Optoelectronic Characterization of Novel Photovoltaic Nanomaterials

by

Andrew Pak Tao Kam

A thesis submitted in conformity with the requirements for the degree of Master of Applied Science

The Edward S. Rogers Sr. Department of Electrical and Computer Engineering
University of Toronto

© Copyright by Andrew Pak Tao Kam 2018
Optoelectronic Characterization of Novel Photovoltaic Nanomaterials

Andrew Pak Tao Kam
Master of Applied Science

The Edward S. Rogers Sr. Department of Electrical and Computer Engineering
University of Toronto

2018

Abstract

Solution-processed nanomaterials such as lead sulfide (PbS) colloidal quantum dots (CQDs) combine various manufacturing benefits and facile spectral tunability. However, the low mobility of CQD films limits its power conversion efficiency in photovoltaic cells. Here, I employ a novel femtosecond transient absorption (fs-TA) technique to determine the mobility of PbS CQD films that have undergone state of the art surface treatments. A significant mobility increase from $3 \times 10^{-2}$ to $5 \times 10^{-1}$ cm$^2$ V$^{-1}$ s$^{-1}$ was determined for iodide passivated and novel perovskite-shelled PbS CQDs, respectively. I performed, for the first time, temperature-dependent ultrafast carrier dynamics in perovskite-shelled CQDs using fs-TA, and determined an activation energy of 14 meV required for carrier hopping. Complementary studies that used time-of-flight measurements to determine the mobility in solar cell configuration corroborated the fs-TA method. Taken together, these results indicate a promising avenue toward improved CQD solar cells.
# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table of Contents</td>
<td>iii</td>
</tr>
<tr>
<td>List of Figures</td>
<td>v</td>
</tr>
<tr>
<td>List of Tables</td>
<td>vi</td>
</tr>
<tr>
<td><strong>1 Introduction</strong></td>
<td></td>
</tr>
<tr>
<td>1.1 Motivation for Photovoltaics</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Motivation for Colloidal Quantum Dots</td>
<td>2</td>
</tr>
<tr>
<td>1.3 Organization of Thesis</td>
<td>5</td>
</tr>
<tr>
<td><strong>2 Colloidal Quantum Dots</strong></td>
<td>6</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>6</td>
</tr>
<tr>
<td>2.2 Background</td>
<td>6</td>
</tr>
<tr>
<td>2.3 Carrier Transport</td>
<td>8</td>
</tr>
<tr>
<td>2.4 Fundamentals of Solar Cells</td>
<td>11</td>
</tr>
<tr>
<td>2.5 Colloidal Quantum Dot Solar Cells</td>
<td>16</td>
</tr>
<tr>
<td><strong>3 Contact and Contactless Methods for Determining Charge Carrier Mobility</strong></td>
<td>20</td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>20</td>
</tr>
<tr>
<td>3.2 Contact Methods</td>
<td>21</td>
</tr>
<tr>
<td>3.2.1 Time-of-Flight</td>
<td>21</td>
</tr>
<tr>
<td>3.2.2 Trap-Free Space-Charge Limited Current</td>
<td>24</td>
</tr>
<tr>
<td>3.2.3 Field-Effect Transistor</td>
<td>25</td>
</tr>
<tr>
<td>3.2.4 Charge Extraction by Linearly Increasing Voltage</td>
<td>26</td>
</tr>
<tr>
<td>3.3 Contactless Methods</td>
<td>27</td>
</tr>
<tr>
<td>3.3.1 Photoluminescence</td>
<td>28</td>
</tr>
<tr>
<td>3.3.2 Femtosecond Transient Absorption</td>
<td>29</td>
</tr>
<tr>
<td>3.4 Summary of Methods</td>
<td>32</td>
</tr>
<tr>
<td><strong>4 Charge Carrier Mobility of Colloidal Quantum Dot Films</strong></td>
<td>34</td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td>34</td>
</tr>
<tr>
<td>4.2 Charge Carrier Mobility from Femtosecond Transient Absorption</td>
<td>35</td>
</tr>
<tr>
<td>4.3 Charge Carrier Mobility from Time-of-Flight</td>
<td>45</td>
</tr>
</tbody>
</table>
5 Conclusion

5.1 Summary ......................................................... 52
5.2 Contributions .................................................... 53
5.3 Future Work ...................................................... 53
# List of Figures

1.1 Global electricity-generating capacity ........................................ 2  
1.2 AM1.5G solar spectrum ....................................................... 3  
2.1 Introduction to CQDs ......................................................... 7  
2.2 Ligand exchange process .................................................... 8  
2.3 Types of charge transport in CQD films .................................. 9  
2.4 Energy band diagram of a p-n junction ................................. 13  
2.5 Typical J-V characteristics of a solar cell .............................. 15  
2.6 Early CQD device architectures ............................................ 17  
2.7 The advent of halide passivation in CQD solar cells ................... 18  
3.1 Schematic diagram of the TOF method .................................. 23  
3.2 Typical photocurrent transients obtained from TOF ................. 23  
3.3 J-V characteristics under SCLC regime .................................. 25  
3.4 Determining mobility from PET .......................................... 26  
3.5 Determining mobility from CELIV ....................................... 27  
3.6 Charge carrier transfer mechanics between donors and acceptors . 29  
3.7 Schematic of the pump-probe technique ................................ 30  
3.8 Energy band diagram of donors and acceptors ........................ 31  
4.1 Experimental setup for fs-TA measurements .......................... 36  
4.2 Absorption spectrum of CQD films ..................................... 37  
4.3 fs-TA spectrum of perovskite-shelled PbS CQDs with 5% acceptor concentrations .......................... 38  
4.4 $\Delta A$ transients of iodide passivated and perovskite-shelled PbS CQDs ......................................................... 39  
4.5 Trap density and trapping lifetime of iodide passivated and perovskite-shelled PbS CQDs ................................. 40  
4.6 fs-TA spectrum for perovskite-shelled PbS CQDs with 5% acceptor concentrations at 80 K ......................... 42  
4.7 Temperature-dependent fs-TA of perovskite-shelled PbS CQDs with 5% acceptor concentrations .......................... 43  
4.8 fs-TA of perovskite-shelled PbS CQDs with a PbS-EDT layer ....... 44  
4.9 Experimental setup for TOF measurements .......................... 46  
4.10 Photocurrent transients of iodide passivated and perovskite-shelled PbS CQDs ................................................. 48  
4.11 Extracting mobility from $t_{tr}$ ........................................... 49  
4.12 Comparison of carrier transport in fs-TA and TOF .................. 51
List of Tables

2.1 Implications for CQDs. .................................................. 16

3.1 Summary of discussed methods for mobility extraction. .................. 33

4.1 Summary of mobilities determined from fs-TA. .......................... 45
4.2 Summary of mobilities determined from fs-TA and TOF. ................. 50
Chapter 1

Introduction

1.1 Motivation for Photovoltaics

Solar energy electricity has only recently passed the milestone of meeting 1% of the world’s electricity needs. Fossil fuels, with their CO₂ emissions, are still used even today to meet nearly 80% of demand [1]. This is true even though the annual available solar energy vastly exceeds the world’s total energy consumption [2]. Over the past decade, the global total number of solar cells installed has increased from about 7 GW to over 300 GW, with the projected global total reaching close to 1 TW by 2021 [3,4]. The relative growth of solar energy compared to the world’s energy consumption is significant (Figure 1.1). The increasing demand for solar cells drives the need for novel technologies that increase the generated power per dollar. This can be realized by improving photovoltaic performance and inventing more scalable and cost-effective materials and manufacturing techniques.
1.2 Motivation for Colloidal Quantum Dots

Bulk crystalline silicon solar cells currently dominate the market with over 90% of the annual generated photovoltaic power in 2016 [5]; however, silicon has an indirect bandgap of 1.12 eV and is unable to absorb light with wavelengths greater than 1100 nm. This limits silicon cells to absorbing about 3/4 of the power available incident from the sun (Figure 1.2).
Figure 1.2 | AM1.5G solar spectrum. The solar spectrum under standardized AM1.5G (air mass 1.5 global) conditions for testing solar cell performance. Since the solar spectrum is dependent on various factors, these conditions correspond to an atmosphere thickness of 1.5, an integrated power density of 100 mW cm\(^2\) at an incident angle of 48.2° \([6]\). The absorption limit of Si is marked on the figure. The remainder of the infrared solar spectrum is left unharvested by cSi, accounting for roughly 1/4 of the integrated power.

Colloidal quantum dots (CQDs) are semiconductor nanocrystals that combine a wide spectral tunability via the quantum size effect, and the manufacturing benefits of solution processed materials. CQDs are favoured for their ability to have its bandgap modified at the time of synthesis. Lead sulfide (PbS) CQDs can be tuned to absorb light from 600 nm up to 3000 nm \([7]\). Importantly, this material platform has the advantage of being compatible with other technologies and substrates, such as flexible substrates for the use in wearable electronics, and in particular, a compliment to widespread silicon photovoltaics. They provide with inexpensive manufacturing routes due to their low temperature synthesis, solution processability, and large-scale deposition compatibility via spray-coating, roll-to-roll printing,
and blade-coating \[8\]. Currently, best performing certified CQDs solar cells exhibit power conversion efficiencies in excess of 12\% \[9\].

