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The Effect of Morphology on Carrier Dynamics in Solution Processed Solar Cells

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THE EFFECT OF MORPHOLOGY ON CARRIER DYNAMICS IN SOLUTION PROCESSED SOLAR CELLS

A DISSERTATION
PRESENTED TO
THE FACULTY OF NATURAL SCIENCES AND MATHEMATICS
UNIVERSITY OF DENVER

IN PARTIAL FULFILLMENT
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DOCTOR OF PHILOSOPHY

BY
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Abstract

This dissertation looks at the charge transport properties of solution processed solar cells and how these properties are effected by the microstructure and morphology of the material. It begins with an introduction and history of the field of solution processed solar cells, focusing on organic photovoltaics and perovskites. The physics and issues of charge transport in these materials are reviewed, and the transport probing techniques of photo-Charge Extraction via Linearly Increasing Voltage (photo-CELIV), Metal Insulator Semiconductor-CELIV (MIS-CELIV), and Resistance Photovoltage (RPV) are detailed.

The photo-CEILV technique is used to probe P3HT devices of varying molecular weights. This material is known to have a microstructure which varies depending on the molecular weight of the polymer. By measuring samples over a range of molecular weights, the mobilities and relative recombination rates are found and a relationship between the microstructure and charge transport is proposed.

The photo-CELIV technique is again used, along with MIS-CELIV and RPV, to measure the mobility of devices made with two related high performing polymers, PTB7 and PBDTTT-EFT. These polymers differ only by the addition of a thiophene ring on the side chain yet Grazing Incidence Wide Angle X-ray Scattering measurements show a significant change in their packing. It is proposed that the decrease in packing distance with the addition of the thiophene ring is responsible for the measured increase in mobility of PBDTTT-EFT which in turn increases the device performance.
The effect of changes to the functional groups of fullerenes on bulk heterojunction morphology is then explored. Samples of three new fullerene derivatives are prepared and compared to PCBM. The changes in film morphology with these materials are studied with Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM) and UV-Vis measurements in order to investigate the origin of their increased open circuit voltage.

Finally, a modified version of the transport probing RPV technique is adapted and used to measure mobility in Perovskite solar cells. Devices treated with two different annealing times are compared showing a doubling in mobility.
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Chapter 1

General Introductions

1.1 Background/History

Photovoltaic technology has developed incredibly rapidly over the last decade. One area of particularly fascinating growth has been in the area of solution processed solar cells; Solar cells whose active layers are formed by deposition from a liquid solution. These photovoltaic materials have several advantages over other materials which either require high temperatures (E.g. silicon) or high vacuum deposition (e.g. CdTe, CIGS) to be fabricated.

The versatility of solution processable materials allows them to be deposited using several different methods. For small area devices, films can be prepared via spin coating. In spin coating a drop of the solution is deposited in the center of a substrate, which is then rotationally accelerated. This rapid spinning (RPMs can vary from $\sim 500$–$\sim 3000$, depending on the recipe) coats the substrate and expels the excess solution. Spin coating is a particularly popular technique for lab scale use due to its ease of use, customizability and versatility[1]. Another deposition technique of growing popularity is blade coating (also known as doctor blading). In blade coating, a small amount of solution is deposited on a sample in front of a flat
level blade which sits just above the surface of the substrate. The solution forms a meniscus between the substrate and the blade, which is then moved forward at a uniform speed, leaving behind a thin layer of solution\cite{2, 3}. This technique is less customizable than spin coating but creates a highly uniform film and, unlike spin coating, it is readily scalable\cite{4}. Additional deposition techniques that are scalable and work well for large area fabrication include spray coating, slot die coatings, and ink jet printing\cite{5}. Lamination\cite{6} can also be used for combining solution processed layers from different substrates. The flexibility of these techniques allows solution processed devices to be produced much less expensively than traditional solar cells.

In addition to the processing flexibility, the high absorption coefficient of these materials allow them to be effective at very small thicknesses, meaning functional devices can be made quite thin. These thin solution processible materials can be deposited on flexible substrates for easier production and used for flexible applications. Polymer materials in particular are well suited for flexible applications because, unlike crystalline materials which crack when they are flexed, polymers stretch. This allows them to continue to function well without generating cracks, even after repeated bending.

Two of the most prominent solution processed technologies are Organic Photovoltaics (OPV) and Perovskite Solar Cells. The technology behind OPVs or polymer solar cells has been in development for decades, with the discovery of the photoelectric properties of organic semiconductors in the 1950s. However, for the vast majority of that time the efficiency was very low, and it took several breakthroughs in order to significantly advance the technology and make it competitive. The 1% efficiency barrier was first approached by C.W. Tang in 1986\cite{7}, who combined a photoabsorbing molecule with an electron accepting copper phthalocyanine in a bilayer device. This created the energetically favorable grain boundary needed to
overcome the electron-hole binding energy, and allowed the dissociation of charge carriers necessary to achieve measurable photoelectron conversion.

The next major breakthrough came in 1992 with the discovery that a C_{60} buckminsterfullerene could be used as the electron acceptor, resulting in ultrafast charge transfer from a conjugating polymer[8]. This was further improved upon in 1995 when the Heeger group discovered that Phenyl-C_{61}-butyric acid methyl ester, PCBM, (a functionalized C_{60} that Hummelen had originally developed for HIV treatment research) could be mixed with the conjugate polymer to form an interpenetrating network of the two materials[9]. This bulk heterojunction (BHJ) dramatically increased the amount of interface between the donor and acceptor comparted with a bilayer device, while still providing pathways for charge extraction.

At this point the field began to grow more rapidly. In 2001, Sean Shaheen et al. of the Sariciftci group discovered that by modifying the solvent used in polymer-fullerene solutions, the domain size of the BHJ could be varied. Optimization of this domain size resulted in a large increase in performance up to 2.5% efficiency[10]. As more photoactive polymers were discovered it was determined that the structure could be further improved via annealing[11]. From here, the efficiencies have continued to climb steadily due to material and device structure improvements[12, 13, 14]. Recently, over the last few years, new active layer materials have rapidly increased performance, with single junction cells surpassing the 10% efficiency mark[15, 16] and multi junction cells reaching device efficiencies of 13.2% [17].

Even compared to OPVs, growth of perovskite solar cells has been very recent and incredibly rapid. The term perovskite refers to crystalline materials with the chemical formula ABX_{3} where the crystalline structure is nominally cubic with the A atoms at the corner positions, the B atoms centered, and the X atoms in face centered positions. In this material, A and B are cations and X is an anion which is mutually bonded to both cations.
The first material of this structure, the perovskite mineral, was discovered in 1839 and, due to their interesting ferroelectric and conductance properties, materials of this type have been studied ever since. Of particular interest are the hybrid-organometallic perovskite materials, where the A atom is replaced by a small organic molecule, most notably methylammonium (CH$_3$NH$_3$ or MA) and formamidinium ((NH$_2$)$_2$CH or FA), and the B atom is a metal such as tin or lead (see figure 1.1). The recent explosion in perovskite research for solar cells began in 2009, when it was discovered that organometallic perovskites with a halide atom in the X place could be used as a visible light sensitizer in a dye-sensitized solar cell (DSSC)[18]. This organometallic halide perovskite can be solution processed at low temperatures from precursor solutions of methylammonium iodide (MAI) and lead iodide (PbI$_2$). These cells used the perovskite (from here on, perovskite will refer to organometallic halide perovskite materials only) to coat a mesoporous film of TiO$_2$ and by enclosing the cell with an organic electrolyte solution, they were able to obtain power conversion efficiencies of up to 3.8%.

