration, the dopant does not alter the inter-dot spacing, as demonstrated by GISAXS (Figure 5.7a). Consistent with the GISAXS data, no observable change in the overall film thickness was observed following doping, confirming the CQD solid is not swollen by infiltration of dopant molecules (Figure 5.7b).
Figure 5.7. (a) Inter-dot spacing found by azimuthally integrating the GISAXS intensities. The spacing achieved after MPA ligand exchange (ca. 3.7 nm) remains unchanged upon doping. (b) VASE was used to precisely measure the CQD film thickness upon doping. A 2-layer stack was fabricated by spin coating on SiO$_2$ wafer. This was followed by the doping step. A ~50% reduction in film thickness was observed after the ligand exchange step\textsuperscript{[137]} however the thickness did not show any observable change upon doping or the subsequent ACN rinse.

5.4 Effect on CQD solar cell performance

Having gained sufficient fundamental insights into the remote electron transfer from the CQDs to Mo(tfd-COCF$_3$)$_3$ throughout the bulk of the CQD solid, we were interested in studying its effects on solar cell performance. Based upon the experimental and computational insights provided in Figure 5.4, we simulate the solar cell performances for undoped, optimally doped and overdoped CQD absorber layers. An untreated MPA film was modeled as n-type with a doping concentration of 1×10\textsuperscript{16} cm\textsuperscript{-3}.\textsuperscript{[75, 116]} The optimally treated film was graded doped from 3×10\textsuperscript{16} cm\textsuperscript{-3} p-type in the last layer to 0 near the TiO$_2$ interface, and overtreated films were considered either as 3×10\textsuperscript{16} cm\textsuperscript{-3} throughout or graded doped from 1×10\textsuperscript{17} cm\textsuperscript{-3} to 0. The simulated $J$-$V$ curves are shown in Figure 5.10b and suggest that doping leads to $V_{OC}$ improvement due to the movement of the Fermi level.
closer to the band edge. Overdoping, however, collapses the depletion region leading to loss of $J_{SC}$ and hence the overall device performance (see Figure 5.8). While these simulations make certain assumptions and simplifications, they suggest that remote molecular doping should influence the performance of CQD solar cells.

**Figure 5.8.** Simulated energy band diagrams inside the CQD absorber layer for various doping scenarios. The Fermi levels are found to get closer to the band edges upon doping. However, overdoping, (c), leads to a collapse of the depletion width causing a reduction in $J_{SC}$ and therefore the overall device performance.

We turn our attention to incorporating the doped CQD solids into solar cells. One of our first trials of arriving at a working doping scheme is illustrated in Figure 5.9a, wherein
every layer in the LbL stack was individually doped. The scheme failed to show performance enhancement (Table 5.3), most likely due to overdoping of the film.

Figure 5.9. An alternate doping scheme was tried involving doping of each individual CQD layer in the LbL stack, shown in (a). The CQD layers were sequentially deposited (Step 1) followed by doping of each individual layer (Step 2). Steps 1 and 2 were repeated till the desired CQD layer thickness (Step 3) was achieved. The final device setup is shown in (b). The device performances, (c), were found to decrease (Table 5.3 below)
Table 5.3. Device parameters for solar cells obtained by doping each individual CQD layer separately.

<table>
<thead>
<tr>
<th>Device</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPA baseline</td>
<td>15.01</td>
<td>0.500</td>
<td>48.0</td>
<td>3.60</td>
</tr>
<tr>
<td>0.01 mgmL⁻¹</td>
<td>14.51</td>
<td>0.491</td>
<td>41.3</td>
<td>2.95</td>
</tr>
<tr>
<td>0.1 mgmL⁻¹</td>
<td>3.54</td>
<td>0.312</td>
<td>26.0</td>
<td>0.29</td>
</tr>
<tr>
<td>1.0 mgmL⁻¹</td>
<td>1.72</td>
<td>0.198</td>
<td>27.1</td>
<td>0.09</td>
</tr>
</tbody>
</table>

The doping strategy adopted successfully is outlined in Schematic 1. The standard procedure of LbL fabrication of the CQD absorber was followed with the difference that only the final CQD film was dipped in the dopant solution for an adjusted time before removal of the solution and solvent washing. This has the benefit of not requiring an extra step to be added to the already onerous LbL process.
Schematic 5.1. Procedure of molecular doping demonstrated in this study. (1) LbL deposition of the CQD absorber layer via spin coating involves sequential deposition of CQDs (capped with OA ligands) followed by solid-state ligand exchange with MPA and a subsequent MeOH washing step. This cycle was repeated typically ten times until the targeted film thickness (~300 nm) was achieved. (2) The film was soaked in the dopant solution (dissolved in ACN) for an optimized time duration before spinning off the excess solution. This was followed by a rinsing step in ACN to wash off any residual dopant and dry the sample (3) for use in subsequent solar cell fabrication steps.
In Figure 5.10c we show the experimentally measured $J-V$ curves for various doping concentrations. The device parameters are summarized in Table 5.4. It is evident that the device performance increases for low doping concentrations, whereas higher concentrations lead to performance degradation.

**Figure 5.10.** (a) Schematic of the depleted heterojunction (DHJ) device architecture employed in this study. (b) Simulated $J-V$ curves showing an increase in overall performance enhancement for solar cells made using optimally doped CQD films, assuming a graded doping architecture. Overdoped films show a performance decrease. (c) $J-V$ curves for solar cells made using CQD films treated with various doping concentrations and treatment times. (d) Averaged device parameters (PCE, $J_{SC}$ and $V_{OC}$), are shown as a
function of the doping concentration for a soaking time of 3 mins. The data highlights that $10^{-2} \text{ mg mL}^{-1}$ is the optimized doping concentration for achieving best performing devices. We observe device performance enhancement for solar cells soaked in low doping concentrations ($10^{-3} \text{ mg mL}^{-1}$). Performance is found to increase with longer soaking times. However, an extended soaking (15 mins) leads to decrease in device performance, an effect we ascribe to overdoping of the CQDs. Next, we test devices with higher doping concentrations ($10^{-2} \text{ mg mL}^{-1}$) and achieve the maximum performance boost for 3 mins soaking time. The PCE of 7.8% obtained for this doping condition is a 24% enhancement over the undoped baseline. We observe that at this elevated doping concentration, overdoping occurs at only 4 mins of soaking leading to performance degradation. Doping the absorber layers with a high concentration (0.1 mg mL$^{-1}$) leads to immediate overdoping of the CQD solid and hence poorly performing solar cells. These experiments indicate that doping with an ACN solution can be effectively carried out in a single step in contrast to the repetitive ligand exchange steps involved in the CQD solid fabrication. The soaking in dopant solution allows the dopants to penetrate and diffuse into the entire CQD film, as indicated by SIMS measurements (Figure 5.6). The optimized doping time and dopant solution concentration pair allows for the optimal dopant concentration levels to be found for any given CQD solid. This is highlighted in Figure 5.10d where the various device parameters are plotted as a function of doping concentration for a soaking time of 3 mins.
Table 5.4. Summary of the device parameters for the various doping scenarios. The reported device parameters ($J_{SC}$, $V_{OC}$, FF and PCE) have been averaged over 5-10 devices. The PCE values in brackets represent the best performing solar cells for each category.

<table>
<thead>
<tr>
<th>Device</th>
<th>Soaking time (mins)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>$R_{shunt}$ (k$\Omega$/cm$^2$)</th>
<th>$R_s$ (\Omega/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPA baseline</td>
<td>18.4±0.9</td>
<td>0.59±0.01</td>
<td>55.6±3.1</td>
<td>6.1±0.2 (6.3)</td>
<td>1.98</td>
<td>8.0</td>
<td></td>
</tr>
<tr>
<td>$10^{-2}$ mg mL$^{-1}$</td>
<td>3</td>
<td>21.3±0.2</td>
<td>0.60±0.00</td>
<td>50.4±1.2 (6.7)</td>
<td>3.49</td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>19.9±0.9</td>
<td>0.62±0.00</td>
<td>53.9±0.5 (6.9)</td>
<td>3.41</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>20.1±0.4</td>
<td>0.63±0.00</td>
<td>59.5±1.6 (7.6)</td>
<td>4.78</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>17.9±0.5</td>
<td>0.63±0.00</td>
<td>60.7±1.5 (6.9)</td>
<td>4.21</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>$10^{-3}$ mg mL$^{-1}$</td>
<td>3</td>
<td>20.8±0.9</td>
<td>0.63±0.00</td>
<td>58.3±0.7 (7.8)</td>
<td>6.29</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>18.0±0.6</td>
<td>0.60±0.00</td>
<td>53.1±2.3 (5.9)</td>
<td>2.78</td>
<td>7.7</td>
<td></td>
</tr>
<tr>
<td>0.1 mg mL$^{-1}$</td>
<td>3</td>
<td>15.7±0.7</td>
<td>0.55±0.00</td>
<td>51.2±2.1 (4.5)</td>
<td>5.89</td>
<td>8.2</td>
<td></td>
</tr>
</tbody>
</table>

The evolution of the device parameters, under illumination and in dark, for the undoped control and the optimally doped solar cells is shown in Figure 5.11. The devices show photostability, however, are found to degrade over a period of several weeks of storage.
Importantly, doped devices do not degrade at a faster pace than the control undoped devices.

![Figure 5.11. Photostability of the various device parameters, (a) J_{SC}, (b) V_{OC} and (c) PCE for the undoped control and optimally doped solar cells are shown. (d) Stability of the devices was also tested over time as they were aged inside the N\textsubscript{2} glove box.]

The shunt resistance, R_{shunt}, for all the better-performing doped devices is higher relative to the undoped controls, which provides evidence for the suppression of trap-assisted carrier recombination. We suggest that the large surface dipoles introduced in conditions of higher doping concentration and the associated valence electron removal, as evidenced by UPS, lead together to the formation of localized energy barriers to efficient charge transport, causing performance degradation. In fact, we observe no change in the absorption of the CQD solids (Figure 5.12) for nearly all doping conditions with the exception of 1.0 mg mL\textsuperscript{-1}, which shows evidence of exciton quenching. Expectedly, a similar quenching is observed in the transient absorption measurements for the highest
doped solid (Figure 5.13), while no changes are observed in the carrier dynamics. These observations agree with the scenario of valence electron removal at high doping concentrations, as discussed above.

Figure 5.12. The absorbance of the films remains essentially unchanged upon doping. A slight decrease in exciton absorption is found for 1 mgmL\(^{-1}\) doping concentration as highlighted in the inset (red spectrum).
Figure 5.13. Transient absorption data for the (a) control (undoped, MPA-exchanged films), (b) optimally doped \(10^{-2} \text{ mg mL}^{-1}\) and (c) overdoped \(1 \text{ mg mL}^{-1}\) films is shown. (d), (e) The overdoped film shows quenching at the exciton wavelength (950 nm).

This is also supported by a quenching of the PL signal at the exciton energy (see Figure 5.14). Hence, only in-gap electron removal through ultra-low doping of the CQD solid leads to PV performance enhancements.
Figure 5.14. PL spectra for CQD films doped with different doping concentrations. The higher concentrations lead to quenching of the exciton emission around 1.25 eV which might be due to the significant removal of CQD valence electrons by the dopant at those concentrations. This is evident from the relatively large shift of the Fermi level for the high doping concentrations ($\Delta E_{\text{VB}}$ in Table 5.2). The spectra have a non-Gaussian shape with the 1.0 mgmL$^{-1}$ doped sample’s spectrum showing the maximum deviation from Gaussian nature. We were not able to ascertain the reason behind this. We observe a reflection peak from the glass substrate around 1.4 eV which was used to normalize the spectra.

The absorber layer thickness in the solar cells reported above is ca. 300 nm which consists of a ca. 250 nm depletion region. In general, doping of the depletion region would lead to a decrease in the depletion width and hence in the solar cell performance. However, it should be possible to optimally p-dope an initially n-type absorber layer, leading to gains in the $V_{\text{OC}}$ without hurting the depletion region. Indeed, as shown recently, the Fermi level of the MPA-PbS CQD solid lies slightly above mid-gap and as such the doping step makes the absorber layer more intrinsic via p-doping, instead of leading to a depletion region collapse. We further tested this hypothesis by fabricating solar cells with thin
absorber layers (ca. 150 nm). Doping of these thin layers involved ~1 min soaking. These thin solar cells also showed performance enhancement (Figure 5.15 and Table 5.5, 5.6) consistent with the picture of “p-doping” leading to the removal of the trap states that lead to n-type behavior for the undoped MPA-PbS CQD layer. This helps us push the limits on the maximum PCE that can be achieved with an MPA-PbS CQD solar cell.
Figure 5.15. (a) Doped solar cells employing a ca. 150 nm MPA-PbS CQD absorber layer. (b) Lower doping concentrations were found to increase the PCE, as shown in Table 5.5 below. The corresponding EQE measurements are shown in (c). (d) The CQD absorber
layer was deposited on room temperature processed TiO$_2$. No high temperature annealing was needed. (e) Doping was found to improve the overall performance (see Table 5.6 below).

Table 5.5. Device parameters for solar cells obtained by doping thin-absorber layer solar cells.