CQDs consist of 100 to 1000 atoms and are grown in solution. Their growth process is not perfect, which leads to a distribution of CQD with different sizes and surface defects. \[10\] The ensuing chemical processes required to achieve nanocrystalline conductive films result in the introduction of additional polydispersity due to CQD etching, aggregation and fusion, leading to more electronic defects and unoptimized charge transport properties.

Thus far, CQDs have been characterized from having low mobilities \((10^1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\) \[11\] compared to high quality bulk crystalline semiconductors \((10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \text{ for Si and GaAs})\) \[12\]. Despite the high absorption coefficient of CQDs, imperfect passivation, and low mobility, resulting in short diffusion lengths – the scale over which charges can diffuse before recombination – on the order of hundreds of nanometers \[13,14\]. The mismatch between the maximum length for efficient charge collection and the thickness required for full absorption, on the order of micrometres, is known as the absorption-extraction compromise.

The development of accurate methods to characterize charge mobility and diffusion length, which can provide with insights to further improve CQD synthesis, surface passivation, and device architecture, is the cornerstone to enable the realization of improved photovoltaic devices based on CQDs.

Due to the lower mobility of CQDs materials compared to bulk crystalline semiconductors, traditional characterization such as Hall measurements are either difficult to realize or not applicable. For low mobility materials, the established methods used include time-of-flight (TOF) \[15,16,18\], steady-state trap-free space-charge limited current (TF-SCLC) \[15,19\], field-effect transistor (FET) method \[15,20\], and charge extraction by linearly increasing voltage (CELIV) \[15,18,21\]. These techniques, however, probe the material within a final device form (or some variant), which may be different from its fundamental mobility. Specifically for CQDs, purely optical methods have been developed to determine the unaltered
mobility from photoluminescence (PL) \[13\], and the novel femtosecond transient absorption (fs-TA) \[22\]. Herein, I aim to study the mobilities determined with a fs-TA purely optical method, compared against TOF requiring a device form, to provide insight on factors limiting transport in CQDs.

1.3 Organization of Thesis

In this thesis, I perform mobility measurements on state of the art halide passivated PbS CQDs and on novel perovskite-shelled PbS CQDs to study their transport behaviour under various conditions. I employ fs-TA to characterize the ultrafast carrier dynamics in CQD films. I extend upon fs-TA measurements to incorporate temperature-dependence, for the first time, on perovskite-shelled CQDs to determine its activation energy required for carrier transport. Lastly, I integrate the CQDs films into full solar cell devices, and quantify the change in mobility with TOF. In doing so, I identified the chief limitations to take advantage of improved, state of the art high quality CQD solids, in existing PV architectures.

Chapter 2 provides an introduction for CQDs, solar fundamentals, and discusses the material properties that affect photovoltaic performance in CQD materials. It also includes a review of the past advances and the current state-of-art CQD solar cells. Chapter 4 discusses the benefits and limitations of contact and contactless methods for characterizing carrier mobility. It describes TOF and fs-TA method giving the required background theory, derivations, and the realization of the measurement. Chapter 5 presents the results of the mobility extraction measurements performed on a novel, perovskite-shelled PbS CQDs compared to the iodide passivation \[23\]. The carrier dynamics of the perovskite-shelled PbS CQDs are further studied with temperature-dependent fs-TA. I conclude in Chapter 7 with future work enabled by our findings for the advancement of CQD materials.
Chapter 2

Colloidal Quantum Dots

2.1 Introduction

This chapter provides an introduction to CQDs photovoltaics. The main types of carrier transport present in CQD films are presented, and the connection between CQD fundamental optoelectronic properties and the underlying solar cell operation are discussed.

2.2 Background

Quantum dots are composed of about 100 to 1000 individual atoms that are arranged in a nanocrystal structure [24]. When the size of a nanocrystal reaches that of about half its exciton Bohr radius – the distance between an electrostatically bounded electron and hole pair – quantum confinement effects appear [25]. For a spherical QD, the type of confinement is similar to that of a quantum well. Changing the size of a QD also changes its bandgap [26] (Figure 2.1). As the size of a QD decreases, its bandgap increases relative to the bulk bandgap of the material, and hence its optoelectronic properties.
Figure 2.1 | Introduction to CQDs. Size tuning of a QD resulting in a change in bandgap. As the QD becomes larger, it approaches the bandgap of the bulk material.

Each CQD has electronic states dependent on its size and shape, analogous to the orbital energy levels of an atom [10]. When CQDs are synthesized, the assembly of atoms vary slightly between nanocrystals. The distribution of CQD sizes and shapes causes in variations in the electronic structure of a macroscopic CQD film, leading to sink states within the energy landscape that result in carrier losses [24]. Dangling chemical bonds on the CQD surface and the presence of oxide species contribute to additional trap states. Since CQDs have a very high surface-to-volume ratio, the passivation of surface traps becomes an important factor in determining its electrical properties.

During synthesis, surface passivating reagents known as ligands are used for colloidal stability, and to control the rate of CQD growth [27]. Typically, ligands optimized for CQD synthesis consist of long chains of organic molecules, such as oleic acid. These long ligands impede electrical transport when the CQDs are assembled in films, and are generally replaced by shorter ligands consisting of only a few atoms in a process called ligand exchange (Figure 2.2). Shorter ligands allow for better coupling between CQDs, and hence better carrier transport [28]. Importantly, these ligands need to provide protection against external agents.
Figure 2.2 | Ligand exchange process. Long organic ligands used for colloidal stability are replaced by shorter ligands which have improved electrical properties. Reprinted by permission from Macmillan Publishers Ltd: Nature Materials [23], copyright 2016.

such as oxygen and moisture that would deteriorate the optoelectronic properties of the CQD film. Halide passivation schemes have been shown to simultaneously provide with improved transport and good passivation.

2.3 Carrier Transport

The electronic structure of an atom consists of discrete energy states. If more atoms are introduced, and the spacing between them is reduced, the wavefunctions of each atom begins to overlap with neighbouring atoms and the electronic states start to split. As the spacing is further reduced, electronic bands will start to form, creating the electronic structure of typical bulk crystalline semiconductors. The electronic structure of CQDs is analogous to that of individual atoms, with each CQD having its own ensemble of discrete energy levels. As a result, carrier transport between CQDs occurs mainly due to hopping or tunneling (Figure 2.3). It is important to note that hopping or tunneling events are a random process, hence the carrier mobility in CQDs is related to the average velocity of carriers over a certain distance, such as the depletion region or active layer [7].
Figure 2.3 | Types of charge transport in CQD films. (a) Depiction of variable range hopping in CQDs. Path I (solid lines) shows hopping between nearest neighbours. Path II (dashed lines) shows hopping between not neighbours. (b) Depiction of tunneling in CQDs. Tunneling between adjacent CQDs favours low energy barriers and small spatial distances where there is a bigger overlap in its wavefunctions [7].

Hopping Transport

In the hopping regime, the transport of carriers between the localized electronic states of CQDs occurs due to thermal activation [7]. For a carrier to hop between energy states $E_i$ and $E_j$, it must acquire sufficient energy $\Delta E_{ij}$ where $\Delta E_{ij} = E_j - E_i$ is the energy difference between the two energy states. The probability of hopping is determined by the energy difference $\Delta E_{ij}$ and the spatial distance between localized states $r_{ij}$. Carrier hopping
favours small distances $r_{ij}$ and large energies $E_{ij}$.

In variable range hopping (VRH), carrier hopping can occur between nearest neighbours (path I) or not between nearest neighbours (path II) (Figure 2.3a). The Mott VRH describes the low temperature conductivity $\sigma$ when hopping via path I dominates as

$$\sigma \propto \exp \left[-\frac{T_0}{T}\right]$$

(2.1)

When hopping via path II becomes more prominent, the conductivity $\sigma$ becomes

$$\sigma \propto \exp \left[-\left(\frac{T_0}{T}\right)^{1/4}\right]$$

(2.2)

where $T_0 = q^2 / \varepsilon \alpha$, $q$ is the elementary charge, $\alpha$ is the localization length, $\varepsilon$ is the dielectric constant of the material, and $T$ is the absolute temperature. In the case where the localization length is much smaller than the spatial distance between hopping states, the overlap between wavefunctions are neglected. In this regime, the Efros-Shklovskii (ES) VRH describes the low temperature conductivity $\sigma$ as

$$\sigma \propto \exp \left[-\left(\frac{T_0}{T}\right)^{1/2}\right]$$

(2.3)

The decrease in conductivity with temperature is less dramatic when Mott-VRH hopping via path II becomes a large contribution of hopping events, as one would intuitively expect.

**Tunneling Transport**

In the tunneling regime, transport between adjacent CQDs occurs due to the quantum mechanical tunneling of electrons. For strongly coupled CQDs, electrons have a higher probability of tunneling through the energy barrier between them. The coupling energy $\beta$ is expressed as

$$\beta$$
\[ \beta \approx h \Gamma \] 

where \( h \) is Planck’s constant, and \( \Gamma \) is the tunneling rate given by

\[ \Gamma \approx \exp \left( -2\pi \Delta x \sqrt{\frac{8 m^* \Delta E}{h^2}} \right) \] 

where \( \Delta x \) is the width of the barrier, \( \Delta E \) is the height of the barrier, and \( m^* \) is the carrier effective mass. Unlike hopping transport, tunneling transport is temperature-independent. Tunneling transport is heavily dependent on the width of the energy barrier, hence the spatial distance between coupled CQDs. For CQDs that are minimally separated in space, there is a greater overlap between wavefunctions, thus resulting in stronger coupling (Figure 2.3b).