It was soon discovered that the charge transport properties[20] allowed for a thicker absorbing layer, and the role of the perovskite material in the cell increased along with device performance up to 6.5% in a sensitized solar cell[21]. Issues with stability and rapid degradation lead to the replacement of the electrolyte with a solid state hole transport material, which created an all solid device[22, 23]. This change also lead to an instantaneous performance jump up to 9.7%[24] and allowed the field of perovskite solar cells to take off. From here device architectures began to change, moving away from a mesoporous scaffolding and towards a more planar OPV like structure with the use of a compact titanium dioxide (TiO$_2$) base layerg[25]. This architecture change, along with developments in electron and hole transport layers, the usage of mixed halides (e.g. MAPb$_{3-x}$Br$_x$) and mixed cation active layers (eg.
Figure 1.1: Crystal structure of a CH$_3$NH$_3$PbI$_3$ perovskite with the methylammonia in the middle, lead atoms in the corners, and the Iodide atoms in purple. Image courtesy of Christopher Eames et al.[19] via Creative Commons.

(Cs/Ma/Fa)Pb(I/Br)$_3$[26] has caused incredibly rapid efficiency growth[27] with devices recently surpassing 20% efficiency[28].

1.2 Solar Cell Physics

There are several ways to generate electricity from sunlight, but most photovoltaic cells with high dielectric constants work as follows: photons are incident upon the absorber material of the solar cell. Photons with energy higher than the material’s band gap are absorbed, while photons with energy lower than the band gap pass through the device without being absorbed. The absorbed photons excite electrons from their valence band into the conduction band, leaving behind a
hole in its place. Inside the conduction band, the electron drops down to the band edge, radiating the excess energy out as heat via lattice vibrations. From there, the thermal energy in the system separates the hole and the electron. The hole, which can be treated as a positively charged particle, and the electron then travel through the device via diffusion and drift from the built-in electric field as shown in the modified Mott-Gurney Drift-Diffusion equation[29] (see equation 1.1). In this equation $J$ is the current density, $\mu$ is the carrier mobility, $\epsilon$ is the permittivity, $d$ is the film thickness, $V$ is the voltage, $q$ is the elementary charge, $k$ is the Boltzmann constant, and $T$ is the temperature.

\[
J = \frac{9}{8} \epsilon \mu \frac{U^2}{L^3} + 4\pi^2 \frac{kT}{q} \epsilon \mu \frac{U}{L^3}
\]  

(1.1)

At the edges of the device the carriers encounter and pass through charge selective barriers. These barriers are either generated by the work function of the contact material, or are deposited as a separate charge selective transport material. Once through these barriers, the charges are collected at the contacts and used for electricity.

1.2.1 OPV Physics

Organic photovoltaics follow this general guideline, however, the use of a polymer blend as their active layer alters the physics of charge absorption and extraction. Unlike crystalline semiconductors, polymer semiconductors have highest occupied molecular orbital (HOMO) and a lowest unoccupied molecular orbital (LUMO) instead of a valence and conduction band. This gives them a defined absorption band with an upper and lower limit which means that while they still absorb a range of photon energies, shorter wavelength photons with energies above the top band edge will pass through the device, instead of being absorbed and losing the excess energy.
as heat. Additionally, the potential variation in polymer design allows the location of said band gap to be highly tunable, enabling the wavelengths of light absorbed by the device to be controlled with modifications to the polymer. These two features give polymer-based solar cells some unique advantages in specific applications. It makes them ideally suited for use as semi-transparent solar cells (e.g. for solar windows), and also makes them ideal for tandem solar cells. Tandem solar cells are solar cells made up of multiple stacked photovoltaic devices each with differing band gaps. This allows a greater range of the solar spectrum to be absorbed without sacrificing the device voltage, and enables the devices to potentially surpass the single device efficiency maximum set by the Shockley-Queisser limit. Since high energy photons can pass through OPV materials instead of being absorbed and losing their excess energy to thermalization, the stacking order of the layers in a tandem device can be altered, which allows for much greater design flexibility. Additionally, OPVs work well in low light conditions[30] which furthers aids their versatility.

The added photoabsorption control of OPVs does come with some drawbacks. The low dielectric constant and lack of rigidity in polymer absorbers compared to their crystalline counterparts means that the polymer chain energetically distorts slightly when a photon is absorbed. This reorganization increases the amount of energy needed to separate the hole and the electron above what is thermally available. Instead of separating from each other, the hole and the electron form a bound neutral quasi-particle inside the polymer called an exciton. These excitons have a lifetime of around 200-400 ps and a diffusion length of \( \sim 6 \text{ nm} \)[31]. In order to dissociate the exciton before it recombines, a second material is added to the active layer. This material is an electron acceptor, the most common of which is a fullerene, usually a C60 buckeyball derivative. When an exciton bumps into the boundary between the polymer and the fullerene, the difference in energy level at the LUMO-LUMO offset is enough to overcome the exciton binding energy of \( \sim 0.2 \)}
eV - ~ 0.3 eV[32] (depending on the polymer). When the binding energy barrier is overcome, the charges go through the charge transfer state and the electron moves over onto the C$_6$0. The rate of this exciton dissociation depends on the reorganization energy of the polymer and can be described by Marcus theory[33, 34]. Once the charges are separated, they can move through their respective materials to the proper contacts to be collected.

In order to have a well-functioning device, the blending of the two materials needs to be optimized such that there is a balance between the probability of an exciton encountering an acceptor-donor interface within its 6nm diffusion distance, and there being a clear channel in their respective materials for both electrons and holes to reach their proper contacts. This is achieved with a solution processed mixture of the polymer electron donor and the fullerene acceptor, called a bulk heterojunction (BHJ). The properties of the BHJ are very important in the performance of the device, however, with the proper solvents, ratios, and contact layers, near 100% internal quantum efficiency (IQE) can be achieved[35].

Even in a nearly optimized bulk heterojunction, there will still be charge carrier pathways which lead to the incorrect contact. In order to prevent these pathways from negatively impacting the device performance, selective transport layers are necessary in OPV devices. OPV devices require either a hole transport layer, an electron selective transport layer, or both. In devices with "standard geometry" where electrons are collected though the metal contact, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) is traditionally used as a hole transport layer (HTL) and a thin layer (10-20 nm) of calcium or lithium fluoride is used as the electron transport layer (ETL). In "inverted geometry" devices where electrons are collected through the transparent contact, zinc oxide (ZnO) is primarily used as the ETL and either oxidized silver, or PEDOT:PSS, or molybdenum oxide[36] are used as the HTL (see figure 1.2). Other oxides, such as nickel oxide[37] can also
be used as transport interlayer. In addition, self-assembled monolayers (SAMs) can be grown on the transparent indium tin oxide (ITO) contact[38, 39]. These SAMs can be modified to directly control their work function and thus act as a selective transport layer.

Figure 1.2: Typical device architecture for A. standard geometry and B. inverted geometry organic photovoltaic devices. The negative electrode is traditionally calcium and aluminum, the positive electrode is traditionally silver. Image courtesy of Brian Bailey

1.2.2 Perovskites Physics

Optimal perovskite devices can have a structure quite similar to that of OPV devices, with the perovskite material substituted in place of the organic bulk heterojunction. However unlike OPVs, the exciton binding energy in perovskite devices has been computationally estimated to be under 50 meV [40] and experimentally measured as low as 5 meV[41]. At these low binding energies, the material can be assumed to be nonexcitonic. There are however, several other interesting charge transport properties of perovskites.

One of the most notable issues in perovskites is the hysteresis shown in device current-voltage measurements, where the shape of the JV curve changes depending on the direction of the scan. The device characteristics are significantly better when sweeping from a positive voltage bias to a negative voltage bias than when swept from negative to positive. In addition to the hysteresis, the measured recombina-
tion rate in perovskite devices is several orders of magnitude lower than expected from Langevin recombination (more on Langevin recombination in section 1.3.4). Additionally, the mobility is much slower than predicted from the effective electron and hole masses of $\sim (0.1 - 0.15) m_0$ where $m_0$ is the free-electron mass[27].