<table>
<thead>
<tr>
<th>Device</th>
<th>J$_{sc}$ (mA/cm$^2$)</th>
<th>Voc (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>R$_{shunt}$ (Ω/cm$^2$)</th>
<th>R$_s$ (Ω/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPA baseline</td>
<td>19.0</td>
<td>0.471</td>
<td>43.6</td>
<td>3.90</td>
<td>957</td>
<td>5.2</td>
</tr>
<tr>
<td>$10^{-6}$ mgmL$^{-1}$</td>
<td>20.3</td>
<td>0.497</td>
<td>47.2</td>
<td>4.76</td>
<td>1096</td>
<td>3.7</td>
</tr>
<tr>
<td>$10^{-5}$ mgmL$^{-1}$</td>
<td>18.6</td>
<td>0.505</td>
<td>45.7</td>
<td>4.31</td>
<td>1318</td>
<td>5.3</td>
</tr>
<tr>
<td>$10^{-4}$ mgmL$^{-1}$</td>
<td>17.6</td>
<td>0.497</td>
<td>46.6</td>
<td>4.09</td>
<td>1264</td>
<td>4.1</td>
</tr>
<tr>
<td>$10^{-3}$ mgmL$^{-1}$</td>
<td>18.7</td>
<td>0.466</td>
<td>42.3</td>
<td>3.69</td>
<td>1206</td>
<td>6.4</td>
</tr>
<tr>
<td>0.1 mgmL$^{-1}$</td>
<td>9.3</td>
<td>0.232</td>
<td>29.5</td>
<td>0.64</td>
<td>337</td>
<td>10.5</td>
</tr>
</tbody>
</table>

Table 5.6. Summary of the device parameters for the room temperature processed TiO$_2$-based solar cells. All the parameters are found to increase for lower doping concentrations. The significant increase in R$_{shunt}$ suggests that doping leads to a reduction in trap-assisted recombination.$^{[96]}$

<table>
<thead>
<tr>
<th>Device</th>
<th>J$_{sc}$ (mA/cm$^2$)</th>
<th>Voc (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>R$_{shunt}$ (Ω/cm$^2$)</th>
<th>R$_s$ (Ω/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPA baseline</td>
<td>17.5</td>
<td>0.434</td>
<td>49.5</td>
<td>3.75</td>
<td>1187</td>
<td>2.1</td>
</tr>
<tr>
<td>$10^{-4}$ mgmL$^{-1}$</td>
<td>19.8</td>
<td>0.511</td>
<td>52.3</td>
<td>5.29</td>
<td>1952</td>
<td>3.1</td>
</tr>
<tr>
<td>$10^{-2}$ mgmL$^{-1}$</td>
<td>18.7</td>
<td>0.492</td>
<td>50.8</td>
<td>4.68</td>
<td>1670</td>
<td>2.6</td>
</tr>
<tr>
<td>1.0 mgmL$^{-1}$</td>
<td>6.2</td>
<td>0.434</td>
<td>35.0</td>
<td>0.94</td>
<td>1808</td>
<td>3.3</td>
</tr>
</tbody>
</table>

5.5 Conclusions

A general, facile and solution process-compatible remote doping strategy for PbS CQD solar cells has been successfully demonstrated. The strategy employs a library of metal-organic molecules which do not require chemical bonding with the CQD surface. High effective EA and low IE complexes, respectively, p- and n-dope the CQD solids. We
demonstrate the advantage of remote molecular doping in the context of solar cells by utilizing a molecule with an EA larger than the ionization energy of the CQDs, enabling remote electron transfer (as also suggested by DFT). We carry out an in-depth study of the effect of doping on the electronic band structure of the CQDs, using UPS. Our study suggests the presence of two contrasting doping regimes – one leading to in-gap electron transfer and the second also resulting in the formation of large surface dipoles; the latter being deleterious to device performance. Exploiting the former – the low doping concentration regime – we suppress effectively clean the CQD band edges, leading to a >20% increase in solar cell performance. Our mechanistic study furthers the fundamental understanding on solution processing-friendly remote molecular doping of CQD solids and presents the most versatile and scalable approach yet for achieving controlled net doping of CQD solids.
Chapter 6

Remote Molecular Doping of the CQD Hole Transporting Layer in n-i-p Solar Cells

6.1 Introduction

In this chapter, we effectively extend the application gamut of the remote molecular doping platform developed in Chapter 5 to include the latest, high-performing CQD solar cells based on an n-i-p device architecture.\textsuperscript{[3]} These solar cells exploit a CQD absorber, exchanged via SolEx (with hybrid perovskites, MAPbI$_3$, or lead halides, PbX$_2$), deposited in a single-step on a ZnO ETL. This assembly is topped by a thin EDT-PbS CQD solid which behaves as the HTL.\textsuperscript{[13, 29]}

We identify a key challenge associated with this promising device architecture. We find that the architecture suffers from an un-optimally doped CQD-HTL that causes limited band bending near the hole-collecting electrode leading to hole extraction issues during device operation. Mildly p-doping the CQD-HTL via a brief soaking step alleviates this issue and improves device performance.

6.2 Issue with the n-i-p CQD solar cell architecture: un-optimally p-doped HTL

The halide-ligand passivated CQD solids are known to exhibit an n-type character, and their Fermi level ($E_F$) is closer to the conduction band edge.\textsuperscript{[3, 94, 122]} This n-character puts restrictions on the ETL, which needs to be highly degenerate in order for sufficient band bending to be retained at the MPP.\textsuperscript{[159]} Importantly, this also suggests that non-optimally doped EDT-CQD solids would lead to similar issues with band bending near the hole-
collecting electrode, affecting charge extraction at the MPP. Doping of the EDT-HTL has however remained largely unexplored thus far.

A controlled electron removal from the EDT-CQD layer (p-doping) should effectively deepen its $E_F$. This would, in turn, result in a favorable band bending at the hole-collecting interface that improves charge extraction and, therefore, the solar cell performance. However, the introduction of p-dopants within the CQD absorber solid can lead to harmful side effects, such as a significant decrease in carrier mobility,\cite{100,160} or a quenching of the exciton absorption.\cite{158} A strategy to controllably dope the CQD HTL without affecting its transport or absorption properties is therefore needed.

We take the view that this could be achieved by remote doping with small redox-active molecules, such as the ones introduced in Chapter 5. If appropriately designed, these molecules would be incorporated throughout the CQD HTL, withdrawing electrons without damaging transport characteristics. We design a facile molecular p-doping recipe to selectively dope the EDT-CQD based HTL. Such a recipe can be extended to a variety of CQD solar cell architectures which rely on a thin CQD solid as the HTL.\cite{9,122-124,159,161-162} We employ the large EA metal-organic complex, Mo(tfd-COCF$_3$)$_3$.\cite{136,163} This molecule, as we have demonstrated in Chapter 5, favors electron withdrawal in other CQD legacy absorber layers.\cite{164} We overcome the obvious technical challenge in these latest architectures of being able to selectively dope the HTL without altering the CQD absorber layer. This approach is demonstrated to work for MAPbI$_3$-PbS and PbX$_2$-PbS CQD absorbers, demonstrating its broad applicability to the latest generation of CQD ligand chemistries. The optimally p-doped HTL leads to an enhancement in the photocurrent and
FF as compared to the undoped control solar cells, which ultimately leads to a ca. 10% increase in PCEs.

The perovskite-shelled CQD solar cell architecture is shown in Schematic 1a. Photon absorption and photocurrent generation take place primarily in the thick MAPbI$_3$-PbS CQD layer.$^3$ Spin-cast ZnO nanoparticles were used as the ETL. Schematic 1b shows the Mo(tfd-COCF$_3$)$_3$ doping procedure. After the deposition of the EDT-PbS CQD hole extraction layer, the device is soaked briefly (~30 s) in an ACN solution of Mo(tfd-COCF$_3$)$_3$. ACN is known to be benign to the surface of CQD$_s$, as expanded upon previously in Chapter 4, unlike other protic solvents such as MeOH,$^{137}$ and was employed as an effective solvent for Mo(tfd-COCF$_3$)$_3$ dopant delivery.$^{164}$ We optimized the soaking time based on previous ACN-based ligand exchanges of OA-PbS CQDs in device architectures employing EDT-PbS CQD as the HTL,$^{3, 9, 29, 31, 122, 159, 161-162}$ where 30-60 s of soaking time leads to a complete ligand exchange.$^{165}$
Schematic 6.1. (a) Solar cell architecture employing a MAPbI₃-PbS CQD absorber layer obtained via a single-step deposition. (b) Schematic depicting the idea behind the doping strategy. A deep-LUMO metal-organic complex is used to extract electrons from the HTL, remotely p-doping the EDT layer. Black dashed lines represent the respective Fermi levels. The green arrow represents the expected electron transfer from the HTL to the dopant that results in p-doping (and not the flow of charges in the operating device).
6.3 P-doping the CQD HTL

To confirm that doping is predominantly limited to the CQD HTL overlayer, we analyzed the dopant concentration (Mo) through the CQD film using SIMS. To achieve detection by SIMS, a 1 mg mL\textsuperscript{-1} dopant concentration was considered since dopant was hard to detect at lower concentrations due to poor signal:noise ratio in the spectra. The 3D distribution of Mo within the CQD solid reveals a strong confinement of the dopant to the top few tens of nanometers, with a concentration that is reduced by two orders of magnitude after 80 nm (Figure 6.1a). Figure 6.1b shows the corresponding SIMS depth profiles. F and Mo dopant species are found to decrease significantly beyond a few tens of nanometers. All the elements show a steep decrease beyond ~150 nm which marks the bottom of the entire CQD layer considered for the SIMS measurements. It should be noted that these SIMS results represent only an approximation to the location of the dopant molecules. Being partially organic, the molecules are expected to be affected by preferential sputtering and matrix effects leading to quantification distortions.

Thus, although Figure 6.1(a) confirms that the dopant molecules are predominantly situated in the EDT-HTL, it is unclear whether a small amount of dopant may have also penetrated into the absorber layer. Nevertheless, we are encouraged by the predominantly near-surface confinement of dopant despite the use of a concentrated dopant solution (two orders of magnitude more concentrated than optimal solutions, as will be discussed below), which provides the stack with a larger supply of dopant for possible penetration into the active layer.
Figure 6.1. (a) 3D distribution for molybdenum from SIMS. (b) SIMS depth profiles for the various elements in the doped CQD HTL capping the CQD light absorber. (c) A PL suppression upon doping is suggestive of electron transfer from the CQD HTL to the dopant molecule. (d) Transient-absorption characteristics of the doped CQD solids remain unchanged relative to the undoped control. (e) TRPL data for the undoped and doped cases.
Successful doping of the CQDs was verified by PL measurements. EDT-PbS CQD films were fabricated on glass substrates for these measurements. Excitation was carried out using a 635 nm diode laser. The measurements confirm electron transfer from the CQDs to the dopant evident from the suppression of the PL intensity (Figure 6.1c). We also performed TRPL on these samples to confirm improvement in charge extraction. p-doped HTLs are expected to demonstrate a reduced carrier lifetime suggestive of enhanced hole extraction, as seen, for example, in a recent report which demonstrated performance enhancement in perovskite solar cells by employing a p-doped HTL.[166] The TRPL results are presented in Figure 6.1e and indicate a shorter lifetime for the doped sample. Fitting with mono-exponential decay functions indicates excited-state lifetimes of ~202 and ~119 ns for undoped and doped samples, respectively. No change in the intrinsic absorption is found as shown through the normalized transient-absorption characteristics (Figure 6.1d).

Efficient p-doping is expected to lead to a deepening of the E_F relative to the band positions and the vacuum level. We employed KP microscopy to characterize the work function difference of the different samples. KP measurements showed an increase in the work function of the CQD solids as the doping concentration was increased (Figure 6.2a). Changes to the overall work function, however, comprise of: i) changes to the E_F and ii) vacuum level shifts originating from surface dipoles. We were interested in determining up to what extent p-doping affects the E_F of the CQD solids without creating a dipole moment. To have a deeper insight into the band structure changes, we resorted to UPS measurements.
Figure 6.2. (a) KP data for the various doping scenarios. The work function of the CQD solids is found to exhibit an increasing trend with doping concentration. (b) Band structures of the CQD solids under various doping scenarios as obtained from a combination of UPS and optical measurements. The dashed black line corresponding to 0 eV represents the vacuum level for the undoped baseline. The gray dash for each band structure represents the corresponding vacuum level. The red and blue bands represent the conduction and
valence bands of the CQD solids, respectively, while the black bars correspond to the $E_F$. The band structures have been put on a common scale according to the top of the VB, for clarity. (c) Excitonic maxima for the various doping scenarios are shown with off-sets. No change in optical band gap is found after doping.