2.4 Fundamentals of Solar Cells

This section outlines the fundamental semiconductor physics underlying solar cell operation. It presents the figures of merit for solar cells and its implications for CQDs.

P-N Junction

A p-type semiconductor is a type of semiconductor that has been doped resulting in a higher hole concentration than electron concentration. Conversely, an n-type semiconductor has a higher electron concentration than hole concentration. A p-n junction is created when a p-type semiconductor is brought into contact with an n-type semiconductor. The excess of holes from the p-type semiconductor diffuse into the n-type semiconductor, and recombine with the dopant sites, resulting in a region depleted of charge. The same effect occurs in the p-type semiconductor for electrons. The resultant region is called the depletion region. The charged dopant ions create an electric field across the depletion region with a built-in potential \( V_{bi} \) that is given by
\[ V_{\text{bi}} = \frac{k_B T}{q} \ln \left( \frac{N_A N_D}{n_i^2} \right) \]  

(2.6)

over the width of the depletion region \( W \) expressed as

\[ W = \sqrt{\frac{2 \varepsilon k_B T}{q^2} \ln \left( \frac{N_A N_D}{n_i^2} \right) \left( \frac{1}{N_A} + \frac{1}{N_D} \right)} \]  

(2.7)

where \( \varepsilon \) is the permittivity of the material, \( k_B \) is Boltzmann’s constant, \( T \) is the temperature, \( q \) is the elementary charge, \( N_A \) is the acceptor dopant concentration in p-type semiconductor, \( N_D \) is the donor dopant concentration in the n-type semiconductor, and \( n_i \) is the intrinsic carrier density of the material.

The quasi-neutral region exists on either side of the depletion region (Figure 2.4). When a photon passes through a semiconductor, there is a probability that the photon will become absorbed by the material resulting in the creation of an electron-hole pair. Photogenerated carriers within the depletion region are swept away by the built-in electric field to the quasi-neutral region. Photogenerated carriers in the quasi-neutral region, along with those swept into it by the built-in field, must diffuse until they reach the electrodes or recombine. The efficient extraction of charges carriers is dependent on the carrier drift length \( L_{\text{drift}} \) and carrier diffusion length \( L_{\text{diffusion}} \), given by

\[ L_{\text{drift}} = \mu E_{\text{bi}} \tau \]  

(2.8)

and

\[ L_{\text{diffusion}} = \sqrt{D \tau} \]  

(2.9)

respectively, where \( \mu \) is the carrier mobility, \( E_{\text{bi}} \) is the built-in electric field, \( \tau \) is the carrier lifetime, and \( D \) is the diffusion coefficient. The diffusion coefficient \( D \) and mobility \( \mu \) are related by the Einstein relation:
Figure 2.4 | Energy band diagram of a p-n junction. Spatial band diagram of a p-n junction illustrating the band bending caused by the built-in electric field, the drift of carriers within the depletion region, and diffusion of carriers in the quasi-neutral region. $E_{c,n}$ and $E_{v,n}$ are the energies of the conduction and valence band in the n-type semiconductor, respectively, and similarly for $E_{c,p}$ and $E_{v,p}$ for the p-type semiconductor. Under illumination, quasi-Fermi levels in the n-type material $F_n$ and in the p-type material $F_p$ are separated by $qV_{oc}$. 
\[
\frac{D}{\mu} = \frac{k_B T}{q}
\]  
(2.10)

It can be seen from Equation 2.8 and 2.9 that efficient extraction of charge carriers out of the p-n junction requires a high mobility and long carrier lifetimes, both of which are impacted by the amount of trap states present \[7\].

**P-I-N Junction**

The p-i-n junction, an extension of the p-n junction, incorporates an intrinsic semiconductor between the p-type and n-type semiconductors. It is the typical architecture of current state of the art CQD solar cells because the intrinsic layer is essentially fully depleted. In this architecture, the built-in electric field extends throughout the depleted region allowing for more efficient extraction of photogenerated carriers.

**Figures of Merit**

The current density as a function of voltage (J-V) characteristics for a solar cell in the dark and under illumination is shown in Figure 2.5. The dark current shows the rectifying nature of the p-n junction. The power conversion efficiency \(\eta\) is determined by the current under illumination, and is given by \[29\]

\[
\eta = \frac{V_{\text{max}} J_{\text{max}}}{P_{\text{inc}}} = \frac{V_{\text{oc}} J_{\text{sc}} \text{FF}}{P_{\text{inc}}}
\]  
(2.11)

where \(V_{\text{max}}\) and \(J_{\text{max}}\) are the voltage and current at the maximum power point, \(P_{\text{inc}}\) is the power of the incident light, \(V_{\text{oc}}\) is the open-circuit voltage, \(J_{\text{sc}}\) is the short-circuit current, and \(\text{FF}\) is the fill factor. \(V_{\text{max}}, J_{\text{max}}, V_{\text{oc}}, J_{\text{sc}},\) and \(\text{FF}\) are all parameters that can be extracted from the J-V characteristic under illumination in order to determine the power conversion efficiency of the solar cell.
Figure 2.5 | Typical J-V characteristics of a solar cell. The quantities related to photovoltaic performance $V_{\text{max}}$, $J_{\text{max}}$, $V_{\text{oc}}$, and $J_{\text{sc}}$ are marked on the plot.

The short-circuit current $J_{\text{sc}}$ is the maximum current per unit that can be extracted from the solar cell. It is dependent on the light intensity, absorption of the solar cell, and carriers lost due to recombination. The open-circuit voltage $V_{\text{oc}}$ is the maximum voltage generated by the solar cell and is expressed as

$$V_{\text{oc}} = \frac{k_B T}{q} \ln \left( \frac{J_{\text{sc}}}{J_0} + 1 \right)$$  \hspace{1cm} (2.12)

where $J_0$ is the reverse saturation current density related to the rectification of the junction.

The fill factor FF is a measure of the solar cell quality, defined as a ratio between maximum output power to theoretical output power \[29]\):

$$\text{FF} = \frac{J_{\text{max}} V_{\text{max}}}{J_{\text{sc}} V_{\text{oc}}}$$  \hspace{1cm} (2.13)

FF is related to the series and shunt resistance of the solar cell. A low series resistance and high shunt resistance is desirable for a high fill factor. It can be seen from Equation \[2.11\]
that $V_{oc}$, $J_{sc}$, and FF all need to be maximized for improved photovoltaic performance.

**Implications for Colloidal Quantum Dots**

Given the figures of merit which encompass the photovoltaic performance, Table 2.1 summarizes their implications for CQDs.

**Table 2.1 | Implications for CQDs.** A summary of how each figure of merit of photovoltaics is affected by the physical properties of the CQDs.

<table>
<thead>
<tr>
<th>Figure of Merit</th>
<th>Fundamental Aspect of CQDs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{oc}$</td>
<td>• Limited by trap states, possibly from surface passivation, film defects, impurities</td>
</tr>
</tbody>
</table>
| $J_{sc}$        | • Dependent on efficient extraction of charge carriers, hence mobility  
|                 | • A requirement that $L_{drift}$ and $L_{diffusion}$ be larger than the width of the depletion and quasi-neutral region, respectively |
| FF              | • Requires minimized series resistance, and maximized shunt resistance  
|                 | • Series resistance dependent on the mobility |

**2.5 Colloidal Quantum Dot Solar Cells**

Early PbS CQD solar cells relied on the use of short organic ligands, exchanged in solid-state, to passivate the CQD surface. Solar cells were based off of Schottky architectures, consisting of p-type CQDs and a metal electrode forming a metal-semiconductor junction (Figure 2.6a), and achieving modest power conversion efficiencies $\eta$ of 3.6% [30]. Schottky devices suffered from poor carrier extraction, as carriers photogenerated at the ohmic side of the device would need to diffuse through the CQD film until it was collected, making it
Figure 2.6 | Early CQD device architectures. (a) Schottky architecture consisting of n-type CQDs and a metal electrode. The depletion region forms at the back of the solar cell at the metal-semiconductor interface. (b) Depleted-heterojunction architecture consisting of a transparent n-type electrode and p-type CQDs. The depletion region forms at the front of the solar cell. Reprinted with permission from [31]. Copyright 2010 American Chemical Society.

susceptible to recombination losses [31]. Depleted-heterojunctions (DH) were developed to overcome the limitations of the Schottky junction. Here, p-type CQDs are deposited on top of a transparent n-type electrode to form the depletion region between the two materials (Figure 2.6b), and achieving η of 5.1%. DHs have the benefit that the depletion region exists on the side of illumination, resulting in a greater number of photogenerated carriers.

The next step in the chief advancement in CQD solar cells was the introduction of solid-state passivation of surface states using halide anions, which allowed the passivation of traps otherwise inaccessible by larger organic molecules (Figure 2.7a). A certified η of 7.0% was achieved using the DH architecture with a hybrid passivated CQD active layer, consisting of both organic and halide ligands [32].