There are several proposed explanations for the hysteresis in perovskites. Three of the most prominent are; the occurrence of ferroelectricity in the samples, the influence of ion transport, and presence of trap states on the surface and at perovskite grain boundaries.

It has been proposed[42] that the application of an electric field during current-voltage sweeps could slowly create ordered ferromagnetic domains caused by the rotation of MA ions. In the proper configuration, these domains could produce interpenetrating percolating pathways of electric potential for the transport of electrons and holes. When swept from the other direction, these pathways would be disturbed, resulting in the reduced hysteresis curve. However, further simulations[43] and experiments[44] indicate that the rotational freedom of MA at room temperature is likely too high to allow this kind of long range order. It is still possible that more local ferroelectric domains are present and that they help to reduce the band gap and enhance charge separation[45], contributing to the low recombination.

A second explanation for the hysteresis in perovskites puts the blame on the occurrence of a large density of trap states on the surface and grain boundaries of the material[46]. This claim is supported by the ability of the hysteresis to be passivated by the deposition and annealing of a PCBM layer on top of the perovskite material in inverted devices. (Note: because they originated as DSSC, the terminology of perovskite devices is opposite that of OPV, and inverted devices refer to devices which collect holes at the transparent bottom contact and electrons at the metallic contact) . The deposition of PCBM on top of the perovskite lowers the electron trap density of states significantly . When the layer is annealed, allowing
the PCBM to interpolate into the domain boundaries, the traps appear to be almost completely passivated and the device no longer shows any hysteresis. However, by attributing the hysteresis to the presence of surface electron traps, this explanation does not fully explain the presence of hysteresis in standard geometry perovskite devices, where electron collection occurs at the bottom of the device.

Other studies have investigated the occurrence of ionic transport in perovskites and its role in device hysteresis [47]. Calculations of the activation energies for iconic migration in MAPbI$_3$ show that while the Pb is immobile in its sublattice and the MA are relatively stable, the I$^-$. ions undergo significant vacancy assisted migration [19]. Additionally, chronophotoamperometry measurements on devices determine that the activation energies for hysteresis is in close agreement with the calculated value for the migration of iodide ions. The diffusion rate of an iodide vacancy is such that the applied electric field during a JV sweep could cause ionic screening, hindering efficient charge collection and significantly reducing the observed photocurrent, whereas an electric field in the opposite direction would mitigate this effect.

There is mounting evidence to suggest that ion migration is the primary cause of hysteresis in perovskite devices [48, 44], however the occurrence of hysteresis over a range of active layer compositions and device structures indicates that full effect may be caused by a combination of factors.

The strong evidence for iconic transport indicates that it is likely the predominant cause of hysteresis in Perovskites but the experimental evidence for the other methods suggest that hysteresis may be a combination of multiple of these effects. The origin of hysteresis in perovskite may be a combination of multiple of these effects.

The origin of low carrier mobility in perovskites compared to other polycrystalline solar cell materials also remains undecided. One explanation for this lower than expected mobility is the occurrence of scattering processes. Increased carrier
scattering can significantly lower mobility, but the long carrier lifetimes and the inverse power dependence of mobility on temperature rules out impurity scattering[49]. This leaves phonon scattering as a potential cause. The moduli of elasticity in Perovskites are relatively low[50] supporting the presence of scattering acoustic phonons. However, some theoretical calculations have shown relatively weak carrier-phonon coupling[51]. Another explanation for the relatively low mobility is the creation of polaron quasiparticles around the charge carriers. Density functional theory calculations show that the rotational freedom of the MA dipoles[20, 45] allow them to align to single charge carriers. These polarons also appear to be strengthened by small local volumetric stain[52]. The polaron formation in perovskites would significantly increase the effective mass of the charge carriers and thereby slow carrier mobility.

The recombination rate in perovskites would also be reduced by the MA rotation, as the dipoles rotate to screen the coulombic interaction between the carriers and encourage charge separation[45]. However, a larger effect on the reduced recombination likely comes from the physical isolation of free holes and electrons. Quantum molecular dynamics simulations show that in perovskites, electrons predominantly reside on Pb atoms whereas holes are located on the I atoms[43]. The MA sublattice does not act as a charge carrier but as a medium which aids in charge separation[52]. This means that once separated electrons and holes will travel down separate atomic pathways towards their respective contacts, greatly reducing the likelihood of carrier recombination.

While the efficiency growth of perovskite solar cells has been rapid, a better understanding of these issues will unlock the full potential of the material and lead to further performance improvements.
1.3 Charge Transport Measurement Techniques

1.3.1 CELIV

One powerful tool to probe carrier dynamics in solar cell devices is Charge Extraction via Linear Increasing Voltage (CELIV). CELIV is a technique that allows for mobility measurements of charge carriers inside fully functional solar cell devices. The technique was developed by Jůska in 2000[53] for use in amorphous silicon, but has since been adapted to organic photovoltaics[54]. The basic concept behind CELIV is that a solar cell device can be treated as a parallel plate capacitor with a dielectric material sandwiched between two conductors. Since the current produced by a capacitor, $I$ is proportional to the derivative of the input voltage, $V$, a linear voltage increase will produce a rectangular current (see equation 1.2, where $C$ is the capacitance).

$$I = C \frac{dV(t)}{dt} \quad (1.2)$$

If there are any dark charge carriers (usually formed by low level trap states or other defects) in the dielectric material between the contacts, these carriers will be swept out as the capacitor is charged. The resulting current will then contain a bump on top of the rectangular voltage pulse. This bump can be analyzed in order to determine the charge carrier mobility and provide other information about the charge carriers, such as the extracted current and recombination rate.

The mobility can be determined by a CELIV extraction with the following derivation:

During CELIV The voltage across a device $V$ is given by the CELIV ramp rate $A'$ times the elapsed time $t$, this is also equal to the integral of the electric field across the device, from 0 to thickness $d$

$$A't = V = \int_0^d E(t, x)dx = E(d, t) * d + \frac{E(0, t) - E(d, t)}{2}l(t) \quad (1.3)$$
where \( l(t) \) is the extraction depleted region. The difference between the electric fields at either side of the device is proportional to the extracted charge \( Q(t) \)

\[
E(0, t) - E(d, t) = \frac{Q(t)}{\epsilon \epsilon_0} = \frac{enl(t)}{\epsilon \epsilon_0}
\]  

(1.4)

where \( \epsilon \epsilon_0 \) is the permittivity of the material, \( e \) is the charge of an electron, and \( n \) is the charge carrier density. Taking the derivative of both sides of this equation yields the extraction current at the edge, which is equivalent to the electric field at the edge times the conductivity.

\[
\frac{dQ(t)}{dt} = en \frac{dl(t)}{dt} = en\mu E(d, t)
\]  

(1.5)

Where \( \mu \) is the charge carrier mobility. Combing equations 1.3, 1.4, and 1.5, gives the relation

\[
A't = \frac{d}{\mu} \frac{dl(t)}{dt} + \frac{en}{2\epsilon \epsilon_0} l(t)^2
\]  

(1.6)

which can be rearranged into the Riccati type equation

\[
\frac{dl(t)}{dt} = \frac{\mu A'}{d} t - \frac{en \mu}{2\epsilon \epsilon_0} l(t)^2
\]  

(1.7)

This shows the depletion rate is dependant on an external field component, \( \frac{\mu A'}{d} t \), and a component from the electric field generated by the charge distribution. For low conductivity materials, the contribution from the extracted charge distribution is negligible, and the equation simplifies to

\[
\frac{dl(t)}{dt} = \frac{\mu A'}{d} t
\]  

(1.8)
integrating both sides with respect to $t$ gives

$$l(t) = \frac{\mu A'}{2d} t^2 \quad (1.9)$$

Which can be solved for the mobility, when evaluated at the transit time, $t_{tr}$, where $l(t_{tr}) = d$.

$$\mu = \frac{2d^2}{A't_{tr}^2} = \frac{2d^2}{3A't_{max}^2} \quad (1.10)$$

given that $t_{max} \simeq t_{tr}\sqrt{3}$.