Figure 6.2b tracks the changes to the CQD band structure for various doping concentrations. The CBM were approximated from the optical band gaps (Figure 6.2c), an estimation which is justified for inorganic materials such as PbS CQDs given their small exciton binding energies. For low doping concentrations ($10^{-2}$ and $10^{-3}$ mg mL$^{-1}$), the $E_F$ of the CQD solids is found to move closer to the VBM, clearly suggestive of p-doping. For larger doping concentrations, however, the $E_F$ is found to saturate well short of the band edge, without leading to degenerate doping of the CQDs. We speculate that this might occur due to a combination of the following factors: a) a fairly high number of trap states inside the band gap, and b) an electrostatic repulsion between the Mo(tfd-COF$_3$)$_3$$^-\text{ counterions}$, formed after the dopant molecules accept electrons effectively p-doping the CQDs. With increasing levels of doping, the anions form increasingly complete monolayers on the surface of the CQDs. Doping will then not only depend on the dopant-CQD energetics (EA of the dopant and VBM of the CQDs), but also on the electrostatic attraction between the positively charged CQDs and the negatively charged dopant anions, and the repulsion between the dopant anions. This remote doping scenario is different from the doping of organic semiconductors, and forces the anions to be close to one another leading to repulsive interactions limiting doping efficiency. Importantly, larger doping concentrations also involve a significant surface dipole formation leading to raising of the vacuum level ($\Delta\Phi$). This has been discussed in detail in Chapter 5. These surface dipoles can potentially form if layers of unreacted dopant molecules start surrounding the CQD surfaces, a scenario which is likely for large doping concentrations.
Importantly, the VB spectrum for the 1 mg mL\(^{-1}\) doping case represents significant deviations from that of undoped CQDs. This might be indicative of the presence of a monolayer of the dopant molecules atop the EDT-HTL for this particular doping concentration (although the SIMS data discussed indicates significant penetration of the dopant into the HTL), since UPS only detects the top ca. 1 nm of the surface. We, however, observe that the VB spectra for lower doping concentrations closely mimic that of PbS CQDs, ruling out any overlayer formation at lower concentrations. The \(\Delta E_F\) measured from UPS agrees well with the magnitude of the shift of Pb 4f core levels to a lower binding energy, as observed in XPS, shown in Figure 6.4. This behavior is similar to that
previously observed when the same dopant was employed to dope absorber layers of MPA-
PbS CQDs (Chapter 5).\textsuperscript{[164]}

Figure 6.4. XPS data. (a) As the doping concentration is increased, the F1s core peak from
the dopant increases in intensity as compared to the Pb 4p\textsubscript{3/2} peak. (b) High resolution XPS
of the Pb 4f\textsubscript{7/2} peaks shows that the core level shifts to lower binding energy for the doped
case, commensurate with the ΔE\textsubscript{F} observed from UPS.

6.4 MAPbI\textsubscript{3}-PbS CQD solar cells

Encouraged by these findings, we made solar cells with doped EDT-PbS layers employing
different dopant concentrations. The various steps involved in this facile molecular doping
procedure are outlined in Figure 6.5. Figure 6.5(a),(b) and (c) show the various device
parameters (J\textsubscript{SC}, V\textsubscript{OC}, FF and PCE) as a function of the dopant concentration used for a
large number of devices. Baseline undoped solar cells yield a PCE in the range of 8.1%,
which are on par with previously reported MAPbI\textsubscript{3}-shelled CQD solar cells.\textsuperscript{[29]}
Figure 6.5. The various steps involved in the doping procedure are shown. The solar cell is fabricated in the standard way: (1) spin coating of the MAPbI₃-PbS CQD ink on the ZnO-coated ITO glass, followed by (2) deposition of the EDT-PbS HTL. This assembly is then (3) soaked in the dopant solution (the desired concentration of Mo(tfd-COF₃)₃ in ACN) for a 30 seconds followed by rinsing with ACN solvent to wash-off excess dopant molecules from the surface of the CQD solid. Device parameters ($J_{SC}$, $V_{OC}$, FF and PCE) as a function of the dopant concentrations are shown in (a), (b) and (c). $10^{-3}$ mg mL$^{-1}$ is found to be the optimized dopant concentration leading to the best performing solar cells. Error bars correspond to the standard deviation over a set of 6-12 devices.

Clear enhancements in $J_{SC}$ and FF are observed at low dopant concentrations ($10^{-3}$ and $10^{-2}$ mg mL$^{-1}$); the PCE shows a maximum of 9.0% for the $10^{-2}$ mg mL$^{-1}$ doped solar cell. The increase is statistically significant based on the increase seen in a number of devices.
Increasing the dopant concentration further leads to a decrease of both $J_{SC}$ and FF, as well as a slight decrease in $V_{OC}$ at the highest concentration, resulting in an overall performance degradation. A concentration of $10^{-2}$ mg mL$^{-1}$ is therefore found to be the optimum dopant concentration, resulting in the most efficient charge extraction. We speculate that as the dopant concentration is increased above the optimum point ($10^{-2}$ mg mL$^{-1}$), the underlying MAPbI$_3$-PbS CQD photoactive layer might become affected, which in turn impairs device performance. We do see a small but non-negligible penetration of the dopant (Mo and F atoms) into the absorber layer for the 1 mg mL$^{-1}$ doped film from SIMS (Figure 6.1b), as discussed above. UPS spectra provide clear clues into the impaired device performance at high doping concentrations. The UPS spectrum of the VB region for the 1 mg mL$^{-1}$ case is suggestive of dopant segregation on the top of EDT-HTL (Figure 6.3). Higher doping concentrations can potentially result in a layer of unreacted dopant on CQD surfaces and act as barriers to charge flow. These high concentrations are associated with formation of large dipoles introducing important shifts in the CQD vacuum level. A severely shifted CQD vacuum level will disrupt charge flow near the Au electrode (the Au work function is 4.6 eV). Also, as has been shown recently in the case of graphene, higher doping concentrations utilizing similar dopants can lead to Coulomb scattering, adversely affecting charge transport.$^{[167]}$
Table 6.1. Device parameters (J_{SC}, V_{OC}, FF and PCE) for the various doping concentrations. Statistics correspond to 6-12 devices. In brackets, the PCE of the best performing solar cells for each category, are shown.

<table>
<thead>
<tr>
<th>Device</th>
<th>J_{SC} (mA cm^{-2})</th>
<th>V_{OC} (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped baseline</td>
<td>20.2 ± 0.4</td>
<td>0.61 ± 0.00</td>
<td>65.6 ± 1.7</td>
<td>8.1 ± 0.1 (8.3)</td>
</tr>
<tr>
<td>10^{-3} mg mL^{-1}</td>
<td>21.2 ± 0.2</td>
<td>0.61 ± 0.00</td>
<td>67.2 ± 0.4</td>
<td>8.6 ± 0.1 (8.8)</td>
</tr>
<tr>
<td>10^{-2} mg mL^{-1}</td>
<td>21.0 ± 0.2</td>
<td>0.61 ± 0.00</td>
<td>68.8 ± 0.9</td>
<td>8.8 ± 0.1 (9.0)</td>
</tr>
<tr>
<td>10^{-1} mg mL^{-1}</td>
<td>20.2 ± 0.4</td>
<td>0.61 ± 0.00</td>
<td>56.5 ± 5.7</td>
<td>6.9 ± 0.8 (7.5)</td>
</tr>
<tr>
<td>1.0 mg mL^{-1}</td>
<td>15.1 ± 0.8</td>
<td>0.59 ± 0.00</td>
<td>62.6 ± 2.3</td>
<td>5.6 ± 0.5 (6.1)</td>
</tr>
</tbody>
</table>

Table 6.1 summarizes the device data shown in Figure 6.5. The J-V curves for the best performing solar cells for each doping condition are shown in Figure 6.6.

Figure 6.6. J-V curves for the various HTL doping scenarios are shown. Low dopant concentrations (10^{-3}, 10^{-2} mg mL^{-1}) improve device performance, whereas a high concentration (1.0 mg mL^{-1}) leads to severe degradation.

The observed device performance enhancement is in good agreement with optoelectronic numerical predictions (Figure 6.7), which predict a FF and J_{SC} increase as the doping
concentration of the EDT layer approaches its optimum value. Table 6.2 summarizes the parameters details employed for the optoelectronic simulations. The simulations were performed with SCAPS.\cite{132}

Figure 6.7. Simulated solar cell parameters as a function of HTL doping concentration.

The device structure was modeled based on an n-i-p architecture. The p-layer represents the modified EDT HTL, the i-layer is the MAPbI$_3$-PbS CQD solid and the n-layer is the ZnO ETL. The acceptor doping concentration of the EDT HTL was varied and analyzed for its impact on the various photovoltaic performance metrics. The MAPbI$_3$-PbS CQD layer consists of a parabolic grading combination of the parameters listed in Table 6.2. The
CQD band-edge for a given exciton peak was calculated from the absorption edge of the exciton peak. The parameters in bold were swept simultaneously.

**Table 6.2. Details of optoelectronic simulation parameters.**

<table>
<thead>
<tr>
<th></th>
<th>HTL</th>
<th>Perovskite-shelled CQD layer (power-law graded)</th>
<th>ZnO layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (nm)</td>
<td>20</td>
<td>200</td>
<td>40</td>
</tr>
<tr>
<td>Band gap edge (eV)</td>
<td>1.02</td>
<td>1.02</td>
<td>3.2</td>
</tr>
<tr>
<td>Electron affinity (eV)</td>
<td>3.9</td>
<td>4</td>
<td>4.3</td>
</tr>
<tr>
<td>Permittivity (Fm(^{-1}))</td>
<td>22</td>
<td>35</td>
<td>66</td>
</tr>
<tr>
<td>CB/VB DOS (cm(^{-3}))</td>
<td>10(^{19})</td>
<td>10(^{19})</td>
<td>5·10(^{19})</td>
</tr>
<tr>
<td>Electron mobility (cm(^{2})V(^{-1})s(^{-1}))</td>
<td>1·10(^{-2})</td>
<td>1·10(^{-2})</td>
<td>5·10(^{-2})</td>
</tr>
<tr>
<td>(N_{\text{donor}}) (cm(^{-3}))</td>
<td>-</td>
<td>10(^{17})</td>
<td>10(^{16})</td>
</tr>
<tr>
<td>(N_{\text{acceptor}}) (cm(^{-3}))</td>
<td>Swept</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Capture cross section (cm(^{2}))</td>
<td>1.2·10(^{-13})</td>
<td>1.2·10(^{-13})</td>
<td></td>
</tr>
<tr>
<td>Position below (E_c) (eV)</td>
<td>0.3</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Density (cm(^{-3}))</td>
<td>10(^{16})</td>
<td>10(^{15})</td>
<td></td>
</tr>
<tr>
<td>CQD-ZnO interface defects (neutral)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capture cross section (cm(^{2}))</td>
<td>10(^{-17})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Position above (E_v) (eV)</td>
<td>0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density (cm(^{-3}))</td>
<td>4·10(^{15})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Importantly, the doped solar cells demonstrate photostability (**Figure 6.8a**). The cells are found to show mild hysteresis, but no increase of the hysteretic behavior is observed upon
doping (Figure 6.8b). We postulate that the observed hysteresis might be linked to the use of perovskite shells.

![Figure 6.8](image)

**Figure 6.8.** (a) $J-V$ curves for MAPbI$_3$-PbS CQD solar cells showing hysteresis. No noticeable increase in hysteresis is detected for the doped cells. (b) Doped cells are found to be stable under light.

The observed enhancement in device performance for solar cells using a p-doped EDT-PbS CQD HTL agrees well with the increase in EQE under short-circuit current conditions (Figure 6.9a). The EQE improvement for the optimally-doped solar cell, especially at the near infrared region, is consistent with the improvement in charge extraction leading to an increase in FF and $J_{sc}$. In order to assess the improvement attained by increased band bending at the MPP, we compare the EQE of undoped and optimally doped solar cells at
these operating conditions (Figure 6.9b). The EQE is found to increase over the entire wavelength spectrum, but the enhancement is more significant in the near infrared (>10% at the exciton peak). This correlates well with the device performance increase attributed to a stronger p-type character of the EDT-PbS layer, as these photocharges are generated closer to this interface. Fabry-Perot interference results in a decrease of EQE around 800 nm in both cases.

Figure 6.9. (a) EQE for the MAPbI₃-PbS CQD solar cells at 0 bias conditions. (b) EQE spectra for the undoped and optimally doped (10⁻² mg mL⁻¹) solar cells taken at V_{MPP} (~0.5 V) conditions. Optimal doping (blue) leads an increase in charge collection compared to the undoped baseline (black) which is especially evident in the near infrared region. This illustrates the beneficial effect of an increased band banding in the photoactive layer at the HTL interface.

The impact of doping on the interfacial band structure at the HTL:absorber interface is schematized in Figure 6.10. For the case of a standard, undoped HTL (Figure 6.10a), the extraction of charges that are photo-generated close to the back interface face an unfavorable energy barrier in the band structure largely leading to carrier recombination. The doped HTL, which we modelled as N_{acceptor}~10^{18} cm⁻³ to better illustrate the mechanism, on the other hand, leads to removal of this ‘kink’ and causes a favorable
bending at the interface (Figure 6.10b). This finding is in good agreement with the observed increase in EQE at the exciton peak (Figure 6.9b), since these are the photons that are absorbed closer to the EDT back-interface.