Following the work of hybrid passivated CQDs, a method was developed for the complete exchange of long organic ligands with smaller halide anions by using tetrabutylammonium
iodide (TBAI) in the solid-state exchange \[33\]. The addition of a PbS CQD layer exchanged with 1,2-ethandithiol (EDT) ligands (PbS-EDT layer) creates an energy barrier which block electrons from travelling toward the hole collecting electrode, and enables better extraction of holes. This architecture resembles that of a p-i-n junction, and resulted in a certified $\eta$ of 8.55%. The introduction of methylammonium iodide (MAI) to the CQDs in ink form prior to the solid-state exchange process further improved the passivation of the CQD surface with halide anions, and resulted in a certified $\eta$ of 10.6% \[42\].

The current state-of-the-art CQD solar cell introduces a ligand exchange in solution phase, improving surface passivation relative to solid-state exchange. Ligand exchange in solution with lead iodide and ammonium acetate allows for a more complete ligand exchange of
organic chains with halide anions, resulting in closely packed CQDs, reducing the centre-to-centre spacing from 3.6 to 3.2 nm relative to PbS-TBAI [23]. Following the same p-i-n architecture with a PbS-EDT layer [33], using solution phase exchanged, iodide passivated CQDs by M. Liu et al. as the PbS active layer have achieved a certified η of 11.28% [23].

Recent, unpublished works by M. Liu introduces cesium lead bromide into the solution phase exchange, which passivates the CQDs with a perovskite shelling. Preliminary measurements of perovskite-shelled CQDs have yielded improved $J_{sc}$, suggesting improved carrier transport possibly due to a lower energy barrier between CQDs, thus improving coupling for hopping and tunneling transport. In this thesis, I aim to quantify the mobility of iodide passivated CQDs along with the novel perovskite-shelled CQDs developed M. Liu. The study of mobility provides insight into the underlying physics, enabling further development towards the next generation of CQD materials.
Chapter 3

Contact and Contactless Methods for Determining Charge Carrier Mobility

3.1 Introduction

Methods for characterizing charge carrier mobility can be generalized into two categories: contact and contactless. Contact methods need an electrical contact to the material of interest – the CQD film in this case – via electrodes. Typically, the mobility is extracted from the measured time- or voltage-dependent current signal. Contactless methods require no electrical contact to the CQD film. The CQD film is typically deposited onto an insulator where it is probed by an optical or a radio-frequency signal to obtain the mobility.

This chapter provides a description of various contact and contactless methods. It compares the benefits, limitations, and range of applications of each method. The time-of-flight and femtosecond transient absorption methods, specifically, are described in detail as they are the main techniques used in Chapter 5. The background theory, derivation of equations, and realization of measurement are provided for both methods.
3.2 Contact Methods

Contact methods have the advantage that they capture a more realistic value of the mobility of CQD films when used in a device due to requiring contact electrodes. Interfacial defects created between the CQD film and the electrodes may reduce the resultant mobility. Contact methods have the disadvantage of more elaborated device fabrication process, requiring the use of electrodes and other design considerations. For example, in time-of-flight (TOF), the method requires the device to be designed such that its RC time constant is at least an order of magnitude less than the carrier transit time through the device [16].

Other contact methods include the steady-state trap-free space-charge limited current (TF-SCLC) [15,19], field-effect transistor (FET) method [15,20], and charge extraction by linearly increasing voltage (CELIV) [15,18,21]. Each method has their own benefits and limitations as it changes the conditions of device operation. For example, in TOF, the charge carriers are photogenerated and swept away by modest electric fields, which mimic typical solar cell operating conditions. In the FET method, the charge carriers are electrically injected and carriers are swept through the material under high electric fields. The near-zero electric field mobility is determined by extrapolation of data obtained under high fields [35], which are not representative of solar cell operating and can skew the measured mobility values. It is important to understand the implications of each method in regard to the measured mobility compared to its actual mobility when used in application. The following subsections discuss the TOF, TF-SCLC, FET, and CELIV contact methods for characterizing carrier mobility that are all applicable to CQD devices.

3.2.1 Time-of-Flight

TOF was developed for use in disordered, non-crystalline molecular systems. It has been widely used in polymer systems [15,17,18] but can also be applied to CQDs [32]. In TOF one measures the transit time of photogenerated charge carriers traversing though a material
the CQD film – of known thickness in order to determine its mobility. The theory behind
time of flight is based on the drift mobility relation \[ \mu = \frac{d^2}{t_{tr} V_{app}} \] (3.1)
where \( d \) is the thickness of the CQD film, \( t_{tr} \) is the transit time, and \( V_{app} \) is the applied
voltage. Varying the film thickness or applied voltage, hence the applied electric field \( E_{app} \),
enables the electric field-dependent mobility to be obtained. TOF also allows for measuring
the dynamics of the opposite charge by changing the polarity of the applied voltage.

In practice, the TOF measurement is realized by sandwiching the CQD film between two
electrodes, one of which must be semi-transparent (Figure 3.1). The sample is illuminated
with a short pulse of light. The photogenerated carriers are swept away by the applied electric
field to their respective electrodes, and the transient photocurrent is measured. Typical
photocurrent transients are shown in Figure 3.2. Under the non-dispersive transport regime –
where mobility does not vary between charge carriers of the same polarity – the photocurrent
transient has a distinct shape. It consists of a sharp peak at the initial light pulse excitation
due to carriers of one polarity being collected immediately by the semi-transparent electrode,
followed by a plateau as the carriers of opposite polarity traverse through the CQD film,
and finally a rapid decrease in current as all the carriers of the opposite polarity reach the
electrode (Figure 3.2a). The transit time \( t_{tr} \) is determined by the kink in the signal where the
plateau reaches the sharp decrease. Under the dispersive transport regime – where mobility
does vary between charge carriers of the same polarity – the photocurrent resembles the shape
of a bi-exponential function and the plateau no longer exists (Figure 3.2b). The transit time
\( t_{tr} \) in this case is determined by the intersection point of the two fitted lines of the fast and
slow component of the transient photocurrent when plotted in log-log axis.
Figure 3.1 | Schematic diagram of the TOF method. Light incident on the sample generates electron-hole pairs which are swept away by the applied electric field, and collected by their respective electrodes. The mobility is measured for the charge polarity that has to travel through film of thickness $d$ [15].

Figure 3.2 | Schematic diagram of the TOF method. Photocurrent transients for (a) non-dispersive transport, and (b) for dispersive transport [15].
A number of considerations that must be taken into account when designing a TOF experiment. The duration of the pulse width $t_{\text{pulse}}$ must satisfy $t_{\text{pulse}} \ll t_{\text{tr}}$. TOF also operates based on the assumption that a two-dimension sheet of charge carriers are generated at the surface of the CQD film, as close to the semi-transparent electrode as possible, which then propagates through the film. This requires the absorption depth to be much smaller than the CQD film thickness $d$ [15], resulting in relatively thicker films. Another consideration when performing TOF is the RC time constant $\tau_{\text{RC}}$, that must be meet the condition $\tau_{\text{RC}} \ll t_{\text{tr}}$. RC time constant constraints are typically satisfied by reducing the capacitance of the device. The device architecture can be optimized such that the device area is decreased, the thickness is increased, while maintaining sufficient photo-response. Other important considerations when the transient photocurrent signal deviates from what is expected could be a result several factors: (a) deep traps, requiring the deep trapping lifetime $\tau_{\text{trap}} \gg t_{\text{tr}}$, (b) inhomogeneous film resulting in variations of mobility throughout thickness $d$, and (c) trapped charges creating local electric field variations [16].

3.2.2 Trap-Free Space-Charge Limited Current

The TF-SCLC method measures the current density-voltage (J-V) characteristics of a semiconductor in the dark. At low applied voltages, J-V characteristics are typically linear, belonging to the ohmic regime where current is transport-limited. At higher applied voltages, the current becomes space-charge-limited where the J-V characteristics follow the Mott-Gurney equation (Figure 3.3) [36]

$$J = \frac{9 \varepsilon \mu V^2}{8 d^3}$$

(3.2)

where $\varepsilon$ is the relative permittivity of the semiconductor, $\mu$ is the carrier mobility, and $d$ is the device thickness. The mobility can be determined by a fit of the J-V curves with Equation 3.2. TF-SCLC has the advantage that it does not require any special device architecture,
such as semi-transparent electrodes or thick semiconductor layers, unlike TOF. TF-SCLC can be readily applied to any semiconductor device giving a mobility for that particular application. However, TF-SCLC assumes that current is only as a result of one carrier type, and applies only for materials where the mobility is independent of electric field.

3.2.3 Field-Effect Transistor

The FET method measures the current-voltage (I-V) characteristics of a semiconductor in FET configuration (Figure 3.4a) in the dark. The I-V characteristics follow the relation (Figure 3.4b) \[20\]

\[
I_{DS} = \mu C \frac{W}{L} \left[ (V_{GS} - V_{TH}) V_{DS} - \frac{V_{DS}^2}{2} \right]
\]

(3.3)

where \(\mu\) is the carrier mobility, \(C\) is the capacitance per area of the gate dielectric, \(W\) is the channel width, \(L\) is the channel length, \(V_{GS}\) is the gate-source voltage, \(V_{TH}\) is the threshold voltage, and \(V_{DS}\) is the drain-source voltage. The mobility can be determined by a fit of
Figure 3.4 | Determining mobility from FET. (a) A bottom-gate top-contact device architecture used for FET mobility measurements. (b) A typical current-voltage curve for a semiconductor in a FET configuration.

the I-V curves with Equation 3.3. For FET measurements, the applied gate voltage can fill the trap states intrinsic to the semiconductor, leading to a measured mobility that is gate-voltage dependent [37,38]. The FET method also measures mobility under relatively high electric field conditions, which may not necessarily be the same for low electric fields.