Unfortunately, for the full range of mobilities, equation 1.7 does not have a simple solution. It can be solved with data fitting [53], numerically [55], or through a complicated analytical solution [56] yielding equations 1.11, 1.12, and 1.13 respectively.

$$\mu = \frac{2d^2}{3A't_{max}^2} \left( \frac{1}{1 + 0.36\frac{\Delta j}{j_0}} \right) \quad (1.11)$$

$$\mu = \frac{2d^2}{A't_{max}^2} \left( 0.860e^{-0.486\frac{\Delta j}{j_0}} - 0.525e^{0.0077\frac{\Delta j}{j_0}} \right) \quad (1.12)$$

$$\mu = \frac{d^2}{2A't_{max}^2} \left( \frac{1}{6.2(1 + 0.002\frac{\Delta j}{j_0})} + \frac{1}{1 + 0.12\frac{\Delta j}{j_0}} \right)^2 \quad (1.13)$$

Where $j_0$ is the base capacitance current and $\Delta j$ is the difference between $j_0$ and the maximum current $j_{max}$. Which of these equations is used is, to some degree, a matter of personal preference. Many papers still use the original data fit equation for simplicity. The work presented here primarily uses the analytical solution.

Often in materials, the dark carriers alone are insufficient to get a signal large enough to accurately measure carrier mobility. In these cases, it is necessary to artificially generate charge carriers in the device. The simplest method for photovoltaic materials is via laser pulse. For our experiment we used a pulsed Nd:YAG
laser, delivering 4-6 ns wide pulses at a frequency of 10 Hz tuned through an optical parametric oscillator (OPO) to a wavelength of 550 nm. Depending on the laser used, the OPO may not be necessary, but ideally the laser wavelength should be near the peak absorption window for your photoactive material. Using an OPO can allow for minimization of the signal while reducing the damage and degradation the device experiences during the experiment.

In order to generate charge carriers for use in photo-CELIV, the pulsed laser must be timed to arrive just before the voltage ramp begins. Despite its relatively short duration (\(\sim 5\) ns) the laser pulse will generate an excess of carriers in the device. These generated carriers will be removed from the device via the built-in field and the resulting current will drown out the CELIV signal unless there is a small delay (\(\sim 5\) \(\mu\)s) between the laser pulse and the CELIV sweep. However, if the delay is too long the built-in field will remove too many of the carriers and there will once again be too small of a signal to produce a good mobility measurement. Additionally, the longer the delay, the more of the charges will be lost due to bimolecular recombination.

This dilemma can be overcome by biasing the device in the reverse direction with a small externally applied voltage in order to counter the charge removal effects of the built-in voltage. A bias voltage of \(\sim 0.3\) V is usually sufficient to keep generated charge carriers inside the device between the laser pulse and the start of the CELIV sweep. Once the timing and the bias voltage have been adjusted correctly, a CELIV sweep can be performed. This will result in the removal of a significant portion of charge carriers and the resulting current bump will be large enough to get reliable measurements for mobility.

There are of course several tricks necessary to perfect the technique, namely the balance between ramp rate, noise, and device stability. A slow ramp rate will decrease the height of the extracted current pulse, which can lead to signal to noise ratio issues, but if the ramp rate is too high, you run the risk of damaging the device.
or forcing charges through the blocking layer. This can create an I=V/R leakage current, which will obscure the measured peak transit time. Most OPV devices will begin to short out with a peak ramp voltage of around 4 V. Additionally, it is necessary to choose ramp time significantly greater than the current transit time. This allows the current bump to achieve a clear maximum, and ideally, return to the base capacitance level, illustrating that all the carriers have been removed. This balance usually has to be achieved experimentally and details of this process are given in appendix A.1.

On top of mobility and transit times, CELIV can also be used to directly measure the number of carriers generated in a given device with a set illumination. This is obtained by integrating the area under the CELIV extraction curve and subtracting out the base capacitance rectangle. For this reason, as well as to get a good $j_0$ value, it is helpful to measure a dark scan of your sample before performing any CLEIV or other measurements on it.

1.3.2 I-CELIV and MIS-CELIV

In cases where it is not possible to use a laser to photo excite the charges; either because a laser of the appropriate wavelength is not available, or because the material is not photoactive enough, or for any other reason, it is still possible to perform CELIV measurements through the use of injection-CELIV (i-CELIV). In i-CELIV a strong reverse bias is applied to the device prior to the CELIV sweep. This voltage forces charges to move in the direction opposite of normal flow in a solar cell and causes the charge carriers to build up against the blocking layer in the cell. The traditional CELIV sweep can then be applied and these built up charges measured as they are removed from the device[57]. This technique requires a highly effective blocking layer. Otherwise the charges will leak through, causing a leakage current and reducing the amount of built up charges, thereby reducing the effectiveness of
the measurement. In addition, the RC spike caused by switching from a negative bias to a positive ramp can have the effect of drowning out the CELIV signal.

A more effective (but also more complicated) variation on the i-CELIV technique is the Metal-Insulator-Semiconductor-CELIV technique (MIS-CELIV)\[58, 59\]. In this experiment, a layer of insulating material (usually magnesium fluoride, MgF$_2$, or silicon monoxide, SiO) is deposited between the semiconducting active layer and the metallic contact during device fabrication. This layer serves as a complete blocking layer allowing a significant build-up of charges when a voltage bias is run against it. These charges are held in the semiconductor on the boundary with the insulating layer and then travel across the device during the CELIV sweep. The mobility of the semiconductor can be found from a MIS-CELIV extraction curve according to equation 1.14 where $d_s$ is the thickness of the semiconductor, $d_i$ is the thickness of the insulator, $\epsilon_s$ is the dielectric constant of the semiconductor, and $\epsilon_i$ is the dielectric constant of the insulator. Alternatively, if the dielectric constants and layer thicknesses are not well known, equation 1.15 can be used.

\[
\mu = \frac{2d^2}{A' t^2_{tr}} \left(1 + \frac{\epsilon_s d_i}{\epsilon_i d_s}\right) \tag{1.14}
\]

\[
\mu = \frac{2d^2}{A' t^2_{tr}} \left(1 + \frac{j_0}{j_{max} - j_0}\right) \tag{1.15}
\]

This technique has the advantage of measuring only the electrons or only the holes depending on the direction of the bias, and the presence/composition of the selective contact on the other side of the device. As such it can be designed to give accurate measurement for either charge carrier, even if the mobilities are similar. However, in order for the MIS-CELIV to work, the insulator needs to block the charges almost completely, even under high bias voltages. At the same time, the maximum thickness of the insulator must be less than half the thickness of the active
layer. Achieving this has shown to be non-trivial, especially for thinner active layer materials.

1.3.3 RPV

Resistance photovoltage (RPV) is a new transient photoconductivity technique which can be used to measure transit time and mobility for both holes and electrons simultaneously in functional solar cell devices. The experimental setup for RPV is similar to that of the time-of-flight (TOF) experiment, in that a photovoltaic device is connected in a circuit to an oscilloscope and carriers are generated via a short laser pulse. However, unlike the TOF measurement, RPV measurements are performed over a range of oscilloscope load resistances, from 10 Ω to 1 MΩ. By increasing this resistance, the circuits RC time is increased. This slows the collection of charges from the device, allowing us to look at the front edge of the extraction voltage transient.