**Figure 6.10.** Schematic shows that an undoped HTL causes an unfavorable ‘kink’ in the band structure at the HTL:absorber interface which is removed upon optimal doping of the HTL. The insets show the scenarios before thermodynamic equilibrium (black dashes represent the Fermi level positions). Charge collection efficiency increases for the optimally doped case.

### 6.5 PbX₂-PbS CQD solar cells

To investigate whether the molecular doping scheme for the CQD HTL demonstrated for MAPbI₃-PbS cells is general in application, we turned our attention to the recently reported PbX₂-PbS CQD based solar cells. These CQDs benefit from a hard nanocrystal surface owing to an increased halide surface coverage, effectively suppressing low-energy phonon modes prone to coupling with electronic transitions and creating carrier traps. The device architecture is shown in **Figure 6.11(a)** and differs from the MAPbI₃-PbS CQD devices in employing a PbX₂-PbS CQD absorber layer. Nevertheless, it employs an EDT-PbS CQD HTL for efficient carrier extraction similar to the MAPbI₃-PbS CQD cells.
investigated above. Doping the CQD HTL with the molecular doping conditions optimized above for the case of MAPbI$_3$-PbS devices, we observed similar device performance increase (Figure 6.11b). Enhancement in $J_{SC}$ and FF (Table 6.3) led to a statistically reproducible ca. 10% relative increase in PCEs compared to undoped control (black curve; PCE = 8.5%) and resulted in 9.5% efficient solar cells (blue curve). A histogram representing device statistics (Figure 6.11c) confirms reproducibility of our PCE enhancements.
Figure 6.11. (a) Solar cell architecture employing a PbX_2-PbS CQD absorber layer obtained via a single-step deposition. (b) J-V curves for the baseline (black curve) using an undoped EDT-PbS CQD HTL and a 10^{-2} mg mL^{-1} doped CQD HTL (blue curve). (c) Histogram showing device statistics for the undoped and doped cases.
Table 6.3. Summary of the device parameters for the PbX2-capping based PbS CQD solar cells for the optimized doping condition of $10^{-2}$ mgmL$^{-1}$. The reported device parameters ($J_{SC}$, $V_{OC}$, FF and PCE) have been averaged over 10 devices. The PCE values in brackets represent the best performing solar cells for each category.

<table>
<thead>
<tr>
<th>Device</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>undoped baseline</td>
<td>21.0±1.1</td>
<td>0.61±0.01</td>
<td>65.5±2.5</td>
<td>8.29±0.20 (8.5)</td>
</tr>
<tr>
<td>$10^{-2}$ mg mL$^{-1}$</td>
<td>22.9±0.5</td>
<td>0.59±0.02</td>
<td>68.0±1.8</td>
<td>9.14±0.18 (9.5)</td>
</tr>
</tbody>
</table>

Figure 6.12. (a) Photostability of the PbX2-PbS CQD solar cells. (b) Performance stability of the PbX2-PbS CQD solar cells is demonstrated.

The doped cells are found to demonstrate acceptable levels of photostability (Figure 6.12a). Importantly, we find that the doped devices remain within 95% of their initial PCEs even after 2 months of storage in ambient environment, closely matching the stability of
the undoped control cells (Figure 6.12b). Although the air-stability of these molecular dopants is well-known,\textsuperscript{[136, 156, 163]} our findings confirm the reliability of optoelectronic devices that employ these dopants.

### 6.6 Conclusions

We have demonstrated that charge-carrier extraction in the latest brand of high performing, single-step deposited PbS CQD based solar cells is limited by the moderate p-type character of the EDT-PbS CQD HTL, which allows only limited band bending under maximum power point operation. We address this problem by introducing a molecular dopant which consists of a large-EA metal-organic complex Mo(tfd-COCF\textsubscript{3})\textsubscript{3}. When incorporated into the EDT-PbS CQD layer, these molecules withdraw excess electrons, conferring a stronger p-type doping to the HTL. This ultimately results in an increased built-in field at this interface that is sustained even at maximum power point conditions, facilitating charge separation and collection. As a consequence, a ca. 10% PCE increase is obtained compared to control samples. Our HTL p-doping recipe involving metal-organic complexes is applicable, in general, to the high-performing CQD solar cell architectures which rely on CQD HTLs for efficient charge collection.
Chapter 7

Breaking the Barrier to Ambient-manufactured, Scalable CQD PV

7.1 Introduction

Several of the CQD solar cells reported in the previous chapters were fabricated in the laboratory of a collaborator at the University of Toronto (UofT), specifically in the dry winter season, with only a few devices (scattered over the previous pages) made in our KAUST laboratory. The reason behind this presents itself as one of the two major challenges on the path to industrial scale-up of CQD PV. Surprisingly, most of the highest-performing CQD solar cells, reported to date, have been fabricated during winters in dry cities (Toronto, Golden, Boston). In contrast, the humidity in our laboratory at KAUST is consistently high throughout the year, reflective of many other laboratories and climates, as will be specified below. This highlights the underlying challenge of ambient manufacturability of these solar cells in realistic environments of uncontrolled and moderate to high humidity. Devices are anecdotally known to be poorly-performing and unstable when fabricated in summers, although this is not reported in the scientific literature. This poses a question mark over the reliability of the CQD PV technology. As Li and Tan, et al., have recently pointed out in the context of CQDs,[27] a modern-generation low-cost PV technology aiming for industrial implementation in ambient air is expected to be invulnerable to high and variable moisture conditions during manufacturing and utilization. The additional state-of-the-art requirement of processing and fabrication in controlled environments hurts the prospects of low-cost solution-processability of CQD PV.[10]
Besides, the fact that there is, to date, no report of scalable fabrication of these solar cells forms the second major challenge to this technology, further jeopardizing the prospects of commercialization. Most of the reports of CQD devices are based on the spin-coating technique. Whereas, this reliance on spin coating is understandable given the simplicity of the coating process and the uniform, smooth and high-quality films that can be realized, it is a lab-based process often involving ~90-99% materials wastage. For industrial manufacturing of CQD solar cells to be possible, spin-coating needs to be replaced with a high-throughput coating technique compatible with scalable, large-area and reproducible processing in ambient air, that approaches negligible materials wastage without compromising film quality and solar cell performance.

In this chapter, we overcome these two challenges and suggest that CQD PV is indeed one of the rare thin film PV technologies that can be scalably fabricated and operated in high humidity ambients (50-65% RH). Our findings advocate that CQD solar cells can now be industrially fabricated in any region of the world without the need of any moisture/humidity control of the ambient. We carry out SolEx of the CQD ink and the subsequent device fabrication in an uncontrolled high moisture environment of our KAUST lab in Thuwal, Saudi Arabia – a very humid region. Our as-prepared solar cells perform poorly (ca. 5% PCEs) as the ambient moisture leads to severe band-bending issues in the device, affecting charge transport. We, however, devise an ‘oxygen-doping’ scheme to heal the interfacial band structure of our solar cells and successfully mitigate the ill-effects of moisture. The scheme allows us to recover our device performances (ca. 10% PCEs). Importantly, our devices exhibit long-term air stability (over 1 year). Next, we employ our oxygen-doping scheme to fabricate roll-to-roll compatible CQD solar cells (obtained via blade-coating and
bar-coating) in high-humidity ambient air, demonstrating performance parity with spin-coating (>10% PCEs). The coating is carried out in a single-step at an industrially-viable speed of 18 meters per minute and, importantly, requires ca. 96% less CQD ink per device as compared to spin-coating, approaching 0% materials wastage.

7.2 CQD PV in dry and humid cities

In Figure 7.1a we present the variation of absolute humidity (AH) over a year for several major cities around the World. The AH embodies the total amount of humidity (g.m$^{-3}$) in a unit volume of atmosphere, allowing for a direct comparison of humidity levels. The RH, by contrast, is used to quantify the human sensation of humidity and the ability to cool down through perspiration. The outdoor AH and RH are shown in Figure 7.1b for the contrasting cases of Thuwal, Saudi Arabia (location KAUST) and Toronto, Canada; although Toronto has a higher RH in winters (due to precipitation), this corresponds to a very low AH when the low winter temperatures are considered. Thuwal, on the other hand, has a very high AH all year round and it is the outdoor AH that should be considered when assessing how much humidity is present in the air. While the reported AH represents outdoor conditions, we have observed that in-lab RH levels at KAUST and University of Toronto (UofT) tend to follow a similar trend to the respective outdoor humidity, as shown in Figure 7.1c. It is probably no coincidence then that the highest-performing CQD solar cells to date have been reported from only a few relatively dry cities, namely Toronto (Canada), Cambridge (MA, USA) and Golden (CO, USA). The AH in Golden is mostly low throughout the year, whereas in Toronto and Cambridge it is low only in the winter season, reflective of many major cities worldwide (Figure 7.1a). The AH tends to be elevated throughout the year in many other regions of the World, including in major cities
such as Singapore, Taiwan, New Delhi, Hong Kong and Shenzhen, to which we refer to as “humid cities”. Thuwal and the nearby major city of Jeddah represent extreme cases of “humid city” as the AH remains very high throughout the year and increases to very high levels in the summer (black line, Figure 7.1a).
Figure 7.1. CQD PV in dry and humid cities. (a) Absolute humidities (outdoor) across some of the dry cities (featuring robust CQD solar cell fabrication) and highly humid cities around the World are compared. Whereas summers are a bottleneck for device fabrication in dry cities, humid cities threaten successful device fabrication and operation almost
throughout the year. (b) Differences between AH and RH are highlighted for Thuwal (KAUST) and Toronto. Although Toronto features high RH in winters (due to precipitation), the overall AH is very low owing to the low winter temperatures. This illustration suggests that while studying and comparing the effect of a variety of atmospheric conditions on solar cell performance, AH should be considered instead of the RH, since the former gives a more holistic picture. (c) Variation of RH and AH for the KAUST and UofT labs is shown. Both labs employ a temperature control (22°C) throughout the year. As can be seen, the in-lab humidities follow a similar trend as the AH in the respective cities.

The impact of fabricating CQD solar cells in ambient air of variable and high humidity conditions is highlighted in Figure 7.2, where the performance of solar cells fabricated at KAUST and UofT by the same operator and using identical materials and processing methods show stark differences. These observations seem to confirm the view in the community that CQD solar cell fabrication is currently limited to highly dry seasonal conditions and is, as such, not suited for cities with higher humidity (Thuwal, New Delhi, Singapore, Hong Kong, Taiwan, etc.). Yet, these cities receive much higher solar irradiance and are therefore better suited for low-cost local manufacturing and deployment of PV panels. It therefore becomes urgent to develop protocols which enable robust fabrication of CQD solar cells under realistic ambient conditions.
Figure 7.2. As contrasting cases, Thuwal, Saudi Arabia (KAUST) and Toronto (University of Toronto) were chosen for a comparative study. The \( J-V \) curves of CQD solar cells freshly fabricated and tested in KAUST (0.1 cm\(^2\)) and UofT (0.05 cm\(^2\)) are shown. Ultra-high humidity in the KAUST lab severely hurts PCEs as compared to the devices made in dry environment of the UofT lab. Temperature in both labs was maintained at 22°C.

7.3 Fabricating CQD solar cells at KAUST: an ultra-high humidity environment

The CQD solar cell architecture is schematized in Figure 7.3a. The inset highlights the SolEx process (elaborately discussed in Chapter 2) and involves exchanging the initial, insulating OA ligands on the PbS CQDs with PbX\(_2\)-PbS in the solution phase. Figure 7.3b shows an X-SEM image of the solar cell.

SolEx and all the following device fabrication steps were carried out in ambient air at KAUST (ca. 50-65% RH, 22°C), where humidity is significantly higher throughout the year than at the UofT (ca. 10-15% RH in winters except in summers when the conditions can be 20-45% RH at the same lab temperature of 22°C). Figure 7.1c gives a rough estimate of RH and AH variations through the year at the KAUST and UofT labs. We first fabricated the devices via spin coating. The various steps involved have been reported elsewhere.\(^{[13]}\)
Solar cells were measured right after Au electrode deposition (called ‘as-prepared’ hereafter). The $J-V$ curve for a typical as-prepared cell is shown in Figure 7.3c (black curve) and corresponds to 4.8% PCE, which is less than half of current state-of-the-art PCEs. This poor result highlights how vulnerable CQDs tend to be to high humidity environments and explains anecdotally why most of the high efficiency CQD solar cells are reported from laboratories where low humidity conditions are achievable seasonally or year round.\cite{27, 31}
Figure 7.3. *Achieving fabrication robustness.* (a) Schematic of the solar cell architecture. Top inset shows a typical ambient humidity value. Bottom inset is a schematic of the SolEx process (b) X-SEM image of the device showing the various layers (c) $J$-$V$ curves for the solar cells under various environmental conditions: as-prepared (black), stored in the nitrogen glove box for 1 day (red), stored in ambient air with ca. 65% RH for 1 day (pink), stored in dry air with 0% RH for 1 day (green), and the best spin-coated solar cell (blue) (d) evolution of device parameters of as-prepared devices as a function of dry air-storage time (e) PCEs for the as-prepared (black) and dry-air stored (green) cells are shown as histograms. Dotted lines show the fitted Gaussians.