3.2.4 Charge Extraction by Linearly Increasing Voltage

The CELIV method measures the current transient after excitation using a triangular voltage pulse in the dark (Figure 3.5a). From the current transient (Figure 3.5b), the mobility can be determined using the relation [21]

$$
\mu = \frac{2 d^2}{3 A t_{\text{max}}^2 (1 + 0.36 \frac{\Delta j}{j_0})}
$$

(3.4)

where \(d\) is the device thickness, \(t_{\text{max}}\) is the time to reach maximum extraction current, \(\Delta j\) is the maximum drift current, and \(j_0\) is the displacement current. CELIV measures the mobility of majority carriers. Like TF-SCLC, it has the advantage that it does not require any special device architecture, unlike TOF or FET; however, since time-dependent electrical signals are involved, the RC time constant of the device and detection circuit must be taken
Figure 3.5 | Determining mobility from CELIV. (a) The device in reverse bias is excited with a triangular voltage pulse. (b) A typical current transient obtained from CELIV illustrating the values of $t_{\text{max}}$, $\Delta j$, and $j_0$ [18].

into account [39]. A limitation of CELIV is that the number of thermally generated, free carriers in the semiconductor are sufficiently high [18, 21, 36].

3.3 Contactless Methods

Contactless methods have the advantage of not requiring special test structures, and also allowing a simpler sample preparation without the need for electrodes. It therefore allows measurement of the intrinsic CQD film mobility without contribution from interfacial defects. Contactless methods require, on the other hand, an exquisite control over the wavelength of the optical excitation so that it closely matches the bandgap of the material. The following subsections discuss the contactless methods that have been demonstrated for CQDs: the
photoluminescence, and femtosecond transient absorption methods.

### 3.3.1 Photoluminescence

In the photoluminescence (PL) method [13], luminescent reporters are introduced into the CQD film in the form of smaller bandgap CQDs. The introduced reporters are denoted as the acceptors, whereas the CQD film of interest is denoted as the donors. The sample is optically stimulated and the photogenerated electrons from the donor diffuse until they are trapped by acceptor, where they radiatively recombine (Figure 3.6). The PL signal is measured and the mobility is determined by the relationship between the ratio of donor to acceptor PL peaks in the spectra $\frac{PL_{\text{ratio}}}{N_t}$ and the acceptor trap density $N_t$:

$$\mu = \frac{d}{6\sigma \tau_{\text{donor}}} \frac{q}{k_B T} \left( \frac{PL_{\text{ratio}}}{N_t} \right) = \frac{d}{6\sigma \tau_{\text{donor}}} \frac{q}{k_B T} \left( \frac{\Delta PL_{\text{ratio}}}{\Delta N_t} \right) \quad (3.5)$$

where $d$ is the film thickness, $\tau_{\text{donor}}$ is the radiative recombination lifetime of the donor CQDs, $q$ is the elementary charge, $k_B$ is Boltzmann’s constant, $T$ is the temperature, and $\sigma$ is the capture cross section. The radiative recombination lifetime of the donor CQDs $\tau_{\text{donor}}$ is determined via time-resolved PL decay [14]. The PL$_{\text{ratio}}$ with respect to $N_t$ should follow a linear relationship, thus multiple acceptor concentrations can be used for a better estimate of the mobility.

The PL method has the advantage that the experimental setup is relatively simple, requiring only a pulsed laser and a spectrometer. The PL method, however, has the disadvantage that for strongly coupled donor CQDs with rapid exciton dissociation, the non-radiative recombination pathway is favoured [22]. Hence, the measurement of the donor to acceptor PL ratio becomes unreliable. Similarly, measuring the radiative recombination lifetime $\tau_{\text{donor}}$ from time-resolved PL decay become increasingly difficult [14]. Another disadvantage in the PL method is the requirement for bright reporters for sufficient PL signal. In addition, charge accumulation in the reporters can lead to other non-radiative recombination processes, such
Figure 3.6 | Charge carrier transfer mechanics between donors and acceptors. Carriers photogenerated in the donor diffuse until they are trapped by the acceptor. Reprinted with permission from [22].

as Auger, and obscuring the interpretation of the results. It is also important that the quantity of acceptors should be kept low enough to not disturb the film morphology. A linear trend between donor to acceptor PL ratios versus acceptor concentration indicates good film morphology.

3.3.2 Femtosecond Transient Absorption

Transient absorption (TA) measures the change in absorption $\Delta A$ of a material with respect to time following excitation using a brief light pulse. In a TA experiment, two light pulses are incident on a sample: the initial light pulse known as the pump, and another light pulse occurring after some time delay known as the probe (Figure 3.7). The pump pulse causes ground state carriers to be photo-excited into higher energy states. When the probe pulse comes in, the now depleted ground state carriers cannot be excited, and hence reduce the absorption of the sample. A spectrometer is used to collect the light from the probe pulse before pump excitation and at some delay after excitation to determine the $\Delta A$ spectra. The $\Delta A$ spectra tends to be at a maximum at time delays immediately after excitation due to a lack of ground state carriers. As the time delay increases, the excited state carriers have time to relax and recombine, decreasing the $\Delta A$ spectra.
Figure 3.7 | Schematic of the pump-probe technique. The pump pulse excites the ground state carriers, and is followed by a probe pulse. The probe spectrum is obtained before and after probe pulse to determine the differential absorption spectrum [40].

The femtosecond transient absorption (fs-TA) method expands upon the PL method. It uses the same donor and acceptor style CQD films but it is a more sophisticated approach because it is not limited by the rapid exciton dissociation of strongly coupled CQDs, which can be resolved in the fs-TA time window. In the fs-TA method [22], the sample is optically stimulated at a wavelength corresponding to the bandgap of the donor. The photogenerated electrons follow the same charge transfer mechanics as in the PL method (Figure 3.8). The TA signal is measured and the mobility is determined by the relationship between its lifetime and quantity of traps.

The theory underlying the fs-TA method follows several assumptions: (a) the difference in conduction band levels between the donor and acceptor are much greater than $k_B T$, where $k_B$ is Boltzmann’s constant, and $T$ is the temperature, such that the charge transfer from the donor to the acceptor is irreversible (Figure 3.8), (b) the carrier lifetime from radiative recombination $\tau_{\text{rad}}$ and non-radiative recombination $\tau_{\text{non-rad}}$ from intrinsic traps in the donor are much greater than the trapping lifetime $\tau_{\text{trap}}$ due to acceptors, and (c) the degeneracy
Figure 3.8 | Energy band diagram of donors and acceptors. The energy band diagram of donors and acceptors used to illustrate charge transfer mechanics. The bandgap difference between the donors $E_{g,\text{donor}}$ and acceptors $E_{g,\text{acceptor}}$ are chosen such that the difference is much larger than $k_B T$ so that acceptor trapping process is irreversible.

Energy states in the acceptor allows for multiple carriers to be trapped in one CQD, and (d) the mechanism of charge carrier transfer in CQDs is due to diffusive hopping under very low to zero electric fields. With those assumptions, the derivation for the fs-TA method begins by expressing the capture rate of carriers into traps $k_{\text{trap}}$ as

$$ k_{\text{trap}} = \frac{1}{\tau_{\text{trap}}} = v_{\text{th}} \sigma N_t \quad (3.6) $$

where $v_{\text{th}}$ is the thermal velocity, $\sigma$ is the capture cross section, and $N_t$ is the trap density. The thermal velocity $v_{\text{th}}$ can be also expressed as

$$ v_{\text{th}} = \frac{d}{\tau_{\text{hop}}} \quad (3.7) $$

where $d$ is the centre-to-centre dot spacing, and $\tau_{\text{hop}}$ is the carrier hopping time between dots. The capture cross section is taken as the geometrical cross section and using a three-dimensional spherical model.
\[ \sigma = \frac{1}{4} \pi d^2. \]  

(3.8)

Under the hopping regime, the mobility \( \mu \) is given by

\[ \mu = \frac{qd^2}{6 \tau_{\text{hop}} k_B T}. \]  

(3.9)

where \( q \) is the elementary charge. From the substitution of Equation 3.6 to 3.9 yields

\[ \mu = \frac{d}{6 \sigma k_B T} \left( \frac{N_i^{-1}}{\tau_{\text{trap}}} \right) \]  

Thus, the mobility can be determined by measurement of TA signal, extracting its lifetime which is assumed to be the trapping lifetime \( \tau_{\text{trap}} \), and calculating the mobility based on the known acceptor trap density.

There are some important considerations that must be taken when performing the fs-TA experiment. The pump power selected should be as low as possible to minimize higher order effects, such as Auger recombination. The repetition rate of the pump and probe pulses must be longer than the carrier lifetimes of the CQD material. It is assumed that sample has returned to steady-state conditions prior to excitation of the next pump pulse. Lastly, the quantity of acceptors used should be low enough to not disturb the morphology of the donor film, thereby minimizing the additional defects introduced to the film. A good indicator of undisturbed film morphology would be a linear trend in acceptor concentration versus trapping lifetime.