To conceptualize this charge collection, one can picture the photogenerated charge in the device as two parallel sheets of charge, one of electrons and one of holes. When the charge sheets move apart from each other and towards their respective contacts, the voltage between them will grow as in a parallel plate capacitor of increasing separation. If we assume one carrier is significantly more mobile than the other, that carrier will transit to its contact first while the other remains relatively stationary. This will cause a steep rise in the extracted voltage. The slower charge will then make its way across the device, further increasing the voltage at a lower rate until it reaches its contact, at which point the voltage transient will reach a maximum and saturate (see figure 1.3). The voltage transient can thereby be used to determine the transit times of each carrier. The transit time of the slower carrier will occur where the voltage transient reaches its maximum, and the faster carrier transit time occurs at the transient’s inflection point. In actual devices the charge
distribution is not a sheet and the mobilities will run a distribution, but the same
principles hold.

Figure 1.3: A simple 1D simulation of an RPV extraction curve with arbitrary units,
showing how to find the transit times of the faster carrier (Transit Time 1) and the
slower carrier (Transit Time 2)

From the transit time, the charge carrier mobility can be determined from equa-
tion 1.16 where $\mu$ is the mobility, $d$ is the device active layer thickness, $t_{tr}$ is the
transit time, and $V$ is the built-in voltage of the device.

$$\mu = \frac{d^2}{t_{tr}V}$$ (1.16)

In the RPV measurement, voltage saturation is necessary to ensure the complete
extraction of carriers transiting the device. When all the carriers are fully extracted,
increasing the measurement time of the voltage curve will not result in any additional
voltage gain. If voltage is not saturated between the 0.5 MΩ and 1 MΩ scans, then
there may still be charges in the device and the transit time of the slower carrier could be underestimated.

Additionally, for the RPV experiment to be accurate, space charge effects must be kept to a minimum. If the photogenerated charge is not significantly less than the capacitance times the voltage, it will redistribute the electric field during extraction, which would change the transit times. To achieve this condition, RPV requires a low intensity laser pulse (\(\sim 10\% \text{ of } \text{Voc}\)). This ensures that the electric field inside the device is kept in a relatively solid state condition and that the mobility measurements are accurate. Used correctly, RPV can provide easy, nondestructive measurements of both holes and electrons in fully functional solar cell devices.

**1.3.4 Recombination**

One of the most important loss mechanisms in photovoltaic devices is carrier recombination. When a photon is initially absorbed in a device, it excites an electron, separating it from a hole. In order to generate electricity from this photoelectric process, it is necessary to get the electron and hole to their respective contacts without them recombining at one of the several separate steps along the way. In polymer solar cells, the creation of an exciton complicates the process further. Once generated, excitons have a lifetime of less than half a nanosecond before they collapse and recombine, emitting either heat or another photon. In order to not recombine, the exciton must move through diffusion to the boundary between the polymer and an electron accepting material within that timeframe. This is ensured primarily by careful optimization of the bulk heterojunction, such that the surface area between domains of the two materials is maximized while still providing sufficiently interconnected domains as to allow a pathway to either contact. If done correctly, near complete extraction can be achieved[35], but this optimization needs to be repeated for every new material.
Once the exciton meets a boundary with a sufficient LUMO-LUMO offset, the electron will transfer to the more energetically favorable material. At this point, the charge carriers form a separated but coulumbically-bound interfacial pair, sometimes called a germinate pair, a bound polaron, a charge transfer exciton, or an exciplexe. This charge transfer state is much more loosely bound than the exciton, and can be separated at a high rate by the built-in field of the device generated via the differences in work function of the two contacts. An applied electric field can be used to increase this charge dissociation. Upon being separated, the charge carriers can move through the materials towards their appropriate contacts via a combination of drift and diffusion. However, it is still possible for nongerminate recombination to occur upon collision with either opposing free charges or trap states. In low mobility materials, such as those used in organic photovoltaics, this recombination can typically be described with Langevin theory. The rate of Langevin recombination is based on the likelihood of two opposing charge carriers essentially running into each other, moving close enough for the Coulomb potential to overcome their thermal energy, thus causing them to collapse together. This Langevin recombination is derived below:

In the case where one charge carrier is significantly more mobile than the other (or simply taking one carrier as the basis of a reference frame), the force applied to the mobile carrier can be described as

\[ F = \frac{e^2}{4\pi \varepsilon \varepsilon_0 r^2} \]  

(1.17)

and the corresponding drift current for that carrier is given by

\[ j = en\mu F = \frac{e^2 n\mu}{4\pi \varepsilon \varepsilon_0 r^2} \]  

(1.18)
where $e$ is the fundamental charge, $n$ is the mobile charge carrier density and $r$ is the radial distance from a fixed charge of the opposite polarity. Now the current generated by these charge carriers flowing into a sphere of radius $r$ around the slower carrier is:

$$I_{\text{rec}} = j \ast 4\pi r^2 = \frac{e^2 n \mu}{\epsilon \epsilon_0}$$

(1.19)

Which represents the recombination current per stationary carrier, $I_{\text{rec}}$. The total recombination current $J_{\text{rec}}$ will be given by this single stationary carrier current times the density of stationary carriers $n_2$

$$J_{\text{rec}} = I_{\text{rec}} n_2 = \frac{e^2 n_1 \mu}{\epsilon \epsilon_0} \ast n_2 = e R$$

(1.20)

which is also the recombination rate, $R$, times the charge of an electron, $e$. In regards to bimolecular recombination, $n_1 n_2$ is the electron density, $n$, times the hole density $p$. As such, the rate of recombination will be

$$R = \frac{e n_1 n_2 \mu}{\epsilon \epsilon_0} = \frac{e \mu}{\epsilon \epsilon_0} \ast np = \beta_L np$$

(1.21)

and $\beta_L$ is the recombination rate factor for Langevin recombination. (*Note: this does not include the intrinsic carrier density $n_0$ in the full equation $R(np - n_0^2)$)

This means that the rate of recombination is primarily dependent of the mobility of the respective carriers ($\beta_L = \frac{e \mu}{\epsilon \epsilon_0}$).

However, in some materials, the actual rate of recombination is less than the recombination rate expected from the Langevin formalism (see Chapter 2). CELIV can be used to directly measure this deviation in recombination rates.

In a fully saturated device, the carrier recombination is a limiting factor in the amount of charges generated. By looking at the peak carrier current extracted during CELIV and comparing it to the base capacitance current, a relative recom-
bination rate can be found. This relative recombination rate is a powerful tool for analyzing charge transport properties in materials.

To find this rate, we start with the time dependent current, which is equal to the base capacitance current \( j_0 \) plus the extraction current \( \Delta J(t) \). This can be given by:

\[
j(t) = j_0 + \Delta j(t) = j_0 + \frac{en(t)\mu}{d} \int_{l(t)}^{d} E(x,t)dx
\]

(1.22)

\[
j(t) = \frac{\varepsilon \varepsilon_0 A'}{d} + en(t)\mu E(d,t) \frac{d-l(t)}{d}
\]

(1.23)

The density of charge carriers in the depleted region is zero, and in the undepleted region it can be given as:

\[
n(t) = \frac{1}{n_0 + \beta t}
\]

(1.24)

where \( n_0 \) is the initial charge carrier density. In a fully saturated device, \( n_0 \) is large and the charge carrier density is recombination limited, thus \( n(t) \) can be approximated as \( \frac{1}{\beta t} \). Additionally, the electric field can be approximated as:

\[
E(d,t) \approx \frac{A't}{d}
\]

(1.25)

At \( t_{max} \), the device is still mostly undepleted, and \( l(t_{max}) < d \), so

\[
\frac{d-l(t_{max})}{d} \approx 1
\]

(1.26)

Applying these approximations to the equations 1.22 and 1.23 yields the equations

\[
j(t) = \frac{\varepsilon \varepsilon_0 A'}{d} + \frac{e\mu A'}{\beta d}
\]

(1.27)
and
\[ \Delta j(t) = \frac{e\mu A'}{\beta d} \]  

From above, the rate of Langevin recombination is given as \( \beta_L \) where
\[ \beta_L = \frac{e\mu}{\epsilon \epsilon_0} \]

So \( \beta_L \) times the base capacitance current can be written as
\[ \beta_L j_0 = \frac{e\mu A'}{d} = \beta \Delta j(t) \]

Rearranging this equation allows us to use CELIV data to determine the Langevin reduction factor, \( \frac{\beta_L}{\beta} \), which indicates the degree of which the recombination rate is reduced below the expected Langevin recombination rate in a measured device.
\[ \frac{\beta_L}{\beta} = \frac{\Delta j(t)}{j_0} \]

This Langevin reduction factor allows for the simple and rapid detection of materials with reduced recombination and is a very useful tool for the analysis of new photoactive solarcell materials.