The $J_{SC}$ of the as-prepared cell is reasonably high, but its $V_{OC}$ and FF are well below expectations (see Table 7.1), providing the first clue suggestive of underlying issues with
charge extraction. We take the view that high humidity conditions can saturate the CQD surfaces in solution, during processing and/or drying in ambient air with H2O molecules, which may hinder the potential action of oxygen doping. To test this hypothesis, we stored the as-prepared solar cells in a variety of environmental conditions, such as N2 glove box, humid ambient, and dry air (ca. 0% RH). Humidity is expected to desorb in the dry environments of the N2 and dry air boxes. The cells were re-tested after one day of storage in these conditions and the J-V curves are shown in Figure 7.3c. Whereas the N2-stored cell (black) remains almost unaffected, the ambient-stored device (pink) shows a moderate enhancement in PCE largely associated with V_OC and FF. By contrast, the solar cell stored in dry air conditions (green) reaches 8.8%, nearly doubling in performance. Significant and commensurate improvements in V_OC and FF are observed. The shunt resistance (R_shunt) is found to increase substantially (from 0.9 kΩ cm^-2 to 5.4 kΩ cm^-2) which might suggest suppression of trap-assisted recombination. There is a decrease in the series resistance (R_s) from 5.9 Ω cm^-2 to 1.8 Ω cm^-2 which can be attributed to efficient charge transport with negligible charge accumulation and recombination. We achieved our best spin coated solar cell performance of 10.2% PCE, shown in Figure 7.3c (blue). We followed the PCE enhancement of the as-prepared devices upon storage in dry air conditions more closely and found that the device parameters increased and saturated within the first few hours (Figure 7.3d), making this a relatively rapid process. Figure 7.3e shows the performance histograms of the as-prepared (black) and the dry air-stored solar cells (green). These results indicate that the performance of solar cells processed in high and variable humidity conditions can be recovered and stabilized easily and simply by briefly storing them in dry air with 0% R.H when coating and manufacturing cannot be carried out in low
and controlled humidity conditions. Importantly, the control experiments point toward changes in oxygen doping as the key culprit for the low and unreliable performance of CQD solar cells fabricated in high and variable humidity conditions, as will be further verified below.

Table 7.1. Device parameters of solar cells exposed to various environmental conditions.

<table>
<thead>
<tr>
<th>Device</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>$R_{shunt}$ (kΩ cm$^{-2}$)</th>
<th>$R_s$ (Ω cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-prepared</td>
<td>22.8</td>
<td>0.49</td>
<td>42.8</td>
<td>4.8</td>
<td>0.9</td>
<td>5.9</td>
</tr>
<tr>
<td>N$_2$, 1 day</td>
<td>22.7</td>
<td>0.50</td>
<td>39.4</td>
<td>4.5</td>
<td>0.5</td>
<td>5.2</td>
</tr>
<tr>
<td>Ambient air, 1 day</td>
<td>23.6</td>
<td>0.54</td>
<td>49.6</td>
<td>6.4</td>
<td>2.0</td>
<td>3.4</td>
</tr>
<tr>
<td>Dry air, 1 day</td>
<td>23.7</td>
<td>0.62</td>
<td>60.1</td>
<td>8.8</td>
<td>5.4</td>
<td>1.8</td>
</tr>
<tr>
<td>Best Cell, (Dry air, 1 day)</td>
<td>25.6</td>
<td>0.65</td>
<td>61.0</td>
<td>10.2</td>
<td>4.9</td>
<td>1.6</td>
</tr>
</tbody>
</table>

7.4 Achieving long-term stability

In order to test the reversibility and long-term stability of the benefits of aging of cells in dry air, we aged them in their respective environments over a period of several months. Figure 7.4a shows the PCEs after 1 day and after 1 month of fabrication, in the form of bars, with percentage PCE increase/decrease shown on top of the bars. The cell stored in N$_2$ (red bars) is relatively stable after 1 month of fabrication. The ambient-stored device (pink bars) shows an initial performance enhancement, as discussed earlier, but sees a slight drop in performance over time. Besides showing the highest PCE gains, the dry air-stored cell (green bars) is highly stable and continues to show almost 8.8% PCE at the end of 1 month of storage in dry air. Figure 7.4b shows the average device parameters of the dry
air-stored cells over a 12-month time frame. The devices retain ca. 70% of their initial performance. Subsequently, we transferred some of these devices, after 1 day storage in dry air, to the ambient high-humidity environment with the aim of testing long-term stability in the humid ambient. The data is shown in Figure 7.4b as black points, and remarkably, also exhibits high stability. These results suggest that the positive effects of a relatively brief storage period in dry air conditions are irreversible and are not lost even after re-exposure to humid air. These devices do not employ any encapsulation and, to the best of our knowledge, are one of the most stable thin film solar cells reported to date.
Figure 7.4. *Long-term stability.* (a) Evolution of PCEs for solar cells corresponding to Figure 7.3c. N$_2$-soaked solar cell fails to show any PCE increase but stays stable over time. The device stored in ambient air initially shows a 36% increase in PCE, however, degrades later. However, the dry air-soaked solar cell stays considerably stable after showing a significant initial increase of >80%. (b) Evolution of device parameters ($J_{SC}$, $V_{OC}$, FF and PCE) for a set of dry air-stored devices (green). As discussed, the device parameters undergo an initial increase before achieving stability over several months. The increase comes primarily from $V_{OC}$ and FF. Also shown is the stability of a set of devices stored in the ambient (black). These solar cells were oxygen doped by storage in dry air for a day, before being transferred to the ambient for a period of several months.
7.5 The issue with the HTL

Understanding how dry air storage influences the device physics should aid us in identifying the physical cause of performance enhancements. Indeed, increases in $V_{OC}$ and FF after storage in dry air are suggestive of issues with interfacial band alignment inside the as-prepared solar cell, which appear to be relieved upon dry air-storage. Hence, this is due either to the interaction of the as-cast PbX$_2$-PbS CQD absorber or the as-cast EDT-PbS CQD HTL with the dry air environment, or possibly both. To deconvolute these possibilities, we first fabricated a control solar cell that employed a PbX$_2$-PbS CQD absorber layer deposited in the dry air environment, while the CQD HTL was deposited in the humid ambient.
Figure 7.5. (a) J-V curves for a solar cell that employs a dry air-coated absorber layer. The as-prepared device exhibits low \( V_{OC} \) and FF (similar to an ambient-coated absorber layer), suggesting that the absorber layer does not benefit from a low-humidity (dry air) fabrication. Dry air-storage of the finished device (after HTL deposition in ambient), leads to PCE increase, as expected. (b) J-V curves for a solar cell that employs a dry air-coated EDT-PbS CQD HTL. The as-prepared device exhibits a high \( V_{OC} \), suggesting that the HTL benefits from a low-humidity (dry air) fabrication. Dry air-storage of the device, leads to further PCE increase.
We observed almost similar behavior in device parameters as in solar cells fabricated entirely in humid air. The $V_{OC}$ and FF were low for the as-prepared solar cell and increased upon storage in dry air (see Figure 7.5a). This hinted towards the fact that the CQD absorber is immune to interaction with the dry air and thus unaffected by deposition in humid air. As the next control, a solar cell was fabricated where the PbX$_2$-PbS CQD absorber was deposited in the humid ambient while the EDT-PbS CQD HTL was coated in the dry air environment. Interestingly, we found a high $V_{OC}$ for the as-prepared solar cell, along with a higher starting PCE of 6.8%. A ca. 5-6 hours’ storage in dry air further increased the $V_{OC}$ and FF leading to a final PCE of 9.3% (Figure 7.5b). Importantly, this result suggests that the humidity levels of the ambient air are not crucial to determining the final PCE of the ambient-manufactured solar cell. Instead, we show that relatively brief storage in dry air conditions can irreversibly undo the harmful effects of high-moisture device processing and fabrication, making the latter acceptable for CQD solar cell manufacturing.

### 7.6 Oxygen-doping of the HTL

Having singled out the CQD HTL as the single biggest culprit for low initial PCEs due to issues with deposition in humid ambient air, we probed deeper into the chemical interactions of these layers with the different ambient environments. We employed photoemission spectroscopy, a highly surface-sensitive characterization tool to study chemical and electronic changes at interfaces occasionally encountered in the field of nanoscience.\cite{122, 137, 153} The sample consisted of the PbX$_2$-PbS CQD absorber layer having a ca. 50 nm EDT-PbS CQD HTL on top, mimicking the solar cell architecture. Figure 7.6a
and 6b, respectively, show the S 2p and O 1s core level peaks for the as-prepared film and also after a day’s storage in dry air, obtained from high-resolution XPS.

Since photoemission spectroscopy probes only a few nanometers below the surface, the information obtained is certainly associated with the EDT-PbS CQD HTL on the top. The complexity of the S 2p peaks suggests that the S atoms are present in a variety of chemical environments. The peaks were deconvoluted into the following components: bound thiolate belonging to sulfur in PbS (red), EDT ligands bound to the surface (green), unbound thiolate (purple) and small amounts of lead sulfite (pink) and lead sulfate (light-green), following literature reports. Interestingly, we found that upon storage in dry air, the amount of bound EDT ligands decreased and the unbound thiolates increased. This was accompanied with an increase in the sulfite and sulfate species (PbSO₃, PbSO₄). These results suggest that the EDT-PbS HTL undergoes oxidation upon storage in dry air, whereby the excess, unwanted bound EDT ligands are removed from the CQD surface leading to the formation of surface oxidation species. This is commensurate with the information gleaned from XPS relative atomic quantification which suggests that O increases by ca. 25 times upon dry air storage (see Table 7.2). An in-depth analysis of the O 1s (Figure 7.6b) shows the formation of sulfate, sulfite and a small contribution from lead oxide (PbO).
Table 7.2. Relative atomic concentrations for the as-prepared and dry air-stored samples (EDT-PbS/PbX₂-PbS).

<table>
<thead>
<tr>
<th>Sample condition</th>
<th>Pb</th>
<th>S</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pb-S</td>
<td>Pb-EDT oxides</td>
<td>Total S-Pb</td>
</tr>
<tr>
<td>As-prepared</td>
<td>19.1</td>
<td>22.3</td>
<td>41.4</td>
</tr>
<tr>
<td>Dry air, 1 day</td>
<td>22.2</td>
<td>11.8</td>
<td>39.0</td>
</tr>
</tbody>
</table>
Figure 7.6. Oxygen-doping of the EDT-PbS CQD HTL. XPS data showing S 2p and O 1s core level peaks for the as-prepared and dry air-stored samples. The films considered for these measurements had the same architecture as the CQD stack used for solar cells (EDT-PbS CQD layer on top of a PbX$_2$-PbS CQD thick film). (a) S 2p core level peaks suggest that upon storage in dry air, CQDs lose some of the EDT ligands (green components) leading to an increase in the unbound thiolate (purple components). This is however, accompanied by an increase in oxidation species (SO$_3$ and SO$_4$) observed at higher binding energies (pink and light-green components). (b) This is confirmed from the O 1s peak which consists of 3 components belonging to PbSO$_3$, PbSO$_4$, and a small contribution from PbO. The as-prepared sample has a negligible amount of O which might correspond to Pb-OH.
For the as-prepared sample, the tiny O 1s peak, centered at 531.2 eV, might correspond to Pb-OH formed as a result of the interaction of moisture and the CQD surface, as has been previously reported.\cite{31} It is possible that this hydroxide species is blocking access of the atmospheric oxygen to the CQD surfaces in the EDT-PbS CQD HTL surface impeding the in situ oxidation process during device fabrication.

\textbf{Figure 7.7.} Pb 4f peak for the dry air-stored sample (EDT-PbS/PbX$_2$-PbS) shows the appearance of a higher binding energy component (orange) which corresponds to the oxidized species. This increases the overall FWHM of the core level.

We have also observed an increase in the FWHM of the Pb 4f core level peak upon dry air storage (\textbf{Figure 7.7}). The effect, although minute, is further confirmation that surface oxidation products are being formed. The formation of some of these oxides has, in fact, been suggested to increase carrier lifetime.\cite{171} This effect is also found, albeit to a lesser extent, in the case of films exposed directly to the ambient after preparation (i.e. without dry air-storage). Oxygen content is found to increase, as do the oxidation products (\textbf{Table 7.3}).
**Table 7.3.** Relative atomic concentrations for the ambient-stored sample (EDT-PbS/PbX<sub>2</sub>-PbS).