### 3.4 Summary of Methods

A summary of the described contact and contactless methods for characterizing charge carrier mobility can be found in Table 3.1. The table outlines the benefits, limitations, and range of applications of each method.
Table 3.1 | Summary of discussed methods for mobility extraction. The benefits, limitations, and range of applications are provided for each method.

<table>
<thead>
<tr>
<th>Type</th>
<th>Method</th>
<th>Benefits</th>
<th>Limitations</th>
<th>Range of Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact</td>
<td>TOF</td>
<td>• Mimics operating conditions of optoelectronic devices, probing the extraction of photogenerated carriers • Applicable for both electron and hole mobility</td>
<td>• RC time constant must be considered • Requires semi-transparent electrode and thicker semiconductor layers</td>
<td>• Inorganic/organic semiconductors</td>
</tr>
<tr>
<td>Contact</td>
<td>TF-SCLC</td>
<td>• Purely electrical experimental setup • Can be applied to existing device architecture without modifications</td>
<td>• Measures mobility of majority carriers only • Applicable for electric field independent mobility</td>
<td>• Inorganic/organic semiconductors</td>
</tr>
<tr>
<td>Contact</td>
<td>FET</td>
<td>• Purely electrical experimental setup</td>
<td>• Measures mobility of majority carriers only • Requires device to be in FET configuration</td>
<td>• Inorganic/organic semiconductors</td>
</tr>
<tr>
<td>Contact</td>
<td>CELIV</td>
<td>• Purely electrical experimental setup • Can be applied to existing device architecture without modifications</td>
<td>• RC time constant must be considered • Measures mobility of majority carriers only • Requires sufficiently high thermally generated, free carriers</td>
<td>• Inorganic/organic semiconductors</td>
</tr>
<tr>
<td>Contactless</td>
<td>fs-TA</td>
<td>• Probes the carrier dynamics of strongly coupled CQDs with good transport properties</td>
<td>• Requires long measurement times due to low excitation powers used to minimize higher order effects (Auger recombination) • Complicated experimental setup</td>
<td>• Inorganic/organic semiconductors</td>
</tr>
<tr>
<td>Contactless</td>
<td>PL</td>
<td>• Simple experimental setup</td>
<td>• Not applicable for CQDs with fast exciton dissociation and good transport properties</td>
<td>• Inorganic/organic semiconductors</td>
</tr>
</tbody>
</table>
Chapter 4

Charge Carrier Mobility of Colloidal Quantum Dot Films

4.1 Introduction

In this chapter, I study the charge carrier mobility of CQD films determined via a contact and contactless method. The results presented show the charge carrier mobility of CQD films measured using the fs-TA and TOF method. Results will also be shown comparing the mobility of CQDs active layers that have undergone two separate chemical ligand treatments: (i) a treatment outlined in the work of M. Liu et al. \cite{23} passivates the CQDs with iodide ligands, and (ii) another novel treatment that introduces a CsPbBrI₂ perovskite shelling around the CQD.
4.2 Charge Carrier Mobility from Femtosecond Transient Absorption

Design of Experiment

The fs-TA experiments were carried out using an apparatus illustrated in Figure 4.1. It consisted of a PHAROS femtosecond laser, ORPHEUS collinear optical parametric amplifier (OPA), and an HELIOS transient absorption (TA) spectrometer. The fundamental pulse emitted by the laser had a pulse width of \( \sim 250 \text{ fs} \), centered at 1025 nm, and at a repetition rate of 2.5 kHz. The fundamental pulse was sent into a 90/10 beam splitter to create the pump (90% power) and probe (10% power) pulse. The pump pulse was passed through the OPA where it could be spectrally tuned, then sent to the TA spectrometer along with the probe pulse.

Inside the TA spectrometer, the pump pulse was sent through an optical chopper at a frequency of half the repetition rate, alternating the passing and blocking of the pump pulse in order to obtain the \( \Delta A \) spectra. The probe pulse was sent through a delay stage that matched the delay of the pump pulse travelling through the OPA, and added an extra 7.5 ns of tuneable delay. The probe pulse was then passed through a sapphire crystal to broaden the spectrum. Filters were used to select a probe spectrum ranging from 900 to 1300 nm. Neutral density filter wheels were used to adjust the power of the pump and probe pulse incident on the sample. After passing through the sample, the probe pulse was collected by a spectrometer to determine the \( \Delta A \) spectra.

The CQD samples were prepared adding fixed amounts of acceptors into an ink of iodide passivated or perovskite-shelled donors. The ink was then spin-coated onto a glass substrate. To satisfy the condition that the difference in conduction band levels between the donors and acceptors are much greater than \( k_B T \), I used \( \sim 950 \text{ nm} \) PbS CQDs with a bandgap of \( \sim 1.3 \text{ eV} \) as the donor for both treatments, and \( \sim 1250 \text{ nm} \) PbS CQDs with a bandgap
Figure 4.1 | Experimental setup for fs-TA measurements. The fundamental pulse was split to produce the pump and probe pulses. The pump pulse was passed through an OPA where it was spectrally tuned, and an optical chopper. The probe pulse was passed through a variable delay, a sapphire crystal to broaden the spectrum. The probe pulse was collected by a spectrometer after passing through the sample to obtain the differential absorption spectra \[40\].

of \(\sim 0.99\) eV as the acceptor (Figure 4.2). This results in a difference in conduction band of \(\sim 300\) meV, which is much greater than \(k_B T\) at 300 K (\(\sim 25\) meV). The acceptor concentrations were selected to be 0.5, 1, 2, and 5% by weight such that there were of high enough concentrations to observe changes in lifetime within the 7.5 ns TA window (limited by the delay stage), but not so high that it would disturb the film morphology.
Figure 4.2 | Absorption spectrum of CQD films. The absorption spectrum of CQD films used in fs-TA, showing the contribution of the exciton peak from the $\sim 950$ nm donor PbS CQDs, and $\sim 1250$ nm acceptor PbS CQDs.

Results from Iodide Passivated and Perovskite-Shelled PbS CQDs

The fs-TA experiment was performed with the pump pulse centered at 950 nm – the bandgap of the CQDs – at low laser powers ($\sim 30$ $\mu$W) to minimize the effects of Auger recombination while maintaining sufficient signal-to-noise ratio (SNR) [23]. The $\Delta A$ spectrum for perovskite-shelled PbS CQDs with 5% acceptor concentration (Figure 4.3a) shows the funneling of photogenerated carriers from the donors to the acceptors, resulting in a large change over time in $\Delta A$ at 1250 nm. Taking the $\Delta A$ value at a specific wavelength (980 nm) and plotting it against the delay time, I obtain Figure 4.3b, which was fitted to obtain the trapping lifetime for a specific acceptor concentration. A wavelength value of 980 nm was chosen in order to observe the electronic states closest to the conduction band edge. The measurements were performed for the various acceptor concentrations, and fitted with an exponential function $y = a \exp(-x / b) + c$ using MATLAB’s nonlinear least-squares formulation (Figure 4.4b). The trapping lifetime $\tau_{\text{trap}}$ was determined by $\tau_{\text{trap}} = b$. The experiment was repeated for the iodide passivated PbS CQDs (Figure 4.4a).
Figure 4.3 | fs-TA spectrum of perovskite-shelled PbS CQDs with 5% acceptor concentrations. (a) $\Delta A$ spectrum at various delay times showing the funneling of carriers from donors to acceptors. (b) $\Delta A$ as a function of delay time probed slightly red of the exciton peak at 980 nm. OD is the optical density.

It can be immediately seen from Figure 4.4 that for the same acceptor concentrations, the perovskite-shelled PbS CQDs has a shorter trapping lifetime than the iodide passivated PbS CQDs, which suggests a faster carrier mobility. The films with 0% acceptor concentrations are flat, thus justifying the assumption that the trapping lifetime is much shorter than the other recombination lifetimes in the donor film, and that the pump pulse power is low enough to not induce Auger recombination. To extract the mobility values from Equation 3.10, the quantity $\Delta N_t^{-1}/\Delta \tau_{\text{trap}}$ must be determined.
Normalized $\Delta A$ transients for different acceptor concentrations (plotted offset from each other) probed at 980 nm for (a) iodide passivated PbS CQDs, and (b) perovskite-shelled PbS CQDs. The trapping lifetime $\tau_{\text{trap}}$ is determined by fitting the differential absorption transient with an exponential function.

The trap density $N_t$ is related to the acceptor concentration percentage $\rho_{\text{acceptor}}$ via $N_t = N_{\text{bulk}} / \rho_{\text{acceptor}}$, where $N_{\text{bulk}}$ is the bulk CQD density $1.87 \times 10^{19} \text{ cm}^{-3}$ \cite{22}. For each acceptor concentration, the corresponding $N_t^{-1}$ was calculated and plotted against $\tau_{\text{trap}}$ (Figure 4.5). The plot was fitted with a linear function $y = a \times x$, and $\Delta N_t^{-1}/\Delta \tau_{\text{trap}}$ was determined as $\Delta N_t^{-1}/\Delta \tau_{\text{trap}} = a$. A linear trend between reciprocal trap density and trapping lifetime indicates that the film morphology has not been affected with the addition of larger bandgap acceptor CQDs. It should also be noted that the mobility could be calculated from a single acceptor concentration (giving $\Delta N_t^{-1}/\Delta \tau_{\text{trap}}$), however, for better accuracy and proof of
Figure 4.5 | Trap density and trapping lifetime of iodide passivated and perovskite-shelled PbS CQDs. Reciprocal trap density $N_t^{-1}$ as a function of acceptor trapping lifetime $\tau_{\text{trap}}$ for (a) iodide passivated PbS CQDs, and (b) perovskite-shelled PbS CQDs. The slope of fitted line $\Delta N_t^{-1}/\Delta \tau_{\text{trap}}$ is marked on the respective plots.