1.4 Motivation and Outline

The field of organic photovoltaics has been rapidly growing in recent years, mostly through the development of new photo-absorbing polymers. To a large extent, however, the development on these new polymers is trial and error. The work presented here is an attempt to add to the analytical framework for design of next generation polymers. Additionally, the development of new perovskite materials as photo absorbing active layers has brought tremendous growth to solution processed...
solar cells, but the understanding of the charge transport in these materials has lagged behind their high efficiencies.

The main work of this thesis is focused on using the tools of CELIV and RPV to investigate the charge transport properties of photovoltaic materials, and to determine how these properties relate to the materials structural and morphological features. This is done with the goal of helping establish a guideline to design and characterize new materials.

Chapter 2 is focused on using Photo-CELIV to determine how adjusting the polymer chain length of P3HT, and thus its molecular packing, effects the mobility and recombination in the material. This chapter further looks at how the semi-crystalline and semi-amorphous mixed domains in P3HT may provide a template for how to produce materials with artificially reduced bimolecular recombination.

Chapter 3 compares two similar molecules using several methods, and looks at how the changes between them affects the crystal packing and its influence on mobility.

Chapter 4 looks at series of new fullerene derivatives and investigates the effect of their solubility groups on film morphology as a potential cause of increased Voc.

Chapter 5 applies some of these same techniques to the new hybrid organometallic perovskite materials, and shows that it is a useful tool in comparing the difference between active layer materials here as well.

In order to perform these experiments, I built a data acquisition, analysis, and graphical user interface program on the IGOR Pro software package. This program interfaces with a function generator, an oscilloscope, and an optional temperature controller. This interface allows the user to use multiple functions including: the ability to create a custom CELIV waveform and remotely control the function generator, to automatically scale and collect data from the oscilloscope, to set data acquisition sweeps and control averaging, and to perform automated data analysis.
This program enabled much faster, better controlled, and more accurate measurements than were previously capable, and allowed the experiments presented here to be performed. More information on this program is available in appendix B.
Chapter 2

Morphology Dependence of Mobility in P3HT

2.1 Introduction

Π-conjugated polymers are a promising material class for many organic electronic technologies, from photovoltaics to transistors to light emitting diodes \[60, 61\]. As the design and synthesis of these materials continues to cause rapid advances in the performance of device platforms, understanding the role of various optimization factors becomes increasingly important. One such factor is the molecular weight of the polymers used in such devices. Variations in molecular weight can directly affect the solid-state structure of polymers such as poly (3-hexylthiophene) (P3HT)\[62, 63, 64\]. At low molecular weights P3HT forms a one-phase, paraffinic structure comprised of unconnected, chain-extended crystallites. As the chain length increases the polymer chains become entangled in solution leading to amorphous interlamellar regions that interconnect the crystalline domains (see Figure 2.1) \[65, 66, 67\]

This change in microstructure has a complicated effect on the charge carrier properties on P3HT. Conventional wisdom would dictate that the change in the
nature of the amorphous phase from paraffinic to semicrystalline microstructure should cause a decrease in mobility, however, in P3HT the opposite appears true. As the microstructure changes with increased molecular weight, the hole mobility has been shown to increase\[66, 67, 68, 69, 70, 71\]. This is believed to be due to improved interlamellar transport along the backbone of the polymer tie chains connecting the crystalline regions\[70\]. While this improvement holds from low to medium molecular weights, at high molecular weights the entanglement density increases\[68\], leading to a large fraction of amorphous regions. These molecularly disordered domains have reduced inter- and intra-chain transport, as well as higher trap densities, limiting interlamellar transport and carrier mobility.

In addition to affecting the mobility, the solid-state microstructure manipulated here with the selection of different molecular weights, can also have an effect on the bimolecular recombination rate in neat polymer semiconductors.
Traditionally bimolecular recombination rates in low mobility disordered solids are described via the Langevin recombination formalism\[72, 73, 74\], in which the rate of recombination is dominated by the probability of the carriers meeting. This rate is given by

\[
\beta_L = e\frac{\mu_e + \mu_h}{\varepsilon_r\varepsilon_0}
\]  

(2.1)

where \(e\) is the electronic charge, \(\mu_e\) and \(\mu_h\) are the mobilities of the holes and electrons respectively, and \(\varepsilon_r\varepsilon_0\) is the dielectric permittivity. However, some polymers, such as P3HT, have displayed recombination rates that are one or two orders of magnitude lower than expected from Langevin recombination when they are blended with an electron accepting material in a bulk heterojunction.\[72, 74, 57, 75, 76, 77\]

The intent of this chapter is to determine to what extent a reduced recombination rate is also present in the neat material, as both a means to a fundamental understanding of the phenomenon and to better inform the structure-property relationship needed for designing materials that perform well in bulk heterojunction blends.

2.2 Results

2.2.1 Photo-CELIV

In order to measure the effect of this microstructure change on the mobility and recombination in P3HT, we used the photo-Charge Extraction with Linearly increasing Voltage (photo-CELIV) technique\[53, 78\]. This technique allows for mobility measurements to be performed on samples with thicknesses and geometries that correspond to the actual usage in photovoltaic devices.

The photo-CELIV technique excites charges in a device with a laser pulse, and then extracts the photo generated carriers with a linear voltage ramp in the reverse
bias direction. By measuring the time and amplitude of the peak current extraction in comparison to the baseline capacitance current in the device, the mobility of the charge carriers can be calculated via equation 2.2 as shown in section 1.3.1

\[
\mu = \frac{d^2}{2A't_{\text{max}}^2} \left( \frac{1}{6.2(1 + 0.002\frac{\Delta J}{j_0})} + \frac{1}{1 + 0.12\frac{\Delta J}{j_0}} \right)^2 \quad (2.2)
\]

Where \(d\) is the device thickness, \(A'\) is the CELIV ramp rate, \(t_{\text{max}}\) is the time from the beginning of the CELIV ramp to the time of peak current, \(j_0\) is the base capacitance current measured from the dark CELIV scans, and \(\Delta J\) is the difference in the peak current and \(j_0\).\[56\] In addition to the carrier mobility, the Langevin Reduction Factor (\(\beta_L/\beta\)) can also be calculated from the CELIV measurement. The Langevin Reduction Factor is the ratio of the measured recombination rate to the Langevin Recombination rate. It can be determined by ratio between the peak extracted current and the baseline capacitance current as shown in equation 2.3.\[57, 75\]

\[
\frac{\beta_L}{\beta} = \frac{\Delta j_{\text{sat}}}{j_0} \quad (2.3)
\]

Photo-CELIV measurements were performed on a series of photovoltaic devices fabricated in an ITO/PEDOT:PSS/P3HT/Aluminum geometry. The weight-averaged molecular weight of the P3HT was varied from \(M_W \approx 13\) kDa to 331 kDa.

Using equation 2.2, we found a hole mobility of approximately \(5 \times 10^{-6}\) cm\(^2\)/(Vs) for low molecular weight material, which increased with increasing molecular weight up to a maximum mobility of \(5 \times 10^{-4}\) cm\(^2\)/(Vs) at \(M_W \approx 47\) kDa (see Figure 2.2). This is within the range of critical molecular weights where entanglements start to occur and the largest lamellar crystal thicknesses are found when crystallizing the material at standard conditions. This \(M_W\) and mobility approximately matches that of commercial samples of P3HT. Further increases in molecular weight resulted
in a slight decrease in mobility to around $1 \times 10^{-5} \text{ cm}^2/(\text{Vs})$, where it plateaued out through to materials of $M_W \approx 331 \text{ kDa}$.