<table>
<thead>
<tr>
<th>Sample condition</th>
<th>Pb-S</th>
<th>Pb-EDT oxides</th>
<th>Total</th>
<th>S-Pb</th>
<th>S-EDT</th>
<th>Un-bound</th>
<th>SO&lt;sub&gt;3&lt;/sub&gt;+</th>
<th>Total</th>
<th>SO&lt;sub&gt;3&lt;/sub&gt;</th>
<th>SO&lt;sub&gt;4&lt;/sub&gt;</th>
<th>Pb-O</th>
<th>Pb-OH</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;O</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-prepared</td>
<td>19.1</td>
<td>22.3</td>
<td>-</td>
<td>41.4</td>
<td>22.2</td>
<td>27.8</td>
<td>5.7</td>
<td>2.3</td>
<td>58.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Ambient air, 1 day</td>
<td>22.5</td>
<td>15.7</td>
<td>1.7</td>
<td>39.9</td>
<td>21.0</td>
<td>18.2</td>
<td>8.3</td>
<td>4.2</td>
<td>51.7</td>
<td>5.4</td>
<td>1.3</td>
<td>1.2</td>
<td>-</td>
<td>0.4</td>
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<td>8.3</td>
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</tbody>
</table>
C1s core peaks for the as-prepared, humid ambient-stored and dry air-stored scenarios also yield interesting trends (Figure 7.8a). A higher BE component (ca. 288.5 eV) corresponding to oxidation species is found for the humid ambient-stored and dry air-stored samples. The component is, however, strongest for the dry air-stored film agreeing with its maximum oxygen content. Importantly, the O 1s core peak for the humid ambient-stored sample shows an additional component (around 533.5 eV) corresponding to adsorbed H2O (Figure 7.8b), which is absent for the dry air-stored film (Figure 7.6b). These findings explain that although directly exposing the as-prepared devices to the humid ambient (without the dry air-storage) can lead to a partial PCE increase owing to an incomplete oxidation (pink J-V curve, Figure 7.3c), the adsorbed H2O causes these devices to be unstable over time. Directly storing the as-prepared devices in dry air leads to a strong oxidation of the HTL without any H2O adsorption on the CQD surfaces. These solar cells, therefore, lead to maximum PCE boost and (green J-V curve, Figure 7.3c) highest stability.
Figure 7.8. (a) High resolution XPS data of C1s peak for EDT-PbS/PbX2-PbS CQD samples for various scenarios. A high BE component (around 288.5 eV, corresponding to oxidation products) is found for the dry air- and ambient-stored samples. For the dry air-stored case, this component is maximum, commensurate with the highest oxygen doping for this case. (b) High resolution XPS data of (a) Pb 4f, (b) S 2p and (c) O 1s for EDT-PbS/PbX2-PbS CQD samples directly stored in ambient after fabrication.

Differences in the oxidation of the HTL under variable high humidity conditions is an important finding and a key to the puzzle since this can have profound implications for the interfacial band structure, directly affecting charge transport across the solar cell.\(^{174-175}\)

We employed UPS to study the impact of oxidation on the HTL energetics. The SE cutoffs and VBM for the as-prepared film and upon dry air storage are shown in Figure 7.9a, b.
Figure 7.9. UPS SE cutoffs (a) and VBM (b) for the as-prepared and dry air-stored films (EDT-PbS/PbX₂-PbS). (c) Band structures derived from a combination of UPS and optical spectroscopy are shown for the two cases. The Fermi level (black) is found to shift towards the valence band (blue) for the dry air-stored sample suggestive of p-doping induced by O. This leads to a scenario, shown in the inset, where oxygen dopes the EDT-PbS CQD HTL tuning band alignment at the hole-collecting interface and reducing carrier recombination.

The CBM were obtained by adding the optical band gaps to the VBM, an approximation justified in the current scenario given the negligible exciton binding energies in PbS CQDs.¹⁴⁶,¹⁵⁵ Figure 7.9c shows the schematic of the respective electronic band structures.
It is found that oxidation of the CQDs in the HTL, in fact, p-dopes the HTL lowering $E_F$ by $\sim 0.2$ eV. This finding suggests that the as-prepared solar cells suffer from an un-optimally doped HTL leading to band alignment issues at the hole-collecting junction, which threatens to increase carrier recombination at the interface. Dry air-storage effectively p-dopes the HTL, tuning the interfacial band alignment suppressing recombination of photo-generated carriers near the back end of the solar cell. This has been schematized in the inset of Figure 7.9c.

As expected based on control device experiments, we find that the PbX$_2$-PbS CQD absorber layer is largely immune to interaction with oxygen. To arrive at this conclusion, we carried out XPS and UPS on the as-prepared and dry air-stored PbX$_2$-PbS CQD films having no HTL on top. We found that there was a comparatively negligible increase in the oxygen content that had no positive impact on the electronic band structure of the absorber layer (Table 7.4, Figure 7.10).

**Table 7.4.** Relative atomic concentrations for the as-prepared and dry-air stored PbX$_2$-PbS CQD absorber. The increase in O is very small as compared to the case of EDT-PbS CQD HTL.

<table>
<thead>
<tr>
<th>Sample condition</th>
<th>Pb</th>
<th>S</th>
<th>C</th>
<th>O</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-prepared</td>
<td>36.3</td>
<td>32.0</td>
<td>21.3</td>
<td>3.2</td>
<td>7.3</td>
</tr>
<tr>
<td>Dry air, 1 day</td>
<td>35.2</td>
<td>28.8</td>
<td>22.0</td>
<td>7.0</td>
<td>7.0</td>
</tr>
</tbody>
</table>
Figure 7.10. High resolution XPS of (a) Pb 4f, (b) S 2p and (c) O 1s showing that the PbX$_2$-PbS CQD absorber layer does not interact with oxygen when stored in a dry air environment. No new chemical species are found upon dry air storage.

Enhanced band bending in the oxygen doped HTL is expected to have direct implications on charge transport. Figure 7.11a shows dark $J-V$ curves for the as-prepared (black) solar cell and upon dry air-storage (green). Upon storage in dry air, the cell exhibits enhanced diode properties in contrast to the as-prepared scenario with an order of reduction in the dark current at reverse bias and leakage current at zero bias, significantly increasing the rectification ratio (the ratio of forward current density to the reversed current density). The ratio of rectification (at ±1 V) after storage is ca. 70 times higher than that for the as-prepared case. The increased rectification ratio demonstrates the enhanced electrical properties of the HTL after oxygen doping. Low dark current results in larger $R_{\text{shunt}}$ (as mentioned earlier) preventing leakage current and leading to improved $J_{\text{SC}}$ and FF. An increase in the dark current under forward bias (above 0.6 V) upon dry-air storage implies improved hole extraction efficiency. These observations explain the enhancement of FF, $V_{\text{OC}}$, decrease of $R_s$ and the increase of $R_{\text{shunt}}$ upon dry air-storage. The enhanced dark $J-V$ characteristics can be directly correlated to the improved performance of the dry air-stored solar cells under illumination.
Figure 7.11. (a) Dark J-V curves for the as-prepared cell (black) and after dry air-storage (green). A significantly reduced current in the reverse bias after dry air-storage implies a higher fill factor, while the S-shape in the forward bias suggests a higher V_{OC}. (b) Nyquist plots of the impedance measurements for the solar cell measured in dark at 0V bias right after preparation (black) and upon dry air-storage. The fitted equivalent circuit is shown in the inset. Recombination resistance is found to increase after 1 day of exposure to dry air, suggestive of enhanced charge transport.

To better understand the mechanism governing charge transport in the as-prepared and oxygen doped solar cells, we resorted to impedance spectroscopy (IS). Figure 7.11b shows the Nyquist plots of the impedance measurements for the as-prepared (black) solar cell and upon dry air-storage (green). These measurements were carried out at 0V under dark conditions. The measurements were performed on the same device before and after oxygen doping. In general, with the exception of a small series resistance R_s, recombination resistance (R_{rec}) and capacitance (C) are the key elements for representation of the charge transport.
transport phenomenon. Capacitance provides insights into the basic mechanism as the photo-generated charge carriers store energy and generate a voltage and current in the external circuit. On the other hand, $R_{\text{rec}}$ should be high enough to allow the accumulated carriers in the capacitor element to flow through the external circuit when the equilibrium state is reached.[179] A low capacitance is, however, undesirable as it will allow the accumulated charge carriers to leak and recombine within the external circuit. The fitted equivalent circuit is shown in the inset of Figure 7.11b. For the as-prepared solar cell, $R_{\text{rec}}$ and $C$ are found to be 0.359 MΩ and 3.55 nF, respectively. Although the device exhibits a high $R_{\text{rec}}$, the low value of $C$ reduces the charge accumulation process due to increased recombination. Upon oxygen doping, $R_{\text{rec}}$ and $C$ are found to be 27.7 KΩ and 17.5 nF, respectively, suggesting that $R_{\text{rec}}$ is now favorable for efficient charge transport due to better flow of substantially accumulated charge carriers in the external circuit (increased value of $C$), suppressing recombination. These observations are in agreement with recent reports on other thin film solar cells.[124, 175]

**Schematic 1** sums up the HTL oxygen-doping picture gleaned from the above experimental insights.
**Schematic 7.1.** Oxygen-doping of the HTL, where dry-air storage of an as-prepared EDT-PbS CQD HTL leads to replacement of a few loosely bound surface-bound EDT by oxygen, resulting in formation of surface oxygen functionalities, effectively lowering the $E_F$ (p-doping) of the solid.

The CQD PV performance achieved herein are compared with a few recent reports in Table 7.5. Besides having two- to three-times larger active area of 0.1 cm$^2$, our devices carry the obvious advantage of fabrication under challenging high-humidity ambient environment which more realistically reflects the conditions in many cities around the World (Figure 7.1a).
### Table 7.5. Device parameters of some high-performance CQD solar cells reported to date on various active areas.

<table>
<thead>
<tr>
<th>Device area (cm$^2$)</th>
<th>Device Parameters</th>
<th>Year</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$J_{sc}$ (mA.cm$^{-2}$)</td>
<td>$V_{oc}$ (V)</td>
<td>FF (%)</td>
</tr>
<tr>
<td><strong>0.01</strong></td>
<td>26.5</td>
<td>0.54</td>
<td>64.0</td>
</tr>
<tr>
<td><strong>0.03</strong></td>
<td>23.5</td>
<td>0.63</td>
<td>65.0</td>
</tr>
<tr>
<td></td>
<td>23.9</td>
<td>0.66</td>
<td>68.0</td>
</tr>
<tr>
<td></td>
<td>22.3</td>
<td>0.64</td>
<td>72.0</td>
</tr>
<tr>
<td></td>
<td>22.2</td>
<td>0.67</td>
<td>69.0</td>
</tr>
<tr>
<td></td>
<td>22.8</td>
<td>0.65</td>
<td>72.0</td>
</tr>
<tr>
<td></td>
<td>24.3</td>
<td>0.64</td>
<td>69.0</td>
</tr>
<tr>
<td></td>
<td>27.2</td>
<td>0.61</td>
<td>68.0</td>
</tr>
<tr>
<td><strong>0.10</strong></td>
<td><strong>25.6</strong></td>
<td><strong>0.65</strong></td>
<td><strong>61.0</strong></td>
</tr>
</tbody>
</table>

### 7.7 Scalable fabrication of CQD PV: Blade-coating

Having overcome the challenge of ambient air fabrication, we took the aim of demonstrating high-performing, scalably-coated CQD solar cells fabricated under similarly high-humidity ambient conditions. We deployed high-speed blade-coating, a high throughput solution coating technique, to print the CQD absorber layers in a single-step under ambient conditions (ca. 50-65% RH). **Figure 7.12a** demonstrates the blade-coating setup employed. Importantly, coating was done at a blading speed of $>15$ m min$^{-1}$, closely mimicking the industrial requirements. This blading speed allowed us to achieve a similar absorber layer thickness (ca. 300 nm) as the spin-coated films. **Figure 7.12b** shows the $J$-$V$ curves for blade-coated CQD solar cells with active areas of 0.1 cm$^2$ (blue) and 0.5 cm$^2$...
Our blade-coated solar cells achieve performance-parity with spin-coated devices (Figure 7.3c), while requiring ca. 96% less CQD material. In other words, blade-coating allows fabrication of ca. 25 solar cells with the same amount of CQD material (by mass) as is needed to fabricate 1 spin-coated solar cell, presenting itself as a very promising platform for scalable fabrication of CQD solar cells. **Table 7.6** compares the CQD materials consumption by some of the standard device fabrication routes and clearly suggests blade-coating as a unique, high-throughput, roll-to-roll compatible CQD printing technique. It also makes the claim that although the recent demonstrations of single-step SolEx-CQD-based absorbers via spin-coating are crucial and have taken the field significantly forward, they have done little to curb materials wastage, since the final concentration of the SolEx CQD ink needs to be high (ca. 200 mg mL⁻¹) in order to achieve a thick absorber layer in a single step. In fact, these single-step spin-coated SolEx absorbers consume almost the same amount of CQD material as the 3-step LbL solid-state ligand exchange approach described in Chapter 4.
Figure 7.12. Blade-coated CQD solar cells. (a) Schematic of the blade-coating technique employed. (b) J-V curves of 0.1 cm² (blue) and 0.5 cm² (green) active area blade-coated solar cells. (c) EQE spectrum of the 0.1 cm² active area blade-coated solar cell. (d) J-V curve of the best flexible CQD solar cell fabricated via blade-coating. (e) Bending stability of the flexible solar cell after several bending cycles at a diameter of 40 mm, and (f) for various bending diameters. Data circled in red corresponds to the failure diameter.
Table 7.6. Comparison of CQD solar cells fabricated via various routes.