The mobility was calculated using Equation 3.10 assuming a value of centre-to-centre dot spacing $d = 3.2 \text{ nm}$ [23], and temperature $T = 300 \text{ K}$. The mobilities of iodide passivated and perovskite-shelled PbS CQDs were determined to be $(3.0 \pm 0.5) \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $(5 \pm 1) \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. The novel perovskite-shelled treatment proves to have significantly improved transport properties compared to the iodide passivation, possibly as a result of reducing the energy barrier required for carrier hopping between CQDs. I further investigate the improvement in transport by studying the activation energy required for transport via temperature-dependent fs-TA.
Results from Temperature-Dependent fs-TA

A liquid nitrogen cryostat was used to control the temperature of the sample to a minimum of 80 K. The same 5% concentration perovskite-shelled PbS CQD film was measured using fs-TA. Figure 4.6a shows the $\Delta A$ spectrum obtained at various time delays. At a temperature of 80 K, the magnitude of $\Delta A$ at the acceptor bandgap (1250 nm) is lower compared to 300 K, suggesting less carriers are being trapped by the acceptors. For the donors, the change of $\Delta A$ with respect to time is slower (Figure 4.6b), due to more carriers remaining in the donors. The results obtained shows that less carriers are leaving the donor sites, and consequently less carriers are being trapped in the acceptors. Since carrier transport is worsened with decreasing temperature, thus requiring thermal activation, the perovskite-shelled CQDs are still likely in the hopping regime.

I then sought to determine the activation energy required for hopping in the perovskite-shelled CQDs. The experiment was repeated for two additional temperatures between 80 K and 300 K (Figure 4.6a). The $\Delta A$ versus time was fit with bi-exponential functions this time for a better fit. The trapping lifetime $\tau_{\text{trap}}$ was determined by the effective lifetime of the two exponentials: $1/\tau_{\text{trap}} = 1/\tau_1 + 1/\tau_2$. An Arrhenius plot was constructed from the trapping lifetime and absolute temperature $T$ (Figure 4.6b). The activation energy $E_a$ was extracted from a linear fit of the Arrhenius plot, following the relation

$$\ln \frac{1}{\tau_{\text{trap}}} = -\frac{E_a}{k_B T} + \ln A$$

(4.1)

where $k_B$ is Boltzmann's constant, and $A$ is a pre-exponential factor typically determined empirically.
Figure 4.6 | fs-TA spectrum for perovskite-shelled PbS CQDs with 5% acceptor concentrations at 80 K. (a) $\Delta A$ spectrum at various delay times showing the funneling of carriers from donors to acceptors. (b) $\Delta A$ as a function of delay time probed slightly red of the exciton peak at 980 nm. OD is the optical density.

An activation energy of (14±8) meV was determined for carrier transport between donor and acceptor CQDs in perovskite-shelled CQDs. A low activation energy required for hopping transport suggests more band-like behaviour of carrier transport. However, further work is required to support the evidence for more band-like transport with more direct measurements of carrier mobility, such as using TOF or other methods.
Figure 4.7 | Temperature-dependent fs-TA of perovskite-shelled PbS CQDs with 5% acceptor concentrations. (a) Normalized $\Delta A$ as a function of time for different temperatures (plotted offset) showing a longer lifetime with decreasing temperature. (b) Arrhenius plot of $\tau_{\text{trap}}$ and $T$ to extract the activation energy.

The Effect of Device Fabrication on the Photoactive Layer: The PbS-EDT Layer

The fundamental mobility values were determined for the CQD films, without the presence of electrodes and other layers normally found in CQD solar cells. It is expected that the carrier transport becomes worse with the addition of other layers in the device due to interfacial defects. In a final solar cell configuration, an additional hole transporting layer based on EDT-treated CQDs is deposited on top of the photoactive CQD film. To get insights on any potential modification of the optoelectronic properties of the perovskite-shelled CQD layer, I further carried out fs-TA experiments on perovskite-shelled CQD films treated with solutions consisting of EDT in acetonitrile \cite{23,42,43} (Figure 4.8). Interestingly, I observed
Figure 4.8 | fs-TA of perovskite-shelled PbS CQDs with a PbS-EDT layer. (a) ∆A transient for various acceptor concentrations (plotted offset from each other) probed at 980 nm. (b) $N_t^{-1}$ as a function of acceptor trapping lifetime $\tau_{\text{trap}}$ showing the slope of fitted line $\Delta N_t^{-1}/\Delta \tau_{\text{trap}}$.

that the mobility was reduced compared to pristine perovskite-shelled CQD films with a mobility of $(1.5 \pm 0.3) \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This represents more than a factor of 3 less than the perovskite-shelled PbS CQDs without the PbS-EDT layer $(5 \pm 1) \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. I ascribed this decrease in mobility to the interaction of EDT and acetonitrile (ACN) with the underlying CQD film, resulting in deteriorated film morphology, reduced passivation, and the introduction of traps [44].
Discussion

The mobility values determined using different CQD treatments and device layers are summarized in Table 4.1. It was found that perovskite-shelled PbS CQDs exhibited a higher carrier mobility than iodide passivated PbS CQDs; possibly due to reduced energy barrier required for transport. An activation energy for carrier hopping of 14 meV was determined for the perovskite-shelled PbS CQDs. Experimental evidence supports the idea of lowered carrier transport with the addition of other layers, such as the PbS-EDT layer. The following subsection aims to study the impact of the entire device stack in standard CQD solar cells using the TOF method.

Table 4.1 | Summary of mobilities determined from fs-TA. Charge carrier mobility of CQD films determined via fs-TA for iodide passivated PbS, perovskite-shelled PbS, perovskite-shelled PbS with PbS-EDT CQDs.

<table>
<thead>
<tr>
<th>CQD Treatment</th>
<th>Charge Carrier Mobility (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iodide passivated PbS</td>
<td>$(3.0 \pm 0.5) \times 10^{-2}$</td>
</tr>
<tr>
<td>Perovskite-shelled PbS</td>
<td>$(5 \pm 1) \times 10^{-1}$</td>
</tr>
<tr>
<td>Perovskite-shelled PbS w/ PbS-EDT</td>
<td>$(1.5 \pm 0.3) \times 10^{-1}$</td>
</tr>
</tbody>
</table>

4.3 Charge Carrier Mobility from Time-of-Flight

Design of Experiment

The TOF experiments were carried out using a more complete apparatus than previous outlined in Chapter 3 as illustrated in Figure 4.9. A 355 nm pulsed laser with a pulse width of 10 ns, and repetition rate of 200 Hz was used to excite the sample. A 1 GHz bandwidth digital oscilloscope was used to measure the transient photocurrent signal, and a source meter was used to apply external bias to the sample. Electrical connections to the sample were
Figure 4.9 | Experimental setup for TOF measurements. A nanosecond laser was pulsed at the CQD solar cell, with a forward bias was applied (Au relative to ITO contact). The applied bias $V_{\text{app}}$ was high enough to overcome the built-in voltage $V_{\text{bi}}$ of the p-n junction to probe the electron mobility. The transient photocurrent was measured on the oscilloscope.

made using pogo-pins soldered onto a printed circuit board (PCB). The PCB was connected to a digital oscilloscope, and source meter through a bias tee with a bandwidth from 5 kHz to 15 GHz: AC connection to oscilloscope, DC connection to source meter, and DC+AC connection to the sample. Precautions were taken to ensure the transient photocurrent signal was not limited by the speed of any equipment.

The PbS CQD sample used the typical device architecture for a CQD solar cell presented in Chapter 2 but with a significantly thicker film. The sample consisted of layers of ITO,
PbS active layer, PbS-EDT layer, and gold all sequentially deposited onto a glass substrate. The thickness of the PbS active layer was designed based on rough estimations of the RC time constant and carrier transit time. A capacitance value of 5 nF was measured for a 500 nm thick PbS solar cell using an LCR meter, and resulting in an RC time constant $\tau_{RC}$ of roughly 250 ns through a 50 Ω load. Assuming a generous upper bound of the carrier mobility on the unknown PbS CQDs of $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$, based on past TOF measurements of differently treated PbS CQDs, the calculated carrier transit time $t_{tr}$ from Equation 3.1 would be 500 ns with a thickness of 500 nm and an applied voltage $V_{app}$ of 0.5 V. In order to satisfy the condition that $t_{tr} \gg \tau_{RC}$, the RC time constant must be reduced and the transit time increased. This was simultaneously achieved by selecting the PbS sample thickness to be twice as thick ($\sim 1 \mu$m), resulting in an estimated $t_{tr}$ and $\tau_{RC}$ to be 125 ns and 2 μs, respectively, making it suitable for TOF. In addition, an absorption coefficient of $10^5$ cm$^{-1}$ at 400 nm gives an optical absorption depth of 100 nm, which is much less than the thickness of the material, thus satisfying the condition for charge generation at the surface.