![Graph A](image1.png)  ![Graph B](image2.png)

Figure 2.2: CELIV measurements of A. mobility vs. molecular weight and B. Langevin recombination reduction factor vs. molecular weight for P3HT devices. Diamonds indicate P3HT from Imperial College of London, triangles from Rieke materials, and squares from Plextronics inc. Error bars indicate experimental spread across several devices.

From equation 2.3 we found that for materials of low molecular weight, which form a one phase structure comprised of chain-extended crystallites, the Langevin recombination reduction factor, $(\beta_L/\beta)$, is close to one, implying that Langevin recombination dominates. However as the molecular weight increases, so does the reduction factor, up to a value of 15 for very high molecular weights ($M_W \approx 331 \text{ kDa}$). This indicates the onset and presence of sub-Langevin recombination in the
semicrystalline material. This suggests that the semicrystalline nature of the neat material is reducing recombination, which in turn may also be the source of decreased recombination in bulk heterojunction P3HT samples.

Photo-CELIV measurements were also performed on P3HT devices with inverted geometry (see figure 2.3). Similar to the standard device, these inverted measurements show an increase in mobility and a decrease in recombination as the material moves from a one phase paraffinic-like structure to a two-phase semi-crystalline structure. However, inverted geometry devices have an electric field distribution which differs from standard devices and is poorly understood. This makes the data harder to decipher and further analysis difficult. In addition, we were only able to obtain measurement for one device each of the 60 kDa and 331 kDa molecular weight devices in the inverted geometry, so the shown values may lack statistical significance.

2.2.2 Admittance Spectroscopy

Admittance spectroscopy measurements were also performed on devices of P3HT of low and high molecular weight to determine their activation energies for charge transport.[79, 80] In admittance spectroscopy, frequency-capacitance analysis is applied to OPV devices over a range of temperature. Capacitance is measured across a large frequency range, and the measurement is repeated from 125 K to 300 K. (see figure 2.4).

This solar cell capacitance behavior can be theoretically modeled using a simplified equivalent circuit structure as shown in figure 2.5 and described in equation 2.4

\[ C = \frac{2G_0G_1C_1 + G_0^2C_1}{(G_1 + G_2)^2 + w^2C_1^2} + C_0 \]  

(2.4)
Taking the derivative of the capacitance with respect to the frequency, and multiplying it by the frequency yields a value for $\frac{dC}{dw}$ shown in equation 2.5.

$$\frac{dC}{dw} = \frac{2w^2C_1^3(2G_0G_1 + G_0^2)}{[(G_0 + G_1)^2 + w^2C_1^2]^2} = \frac{2R_t^4C_1^3(2G_0G_1 + G_0^2)}{(\frac{1}{w} + wR_t^2C_1^2)^2}$$

(2.5)

where $R_t = 1/(G_0 + G_1)$ and $w$ is the angular frequency applied to the signal. The extreme point of this function occurs when the frequency is equal to the value of $w_0 = 1/R_tC_1$. We can perform the same derivative calculation on our measured data to find $w_0$ as shown in figure 2.6.

Figure 2.3: CELIV measurements of A. mobility vs. molecular weight and B. Langevin recombination reduction factor vs. molecular weight for P3HT devices with an inverted geometry. Shapes indicated different suppliers, error bars indicate experimental spread across several devices.
In thin devices or devices with strong depletion regions, $G_0$ is much larger than $G_1$, which means that $R_t \approx R_0$. Most OPV devices follow these criteria and can thus be considered fully depleted. From these conditions, we expect Shockley-Read-Hall recombination, which has previously been observed in P3HT:PCBM\cite{81}. Since $G_0 \gg G_1$ in most cases, the time constant will be equal to $R_0C_1$ in the equivalent
Figure 2.6: Derivative of the admittance spectroscopy measurement, multiplied by the frequency. $w_0$ values are found at the minimums of the curves. Colors are indexed to scan at various temperatures.

circuit. This can be considered the Shockley-Reed-Hall lifetime, $\tau_p$, where $\tau_p = R_0 C_1$ and $1/\tau_p$ can be given by equation 2.6.

$$\frac{1}{\tau_p} = v_{th} \sigma n_i \exp\left(\frac{E_t - E_i}{kT}\right)$$  \hspace{1cm} (2.6)$$

where $v_{th}$ is the average thermal velocity, $\sigma$ is the capture cross section, $n_i$ is the intrinsic carrier concentration, $E_t$ is the trap energy level, and $E_i$ is the intrinsic Fermi level. Thus the value of the frequency $w_0$, found at the extreme point of $wdC/dw$, is the same as $1/\tau_p$. We can use equation 2.7 to calculate the activation energy, $E_A$, of charge transport in a material, where the activation energy is the difference between the intrinsic Fermi level and the trap energy level.

$$w_0 = v_{th} \sigma n_i \exp\left(\frac{-E_A}{kT}\right)$$  \hspace{1cm} (2.7)$$
Using this technique, the activation energies of charge transport were measured for molecular weight 20 kDa and 55 kDa P3HT (See figure 2.7). The largely paraffinic low molecular weight sample ($M_W \approx 20$ kDa) had a charge transport activation energy of 50.5 meV, whereas the semicrystalline higher molecular weight material ($M_W \approx 55$ kDa) had a charge transport activation energy of 71.6 meV. This increase in activation energy with increased molecular weight indicates deeper electronic defect states in the material. This is likely caused by trap formation due to increased energy level barriers between the ordered and disordered domains in the latter material.

Figure 2.7: A plot of the natural log of $w_0$ vs $1/T$. Activation energy, $E_A$, can be found from the slope. The red line is from a standard geometry device made with neat P3HT of molecular weight 20 kDa, the blue line is from standard geometry device made with neat P3HT of molecular weight 55 kDa.

2.3 Conclusions

One hypothesis for the reduced recombination in P3HT of higher molecular weight is the effect of the solid-state microstructure on charge separation. Charge generation in neat polymers predominantly occurs at the grain boundaries between
ordered and disordered regions, and the low mobility of electrons means they are essentially held stationary at the point of generation\cite{67}. In low molecular weight polymers, the paraffinic one-phase structure does not create any significant barrier to recombination between the holes and electrons. However at higher molecular weights ($M_W > \sim 40$ kDa), when the material develops a two-phase structure composed of defined amorphous and crystalline domains, an energy difference is developed between the two domains and holes are preferentially pulled in to the crystalline regions. This creates a physical separation between the mobile holes and the two main sources of recombination, the stationary electrons at the grain boundaries and dark carriers which occur in high densities in the disorder areas of the material. By increasing the molecular weight of the material, and thus the degree of semicrystallinity, the presence of this separation is heightened. This allows the holes to reside in well-defined crystalline regions and travel between them along the backbones of polymer tie chains. Such a spatial separation would decrease the encounter frequency between electrons and holes and cause sub-Langevin recombination.

This picture is in agreement with those advanced in previous studies on the molecular weight dependence of mobility in P3HT, with the optimal mobility occurring at a mid-range molecular weight, where the chain length is sufficiently long to allow tie chain backbone transport between crystalline domains, but not so long as to create an excess of entanglement-based traps\cite{82, 70}. It also indicates that sub-Langevin recombination is present in neat P3HT and is likely due to the semicrystalline microstructure present at mid and high molecular weights. This shows that polymer semi crystallinity may be a promising avenue of design for future low recombination high performing materials.