<table>
<thead>
<tr>
<th>Deposition scheme</th>
<th>Fabrication method</th>
<th>Device area (cm²)</th>
<th>CQD amount required (mg/cm²)</th>
<th>PCE (%)</th>
<th>Year</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>65-85 LbL</td>
<td>Spray</td>
<td>0.05</td>
<td>15.5</td>
<td>8.1</td>
<td>Nov., 2015</td>
<td>[180]</td>
</tr>
<tr>
<td>10-12 LbL</td>
<td>Spin</td>
<td>0.05</td>
<td>5.8</td>
<td>10.8</td>
<td>Apr., 2016</td>
<td>[159]</td>
</tr>
<tr>
<td>3-LbL</td>
<td>Spin</td>
<td>0.05</td>
<td>3.8</td>
<td>6.8</td>
<td>June, 2014</td>
<td>[137]</td>
</tr>
<tr>
<td>Single-step</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Blade</td>
<td>0.10</td>
<td>0.1</td>
<td>10.3</td>
<td></td>
<td>This work</td>
</tr>
</tbody>
</table>

A histogram of blade-coated solar cell performances (over 50 devices) is shown in Figure 7.13.

**Figure 7.13.** Device statistics for blade-coated solar cells (active area = 0.1 cm²) demonstrating high reproducibility.

Making use of this high-throughput coating technique, we also demonstrate flexible CQD solar cells on plastic substrate. Such a technology is of particular interest for niche applications such as wearable electronics, portable devices and other in-door
applications.\textsuperscript{181-183} Since these applications do not demand high power input, naturally, the requirement on PCEs is relaxed while becoming stricter on mechanical bending durability. Towards this goal, we fabricated solar cells on polyethylene terephthalate (PET) substrates with active areas of 0.1 cm\(^2\). Our best flexible solar cell gives 7.7 % PCE, the highest reported CQD solar cell in this category. Figures 7.12d-f show the \(J-V\) curves of the best flexible device along with their associated bending stability. \textbf{Table 7.7} summarizes the blade-coated solar cells fabricated on glass and PET substrates under high-humidity ambient conditions.

\textbf{Table 7.7}. Device parameters of blade-coated CQD solar cells reported in this work.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Active area (cm(^2))</th>
<th>(J_{SC}) (mA cm(^{-2}))</th>
<th>(V_{OC}) (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass/ITO</td>
<td>0.1</td>
<td>25.4</td>
<td>0.65</td>
<td>62.9</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>21.5</td>
<td>0.60</td>
<td>55.5</td>
<td>7.2</td>
</tr>
<tr>
<td>PET/ITO</td>
<td>0.1</td>
<td>23.4</td>
<td>0.56</td>
<td>58.4</td>
<td>7.7</td>
</tr>
</tbody>
</table>

\textbf{7.8 Modified SolEx process}

Aiming to expand the scope of CQD PV’s scalability, we considered the latest brand of CQD solar cells that employ a modified SolEx process. These modifications have recently resulted in PCEs of 12.5\%, achieved via spin-coating and active areas of 0.05 cm\(^2\).\textsuperscript{184} Specifically, these record-devices were achieved in the dry-winter season at UofT. In this part of the chapter, we discuss the key role that we played in the SolEx process modification that are part of a study currently under review and go on to demonstrate its scalable coating in the following section.\textsuperscript{184} The modified SolEx ink exhibits enhanced charge transport properties leading to better diffusion lengths, resulting in high-
performance solar cells. Next, we utilize these inks to fabricate solar cells, in our KAUST lab, on active areas of 0.1 cm$^2$ using high-speed wire-bar coating, another roll-to-roll compatible solution-printing technique.

The SolEx recipe used in this chapter, so far, employs BTA solvent for the final dispersal of CQDs after the solution-exchange. BTA is a fairly volatile solvent with a boiling point of ~78°C. This ensures fast drying of the CQD ink during film fabrication (spinning/blading) leading to a smooth solid. However, the optimized absorber layer thickness in this case is ~350 nm which is well below the absorption limit for a CQD solar cell.$^{[13]}$ Any further thickness increase was met with device performance degradation due to limitations on carrier diffusion length. It was, therefore, reasoned to engineer the SolEx process so as to enhance charge transport in the resulting solid.

It was found that the BTA-deposited CQD inks contained high amounts of PbI$_2$ on the CQD surfaces, sufficient to result in monolayer formation. Hybrid amines (a mixture of BTA, amylamine and hexylamine) were used to form a PbI$_2$:hybrid amine complex that would confine the growth of PbI$_2$ to a 2D matrix enveloping the CQD surface. These 2D matrix engineered CQD inks were then utilized to form the absorber had enhanced optoelectronic properties and effectively allowed depositing ~600 nm thick absorbers leading to enhanced PCEs.
Figure 7.14. Modified SolEx recipe (a) The liquid-to-solid transformation during spin-coating was studied by in-situ optical absorption for the CQD inks dispersed in hybrid-amine and butylamine. Also shown (dashed lines) are the corresponding dry film thicknesses. The thinning behavior provides the first insights into important solvent-solute interactions mediating the solidification. This demonstrates the CQD ink solidification follows a sol-gel process reminiscent of lead halide perovskites. (b) To confirm that these changes are related to the hybrid amine, a simple experiment was designed to compare the drying rates of the various solvents involved in the study. Constant volumes of the solvents were placed on a weighing balance and the mass loss tracked as a function of time. Addition of amylamine (blue) and hexylamine (pink) to butylamine (black) decreases the drying rate of the hybrid amine (green) as compared to the case of pure butylamine (black) suggestive of an increased viscosity.

As a first investigation into the differences between the two recipes, we compared the liquid-to-solid transformation of the solution-exchanged CQD solutions in hybrid amine and BTA using in-situ optical absorption. The comparison is shown in Figure 7.14a and suggests that the hybrid amine CQD ink leads to a thicker solid as compared to the BTA-only case. This finding necessitated a deeper look into the solvents used. We performed a simple experiment to track drying rates of pure solvents in real-time (Figure 7.14b). The hybrid amine was found to dry at a slowed rate as compared to BTA,
suggesting that the enhanced viscosity of the hybrid amine is responsible for a thicker CQD solid.

Figure 7.15. The device fabrication recipe requires a post-annealing step for the PbX$_2$-PbS CQD absorber layer for 10-15 mins at 80°C. Absorber layers for these measurements were spin-cast. (a) 2D plot showing the in-situ evolution of absorbance spectra as a function of the annealing time revealing important changes and increases. (b) Also shown is the commensurate increase in CQD film absorption at 500 nm (visible) and 940 nm (excitonic peak). (c) These changes are found to be associated with a mass loss (confirming the loss of volatile species), as determined from TGA. (d) In situ spectroscopic ellipsometry shows that the absorber layer loses ca. 40% of its initial thickness (volume) after 10 min of annealing, indicating that a volatile species was trapped within (first hint of sol-gel process like MAPbX$_3$ and PbX$_2$ systems).

The device fabrication protocol involves a post-annealing of the CQD absorber solid to ~80°C for 10-15 mins.$^{[184]}$ We were interested in understanding the importance and role of this post-annealing step. This post-annealing is crucial to getting working solar cells; un-
annealed absorbers lead to poor devices (black $J-V$ curve in Figure 7.17c). Intrigued by these initial findings, we carried out an exhaustive in-situ characterization of the annealing step. Figure 7.15a shows the evolution of the absorption spectrum of the CQD film (hybrid amine) during annealing. The solid is found to undergo significant absorption enhancement with time, as shown in Figure 7.15b for the visible (500 nm) and exciton (940 nm) wavelengths. These optical changes, during post-annealing, hint towards an enhanced interaction of the hybrid amines, which are apparently trapped within the deposited absorber, with the CQD surface (PbI$_2$), as initially proposed. In fact, TGA results (Figure 7.15c) confirm mass-loss of volatile species during this annealing step, which when combined with the in-situ thickness decrease (spectroscopic ellipsometry results, Figure 7.15d) suggests a ~50% densification of the hybrid amine deposited solid. This film densification agrees well with the absorption enhancement in Figure 7.15a.

Having confirmed that there are crucial interactions of the hybrid amine with the CQD surface (similar to a sol-gel behavior) during post-annealing which are absent/diminished in the BTA-only case, we were naturally interested to know the chemical nature of this post-annealing modification. We, therefore, carried out XPS and UPS to probe the origins of these changes. To our surprise, we did not find any signature of amines in the hybrid amine CQD solid. Also, no changes in the chemical composition were detected post-annealing. (Figure 7.16a, b, c and Table 7.8). Since these measurements are carried under UHV conditions ($\sim 10^{-10}$ mbar), it is possible that the solvated amines are getting de-gassed from the CQD surfaces. To confirm this, we compared the film thickness of a CQD film right after fabrication and upon storage in UHV for a few hours. We, indeed, found the film thickness to decrease substantially from ~650 nm to ~450 nm, suggesting that the
CQD surfaces had lost the coordinating amines, explaining why no amine signatures are detected by XPS.

**Figure 7.16.** High resolution XPS (a) Pb 4f, (b) S 2p and (c) C1s peaks before and after annealing. No changes in chemical composition were detected, as shown in the Table 7.8. UPS measurements were performed to study the effect of annealing on the electronic structure of the absorber layer. (e) SE cutoffs suggest that the work function of the film decreases by 0.2 eV upon annealing. (f) VB onsets suggest that the film becomes relatively more n-type upon annealing. The modification of the absorber’s band structure is summarized in (g).

**Table 7.8.** Relative atomic concentrations of the un-annealed and annealed absorber layers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pb</th>
<th>S</th>
<th>C</th>
<th>O</th>
<th>I</th>
<th>Br</th>
<th>O/Pb</th>
<th>S/Pb</th>
<th>I/Pb</th>
<th>Br/Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-annealed</td>
<td>33.4</td>
<td>28.3</td>
<td>19.4</td>
<td>3.4</td>
<td>5.4</td>
<td>10.2</td>
<td><strong>0.10</strong></td>
<td><strong>0.85</strong></td>
<td><strong>0.16</strong></td>
<td><strong>0.31</strong></td>
</tr>
<tr>
<td>Annealed</td>
<td>31.2</td>
<td>26.4</td>
<td>22.5</td>
<td>5.1</td>
<td>5.3</td>
<td>9.6</td>
<td><strong>0.16</strong></td>
<td><strong>0.85</strong></td>
<td><strong>0.17</strong></td>
<td><strong>0.31</strong></td>
</tr>
</tbody>
</table>
The SE cutoffs and VB spectra measured by UPS are shown in Figure 7.16e, f, respectively, and suggest that the CQD solid undergoes an n-doping upon annealing with the $E_F$ moving closer to the CB by ~0.2 eV. The changes to the band structure are schematized in Figure 7.16g. Importantly, these changes to the $E_F$ near the absorber:HTL junction can have significant implications on hole-extraction. These findings are in line with the observation of enhanced n-type electron mobility of the hybrid amine CQD solids found from FET measurements in our collaborator lab (UofT). These measurements highlight the fact that although a UHV storage can remove the amine solvates from the CQD film, a post-annealing is indeed required to render the film n-type, and to enhance its optoelectronic properties (absorption, diffusion length).
7.9 Scalable fabrication of CQD PV: Bar-coating

Figure 7.17. (a) Schematic of the wire-bar coating setup.\[188] (b) X-SEM confirms that the hybrid amine SolEx recipe leads to realization of thick absorbers, with thickness >500nm. (c) Bar-coating was used to deposit the absorber in a single-step. A solar cell employing an un-annealed absorber performs poorly (black). The performance evolves with annealing of the device, but is found to be eventually limited since the EDT-HTL is also annealed in these tests. Since, the active layer is sandwiched and the annealing process involves solvent removal, the optimum annealing timescale is understandably different than 10 minutes. These absorbers are coated at speeds of 18 m min\(^{-1}\). The best device is obtained when the absorber is annealed before the deposition of the HTL (dashed black). (d) Histogram showing reproducibility of high-performing solar cells obtained via wire-bar coating.

Figure 7.17a shows the schematic of the setup used for wire-bar coating the CQD absorber. The setup employs a wire with coils that traps the solution to be coated. The trapped solution is then dragged along the surface of the substrate as the wire is move along in the direction of the black arrow. The coating was carried out at speeds of 18 m min\(^{-1}\), similar
to blade-coating, and the film thickness was optimized to be similar to spin-coated films (>500 nm), as confirmed by X-SEM shown in Figure 7.17b. These high thicknesses for the 2D matrix engineered CQD inks, as suggested previously, are a clear advantage over the older SolEx recipe that employed BTA and yielded ~300 nm thick absorbers.

We first fabricated a solar cell avoiding the post-annealing step. As can be expected from the spectroscopic insights gleaned so far, these solar cells underperformed, as evident from Figure 7.17c (black curve). We ascribe this observation to the fact that in the absence of post-annealing the absorber suffers from: poor light absorption, poor density, inefficient n-character and electron mobility and excess hybrid amine in the CQD surface matrix. As the device is annealed, performance increases, however, since the EDT-PbS CQD HTL is also annealed, the performance is finally limited. Also, since the absorber is sandwiched and the annealing process involves removal of volatile species, the optimum annealing timescale is different than 10-15 mins. The observed trend in J-V curves, however, captures a complete picture of the formation of the 2D matrix on the CQD surfaces accompanied with the enhancement of optoelectronic properties.