In the experiment, the PbS CQD sample was illuminated from the glass side and forward biased with respect to the gold electrode. Electron-hole pairs that are photo-excited are swept away by the applied electric field to their respective electrodes. Since the ZnO thickness is roughly 150 nm, the holes are immediately collected by the ITO electrode, compared to the electrons that must travel through the much thicker PbS layer to reach the gold electrode. In this electrode configuration, the electron mobility is probed via TOF.

**Results and Discussion**

TOF enables us to study the effect on mobility of the CQD active layer when used in the standard CQD solar architecture. From the results of Chapter 3, it was found that the addition of the PbS-EDT layer reduced the mobility of CQD film. I expect the mobility to further decrease with the addition of the ITO electrode, ZnO layer, and gold electrode. Since
Figure 4.10 | Photocurrent transients of iodide passivated and perovskite-shelled PbS CQDs. Experimental data obtained from TOF of (a) iodide passivated and (b) perovskite-shelled PbS CQD solar cells. The intersection of the two dashed lines indicate the carrier transit time.

The PbS CQD sample is now a full CQD solar cell, but with a thicker active layer, there exists a built-in field. The built-in field was taken into account by sweeping the applied voltage at values greater than 0.5 V in order to observe the kink in the photocurrent transient marking the carrier transit time. The power of the laser pulse was set to 10 µW—a lower power than the fs-TA because these CQD films have higher photo-response in the ultraviolet spectral regime—to minimize any higher order effects.

Figure 4.10 shows the raw data taken from TOF measurements for iodide passivated and perovskite-shelled PbS CQD solar cells, respectively. The carrier transit time $t_{tr}$ was determined by the intersection of the two lines in the log-log plot for each applied bias. The thickness of the device was determined via profilometer measurements by scratching the CQD device. A thickness of 1.15 µm and 1.01 µm was obtained for the iodide passivated and perovskite-shelled PbS CQD solar cells. The ratio of device thickness $d$ to carrier transit
Figure 4.11 | Extracting mobility from $t_{tr}$. The mobility was determined as the slope of the line fitted to the ratio of $d/t_{tr}$ versus the $E_{app} = V/d$. (a) The mobility of iodide passivated PbS CQD solar cell. (b) The mobility of perovskite-shelled PbS CQD solar cell. 

The mobility was determined as the slope of the line fitted to the ratio of $d/t_{tr}$ versus the $E_{app} = V/d$ (Figure 4.11). The plot was fitted with a linear function $y = ax + b$, where the mobility is given by $\mu = a$ from Equation 3.1. It should be noted that the value of the built-in field does not matter in determination of mobility, since it only shifts the plot left or right, keeping the slope unchanged.

A mobility of $(4.0 \pm 0.2) \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $(5.1 \pm 0.3) \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was obtained for iodide passivated and perovskite-shelled PbS CQD solar cells, respectively. It follows the trend that the perovskite-shelled PbS active layer device exhibits a higher mobility – nearly a factor of 1.3 times – than the iodide passivated PbS CQDs even in device form. When compared to its fundamental mobility values obtained via fs-TA measurements, the mobility of iodide passivated PbS CQDs loses almost a factor of 10, whereas the perovskite-shelled PbS CQDs loses a factor of $\sim 10^2$ with the addition of other layers necessary for CQD solar cell operation (Table 4.2).
Table 4.2 | Summary of mobilities determined from fs-TA and TOF. Fundamental charge carrier mobility of CQDs films determined via fs-TA compared with mobility of CQD films when used in a device from TOF.

<table>
<thead>
<tr>
<th>CQD Treatment</th>
<th>Charge Carrier Mobility (cm² V⁻¹ s⁻¹)</th>
<th>fs-TA</th>
<th>TOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iodide passivated PbS</td>
<td>(3.0 ± 0.5) × 10⁻²</td>
<td>(4.0 ± 0.2) × 10⁻³</td>
<td></td>
</tr>
<tr>
<td>Perovskite-shelled PbS</td>
<td>(5 ± 1) × 10⁻¹</td>
<td>(5.1 ± 0.3) × 10⁻³</td>
<td></td>
</tr>
</tbody>
</table>

The vast difference in mobility values can be attributed to the location in the band structure where each of these methods probe. In fs-TA, the measured mobility is the interaction of charge carriers hopping between donor CQDs until it becomes trapped by an acceptor, which is localized to tens of CQDs (Figure 4.12a). The mobility is inferred from the diffusion of carriers under very low to zero electric fields. In TOF, the measured mobility depends on charge carriers traversing the entire length of the PbS CQD active layer plus PbS-EDT layer under the presence of an electric field (Figure 4.12b). The mobility measured by TOF is dependent on other layers present in the device. The behaviour of carriers is also probed on a much larger length scale, thus increasing their susceptibility to impurities, film defects and interface defects that impede transport.

From past works, carrier mobilities of 10⁻³ cm² V⁻¹ s⁻¹ [46] and 10⁻¹ cm² V⁻¹ s⁻¹ [47] have been determined for PbS-EDT and ZnO, respectively. Both the PbS active layer and ZnO layer possess higher carrier mobilities, by at least an order of magnitude, relative to the PbS-EDT layer. The measured TOF mobilities, and hence the CQD device architecture, are likely limited by the transport properties of PbS-EDT layer. The combination of low PbS-EDT mobility and the effect of EDT and ACN deteriorating the underlying PbS film during processing contribute to the large difference in fs-TA and TOF results.
Figure 4.12 | Comparison of carrier transport in fs-TA and TOF. (a) In fs-TA, the measured mobility is of carriers hopping between tens of CQDs. (b) In TOF, the measured mobility is of carriers traversing through many, many CQDs through the PbS active layer and PbS-EDT layer.

One limitation of the TOF method is the requirement for relatively thick films. Typical CQD active layers for solar cells are in the range of 200-400 nm [23,42,43]. In the experiment, I used films with a thickness of $\sim 1 \mu m$. The deposition of thicker CQD films resulted in poor film formation. I varied the deposition technique, by increasing CQD concentration in ink form prior to spin-coating and spin-coating multiple layers, but the quality was still low. Micro-cracks were observed in the films used in TOF, which likely introduced additional traps, and resulting in an underestimated mobility.

To conclude, it was found that the mobility of perovskite-shelled PbS CQDs was slightly higher than the iodide passivated PbS CQDs in device form. The mobility of the devices, when compared to film mobilities from fs-TA, are largely limited by the mobility of the PbS-EDT layer and traps from poor film formation. The mobility results obtained motivates further work in improving the device architecture. Closing the gap between the fundamental mobility of CQDs and when it is used in a device could greatly increase solar cell efficiency.
Chapter 5

Conclusion

5.1 Summary

In this thesis, I provided an overview of CQD materials and its application for optoelectronic devices. I used fs-TA to characterize the novel, state of the art perovskite-shelled PbS CQDs, which have shown significant improvements in carrier mobilities compared to the iodide passivation. I quantified, for the first time, the activation energy required for transport in perovskite-shelled PbS CQDs. The strategy to achieve this utilized temperature-dependent fs-TA. I studied the effects of the PbS-EDT and found that it hindered the effective mobility. I was then interested to quantify the effect on transport due to the remaining layers. Full CQD solar cells were fabricated from the PbS CQD films, and the mobility was determined via the TOF method. For types of PbS active layers, the mobilities in device form was found to be lower by a factor of $10^1$-$10^2$. This large difference was attributed to TOF measuring the effective mobility of the entire device stack, with contributions from the PbS-EDT and ZnO layers, and additional traps between the interfaces. The work in this thesis has provided insights on effects that limit transport in CQDs, and contributing to the development of the next generation of CQD materials.
5.2 Contributions

In this thesis, I quantified the mobility of the novel perovskite-shelled PbS CQDs and compared it against iodide passivation. With fs-TA, I found that the mobility of the perovskite-shelled CQD films were significantly higher (by a factor of 10), possibly due to a lower energy barrier required for carrier hopping. I sought to quantify this by performing temperature-dependent fs-TA and determined an activation energy of 14 meV. I then investigated the effects of the PbS-EDT layer on CQD films, and determined a decrease in mobility by 3 times. With TOF, I studied the CQD films in full device form, and found the mobility decreased even further (by a factor of 10-100) likely due to interfacial defects and other impurities. I conclude that this novel perovskite-shelled has remarkable transport properties, making it favourable for highly efficient solar cells. However, the issues present in the device architecture limit this material from achieving its full potential.

5.3 Future Work

The results obtained in this thesis indicates further work needs to be done to improve the device architecture surrounding the CQD films when used in a device. Specifically, improving the transport properties of the PbS-EDT layer through modified surface passivation and processing techniques. An experiment could be conducted with fs-TA to determine the mobility of purely PbS-EDT films, and compare it against ref. 46 and the results obtained through TOF to obtain a greater understanding of what is limiting transport.

The formation of thicker CQD films needs to be improved by reducing micro-cracks. One possible avenue is the engineering of CQD inks and deposition techniques for optimal film formation without compromising performance. The enhancement in high quality, thick CQD films not only allows for more accurate TOF results, but would increase the performance of CQD solar cells through increased absorption.
On the measurement front, fs-TA could be performed with lower acceptor concentrations. The charge carriers would be able to hop between more donors before reaching an acceptor, mimicking the effects of longer range transport. The smaller the acceptor concentration, the more the carriers behave in the absence of introduced acceptors, thus probing a more accurate mobility.
References