J-V curves for the best bar-coated device, involving a post-annealing step, are shown as the dashed black curve in Figure 7.17c. This solar cell corresponds to a J_{SC} of 27.81 mA cm^{-2}, V_{OC} of 0.633 and a FF of 59.6%, leading to a 10.5% PCE. The success of the device resides in an enhanced current density, owing to thicker films, without compromising on charge extraction (high FF) due to better diffusion lengths in these modified SolEx CQD inks.
7.10 Conclusions

We have overcome two crucial challenges that currently hinder industrial scale-up of CQD PV, namely manufacturability in high and variable humidity conditions and scalability to large areas with low material consumption and without compromising solar cell performance. We have demonstrated air-stable CQD solar cells fabricated in a high-humidity ambient environment of ca. 50-65% R.H. Our initially ca. 5% PCE solar cells transform into highly stable, ca. 10% PCE devices upon brief storage in a dry air environment, dramatically improving the manufacturability of CQD solar cells in variable and high humidity ambient air conditions. We have thrown light on the underlying process and shown that the as-prepared solar cells suffer from an un-optimally self-doped HTL in high humidity conditions leading to issues with charge transport across the device. Storage in dry air produces oxidation species and p-dopes the HTL thereby relieving band misalignment and effectively leading to high-performing solar cells. Our best solar cell of 10.2% PCE at 0.1 cm² active areas is the highest performing CQD solar cell fabricated under an ambient of ca. 50-65% RH. Next, we overcome the scalability challenge by demonstrating >10% solar cells via two roll-to-roll compatible solution-printing techniques: high-speed blade coating and wire-bar coating. The CQD absorber layers are printed at speeds of >15 m min⁻¹, mirroring the industrial requirements, curbing ca. 96% CQD materials wastage compared to spin-coating. Our study breaks a long-standing three-way trade-off between high-moisture resilience of manufacturing, ambient air scalable manufacturing, and high PCEs of the CQD PV technology, and brings it a significant step closer to industrial implementation for outdoor and indoor applications.
Chapter 8

Conclusions and Future Perspectives

8.1 Summary

In this thesis, we have shone light on the importance of the process-structure-property-performance relationship in PbS CQDs. Using a suite of characterization techniques, we have delved deeper into the role of CQD surfaces in the carrier trapping phenomenon. Our studies highlight that surface traps have, so far, been directly responsible for rendering CQD PV unscalable and industrially incompatible, limiting its fabrication only to low-humidity environments via wasteful and tedious methods. Our understanding of CQD surfaces have led us to several successful trap management protocols and have finally allowed us to achieve scalable, industry-compatible fabrication and operation of CQD PV in ambient environments of high, uncontrolled humidity – a demonstration that has so far eluded the community, ever since the first reports of CQD solar cells emerged in 2005.

As detailed in Chapter 2, the field of CQDs took a boost in 1993 with the demonstration of the hot-injection synthesis. However, it was not until 2003, when facile synthesis of PbS CQDs was reported, that this thin-film PV started garnering interest. Lead chalcogenide CQDs, of which PbS CQDs are a class, perfectly fit the requirements of a solar cell absorber by exhibiting intense light absorption, charge carrier mobilities, high dielectric constants and low exciton BEs. Underpinned by rampant forays into ligand passivation and smart device architectures, CQD PV has strengthened over time and currently stands at 12.5% PCE.
At the start of this PhD, solid-state ligand exchange was the routine strategy to realize electronically coupled PbS CQD solids that could be directly used as absorber layers in solar cells. This would typically require 10-12 LbL deposition cycles in order to achieve the target absorber thickness, and as such, was a very highly wasteful and time-consuming protocol. This encouraged us to perform an exhaustive investigation into the nature of the solid-state exchange process, which we discussed in Chapter 4. We probed the interaction of the linker and solvent molecules with the CQD surfaces and gained important insights into how these interactions shaped the property and performance of CQD solar cells. We realized that the protic nature of the process solvent used in the solid-state exchange, MeOH, was in fact directly responsible for leaching-off surface halide passivants and resulting in surface traps, which became evident for longer exposures of the solvent with the CQD surface. This explained the reason behind the reliance of the CQD PV community on the 10-12 LbL approach: this approach, although unscalable, entailed a 3s exposure of the CQD surfaces to the MeOH solvent, thereby limiting the surface damage. We, then, designed an alternative solid-state exchange by replacing MeOH with ACN, and experimentally confirmed that the aprotic solvent was benign to the CQD surfaces even for extended exposures. Stimulated by this modified recipe, we fabricated CQD solar cells in as few as 3 LbL cycles, with each individual thicker layer requiring 60s of exchange time, and achieved performance parity with the then-standard of 10-12 LbL MeOH-exchange based solar cells.

We realized that controlled net doping of CQD solids had not previously been demonstrated in the context of solar cells. Remote dopants can be used to efficiently dope the solids without resorting to chemical modifications of the CQD surfaces. We envisaged
employing metal-organic molecules as remote dopants to efficiently affect n- or p-doping of the solids, depending of the energetics of the dopants employed. This topic was dealt with in Chapter 5, where a library molecules was demonstrated as of n- and p-dopants, by studying shifts in $E_F$ of the CQD solids. The recipe involved a single-step dipping of the solids into the dopant solution for an optimized duration. Taking the advantage of this facile remote doping strategy, we aimed at p-doping the CQD absorber layer in the context of the p-n heterojunction solar cells. The MPA-PbS CQD film, an efficient absorber solid in this architecture, is known to possess a shallow $E_F$ giving it a slight n-character. We, therefore, argued that a mild p-doping can, in essence, render it intrinsic leading to enhancement of $V_{OC}$, without significantly hurting the depletion region. This was realized by a long-soak of the CQD solid in the solution of a carefully selected deep EA molecule, Mo(tfd-COCF$_3$)$_3$, to affect charge transfer of in-gap electrons uniformly from within the CQD absorber resulting in a trap passivated, intrinsic MPA-PbS CQD film. These optimally doped solar cells exhibited improvements in all device parameters, resulted in 7.8% PCE solar cells (versus 6% controls) and demonstrated that remote molecular doping could be used as facile trap passivation strategy for CQD absorbers.

In Chapter 6, we extended the application gamut of the remote molecular doping recipe to include the latest, high-performing CQD solar cells that utilize CQD absorbers achieved via SolEx in an n-i-p architecture. These solar cells employ an EDT-PbS CQD solid as the HTL to block the egress of photo-generated electrons towards the hole-collecting electrode, enhancing charge collection and leading to high-performing devices. Besides, the absorbers feature single-step spin-coated MAPbI$_3$ or PbX$_2$-PbS CQDs bringing CQD PV a step closer to scalable fabrication. We, however, realize that these promising architecture
suffer from an un-optimally doped HTL restricting band bending near the hole-collecting junction at the MPP limiting charge collection. We argued that selectively remote p-doping the HTL with Mo(tfd-COCF$_3$)$_3$ can alleviate band bending issues at the hole-collecting absorber:HTL junction. The obvious challenge of leaving the CQD absorber beneath unaltered, yet being able to effectively p-dope the HTL was overcome by restricting the single-step soaking to a short duration of 30s. The doping recipe efficiently deepened the $E_F$ of the HTL, as evidenced by UPS and KP measurements, and led to realization of 9.5% efficient solar cells.

Several of the CQD solar cells reported so far in this thesis were fabricated in the laboratory of a collaborator at the University of Toronto in the dry winter season when the humidity levels inside the lab are very low. This is, in fact, true for most of the high-performing CQD solar cells reported in literature so far: fabrication has been carried out in cities such as Toronto, Golden and Boston, which remain substantially dry part of the year (Toronto, Boston) or throughout (Golden). Fabrication and operation of efficient solar cells in a high humidity environment, such as our laboratory at KAUST, presents itself as a serious challenge to the field of CQD PV.

A second important challenge in the field is to achieve scalability of the device fabrication process. Although SolEx CQD inks have helped realize single-step deposition of the absorbers, all the demonstrations, to date, have employed spin-coating, leading to materials consumption at par with the 3 LbL deposition scheme we demonstrated in Chapter 4. SolEx CQD inks offer a path to depositing the absorber in a single-step via a roll-to-roll compatible technique such as blade- or bar-coating.
These two major challenges combine to render CQD PV an unreliable solar power conversion technology and threaten to impede its adoption, even as the device performances continue to soar. In Chapter 7, we took the aim to evaluate and address these two challenges. We gleaned crucial insights into the effect of high-humidity on CQD surfaces, and realize that the high moisture in our KAUST laboratory leads to an un-optimally doped HTL, drastically impeding charge collection and resulting in ~5% PCE as-prepared solar cells. These solar cells were comparatively much lower in performance than the best-reported devices employing this architecture (~11% on 0.05 cm² active areas). We then devised an ‘oxygen-doping’ recipe to overcome the ill-effects of high moisture and recover the PCEs of our as-prepared solar cells. The devices were stored in a dry-box for a day; upon re-measuring, PCEs of ~10% were obtained (active areas of 0.1 cm²). Using spectroscopic insights, we were able to explain the mechanism behind this performance recovery: during dry-air storage, the moisture on the CQD surfaces desorbs over time making way for oxygen to attach to the surface, cleaving some of the EDT ligands in the process. This leads to an effective deepening of the E_F of HTL and betters charge collection across the device.

Having solved the intrinsic issue of ambient manufacturability of CQD PV, we resorted to fabricating the CQD absorbers using blade- and bar-coating techniques in a single-step. The coatings were carried out at industrially viable speeds of >15 m min⁻¹ and required 1/25th the CQD material needed for spin-coated absorbers. Utilizing these roll-to-roll compatible coating techniques, we were also able to demonstrate large-area solar cells (0.5 cm²) and flexible devices exhibiting excellent bending durability.
To sum up, this thesis has aimed at developing an understanding of surface traps in the context of CQD solar cells and inventing efficient protocols to mitigate them, such as solvent engineering, remote molecular doping and oxygen doping, with an eye on scalable manufacturability in realistic ambient air conditions. We reach the culmination of our efforts by exploiting this understanding to finally break the barrier to ambient-manufactured, scalable and efficient CQD solar cells.

8.2 Future directions

An area that currently needs serious attention in CQD PV is the issue of low $V_{OC}$ which has consistently continued to remain at ~50% of the band gap, even as the PCEs have soared over the last few years thanks to concomitant gains in $J_{SC}$ and FF. Surface traps play a core role in limiting $V_{OC}$, and as has been expounded upon in this thesis, probing the immediate surface environment of the CQDs (process solvents, linkers, molecules, moisture) can lead to novel ways of smartly managing traps and pushing the limits on the device performance and scalability. It is believed that the findings presented herein will arouse interest towards a more exhaustive understanding of the CQD surfaces leading to further possible gains in the $V_{OC}$ and hence the overall PCEs. The latest suite of device architectures and matrix-engineered PbS CQDs allow efficient harvest of solar light and subsequent charge extraction over ~600 nm thick absorbers, directly benefiting from superior carrier diffusion lengths. Efforts to further increase $V_{OC}$ in these architectures can definitely place CQD PV in reach of the 15% PCE limit.

A major effort in this thesis has been the realization of ambient-manufactured, scalable CQD solar cells compatible with industrial requirements of roll-to-roll manufacturing in
uncontrolled humidity environments. These devices, however, still require the deposition of a CQD HTL that has to be spin-coated atop the scalably-coated SolEx absorber, followed by solid-state exchange. This leaves room for a smarter design that can replace the CQD HTL with a thin SolEx layer that is humidity-resilient and can be scalably-deposited. Another option might be to do away with the HTL and tailor the band structure (via surface dipoles and graded doping) at the top of the SolEx absorber near the hole-collecting electrode. Such an architecture will combine the merits of an n-i-p configuration that the CQD HTL currently allows, with the opportunity to scalably coat the full device and large-area modules.

The field, we believe, also lacks efforts towards fabrication of tandem solar cells, with the best CQD tandems only recently reaching ~9%. CQDs offer a cost-effective path to efficient utilization of the solar spectrum by the virtue of band gap tunability. The recent success with SolEx CQD absorbers presents an interesting avenue of utilizing these robust materials to build tandem solar cells, which can be scalably printed. Combining CQD solids with different band gaps as top and bottom cells can help push PCEs >15%.

Finally, we believe that developments reported in this dissertation have placed PbS CQD PV on a firm ground with respect to understanding of surface trap mitigation, ambient-manufacturability and scalable fabrication. It, therefore, becomes easier than ever to make a switch to an environmentally-friendly, non-toxic alternative. A recent highlight has been solar cells employing ultra-thin films (~35 nm) of AgBi$_2$S$_3$ CQDs as absorbers with PCEs >6% on active areas of ~0.016 cm$^2$. Due to their intense absorption, solution-processability
and, most importantly, non-toxicity, AgBi$_2$S$_3$ CQDs offer a very interesting path forward for thin-film PV.
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