Our work confirms that molecular weight has a significant effect on both the mobility and the recombination behavior in semiconducting polymers and molecular weight optimization needs to be considered when optimizing a material system.
for use in OPVs. It also suggests that the semicrystalline microstructure of the neat polymer may explain the sub-Langevin recombination in a bulk heterojunction comprising this material.

2.4 Experimental

Devices of molecular weight 13 kDa, 20 kDa, 25 kDa, 47 kDa, 55 kDa, 60 kDa, and 331 kDa (Molecular weight 55 kDa is from Plextronics inc., weights 25 kDa and 60 kDa are from Reike Materials chemicals, weights 13 kDa, 20 kDa, 47 kDa, and 331 kDa, were provided by the Stingelin group at the Imperial College of London. The polydispersity index (PDI) for all samples was ≤ 2.) were fabricated for photo-CELIV and impedance measurements as follows: Glass substrates coated with patterned Indium Tin Oxide (ITO) were sonicated in acetone and isopropyl alcohol for 10 minutes each. They were then treated with a Jelight UV-ozone cleaner for 1 hour. PEDOT:PSS (Clevios 4083) was spin-coated on top of the ITO via two depositions at 2000 rpm for 45 seconds each and then annealed at 110 °C for 10 minutes yielding a total thickness of 60 nm. Solutions of pristine P3HT were prepared for each molecular weight at 20 mg/ml of chlorobenzene and stirred overnight at 60 °C. The solutions were deposited on top of the PEDOT by spin-casting at 600 rpm for 60 s. Finally, a 100 nm thick layer of aluminum was evaporated on top of the sample at 1 × 10⁻⁷ Torr via an Angstrom Engineering EvoVac deposition system, using a shadow mask to yield devices with an area of 0.101cm². The completed devices were annealed for 10 minutes at 130 °C in a nitrogen environment. Photo CELIV measurements were carried out using a Continuum Surelite Nd:YAG laser, delivering 4-6 ns wide pulses with a wavelength of 532 nm at a frequency of 10 Hz. An Agilent 33220A Function Generator, triggered by the laser, produced a sawtooth pulse ramp of -2 V over 30 µs. The baseline voltage was offset by 0.3 V in order to neutralize the built-in field inside the device prior to the sweep. The resulting
current response was read by a Tektronix DPO7254 Digital Phosphor Oscilloscope. Measurements were averaged over 500 sweep iterations and analyzed in IgorPro. Devices were packed in nitrogen for the measurement.
Chapter 3

Effect of Side Chain Structure in Benzodithiophene-Thienothiophene Low Bandgap Polymers

3.1 Introduction

As the efficiencies of organic photovoltaic (OPV) devices continue to improve, much of the progress is being achieved through the creation of new photoactive polymers. The most successful of these new materials have been conjugated co-polymers with alternating electron rich and electron poor blocks. The selection of the polymer backbone units has been the primary focus of new polymer development and has allowed for increased photoabsorption, charge transport, and efficiency, with the side chains mainly used to provide solubility to these ridged $\pi$-conjugated polymers. However, recent studies have shown the important role side chains play in determining the polymer self-assembly and film morphology. Modifying the conjugated
side groups can have a significant effect on the electronic properties of the polymer films [83, 84, 85]

Predominant among new high performance OPV materials are polymers made with a Benzodithiophene (BDT) unit coupled with an electron deficient unit. The polymer created from BDT and Thienothiphene (TT) with branched 2-ethyhexyl side chains, forms a particularly high performing polymer named PTB7[86]. When a thiophene ring is substituted into the side chain, the resulting polymer called PBDTTT-EFT, or PTB7-Thiophene (see figure 3.1), is even higher performing. In this chapter we will investigate how this substitution effects the microstructure of the polymer, the polymer’s hole mobility, and how this change relates to the increased performance.

Figure 3.1: The chemical structure of A. PTB7 and B. PBDTTT-EFT. The polymers have identical molecular structure except for the addition of a thiophene ring on side chain of the PBDTTT-EFT devices.
3.2 Results

3.2.1 Neat Polymer

To probe the origin of increased performance in PBDTTT-EFT, we performed a series of mobility measurements on films comprised of neat PTB7 and PBDTTT-EFT. These measurements are performed with the photo- Charge Extraction with Linearly Increasing Voltage (p-CELIV). P-CELIV is an in situ full device mobility and recombination measurement technique in which charges are generated in the device with a laser pulse then extracted via a linear voltage ramp. This voltage sweep extracts the charge carriers in the device and by measuring the amplitude and peak time of the extracted current, the bulk mobility of the material can be calculated [53, 56]. Neat polymers were used for the active layer in order to ensure that the measured value corresponded to the hole mobility, as p-CELIV measures only the fastest charge carrier in a device. From this, we obtained an average mobility of $1.2 \times 10^{-5}$ cm$^2$/Vs for PTB7 and $7.0 \times 10^{-5}$ cm$^2$/Vs for PBDTTT-EFT.

In order to compare the crystal structures of the polymers, samples of both materials were prepared as neat polymers and were deposited on top of ZNO for Grazing-incidence wide-angle X-ray Scattering (GIWAXS) [87]. In both polymers, the X-ray measurements show strong aromatic ($\pi$-$\pi$) stacking. In neat PTB7 the $\pi$-$\pi$ stacking is somewhat isotropic favoring the $q_z$ orientation. This indicates a slightly face-on orientate, but with substantial spread. The PBDTTT-EFT on the other hand has a significantly higher degree of order and is very strongly concentrated in the $q_z$ orientation, indicating a strong face-on orientation (see figure 3.2).

$$d_{\pi-\pi} = \frac{2\pi}{q_z} \quad (3.1)$$

In neat PTB7 the $\pi$-$\pi$ stacking peak is at a value of $\sim 1.5$ Å$^{-1}$. This gives a spacing of around 0.42 nm using equation 3.1, where $d$ is the stacking distance.
and q is the GIWAXS reciprocal space peak. In neat PBDTTT-EFT GIWAXS measurements show a $\pi-\pi$ stacking peak of $\sim 1.65 \text{Å}^{-1}$ giving a spacing of 0.38 nm.

Figure 3.2: Grazing Incidence Wide Angle Scattering (GIWAXS) images of diffraction peaks in reciprocal space for A. neat PTB7, and B. neat PBDTTT-EFT on ZnO Substrates. Both materials show predominately face on orientation, with the PBDTTT-EFT image indicating increased crystallinity and decreased $\pi-\pi$ stacking distance relative to PTB7. (Measurements performed by the Chabinyc group at UCSB.)

3.2.2 Bulk Heterojunction Blends

To confirm that neat polymer mobility difference also occurs in bulk heterojunction (BHJ) devices, Metal Insulator Semiconductor-CELIV (MIS-CELIV) measurements were performed. The MIS-CELIV technique is a variation on CELIV in which a layer of insulating material (in our case SiO) is inserted into the device in between the semiconducting active layer and the metallic contact. A voltage bias is applied to the device and charges are built up in the semiconductor on the boundary with the insulator. This charge build-up replaces free charges generated via the laser pulse of P-CELIV. A CELIV sweep can then be performed moving those
built up charges across the device and extracting them. This experiment allows for the selective extraction of either holes or electrons, allowing their mobilities to be measured independently instead of predominately measuring the speed of the faster carrier as in P-CELIV [59, 88]. From our MIS-CELIV measurements we found a hole mobility in PTB7 of $1.46 \times 10^{-6}$ cm$^2$/Vs and a mobility of $8.11 \times 10^{-6}$ cm$^2$/Vs in PBDTTT-EFT, each approximately one order of magnitude smaller than in the neat films, but with the same relative improvement evident in PBDTTT-EFT.

The insulating layer required for MIS-CELIV, however, has some drawbacks in that it prevents the device from being fully functional and diminishes the built-in field. In order to test the mobility difference in a fully functional device, the relatively new technique of Resistance Photovoltage (RPV) was used. In RPV the device is hit with a reduced intensity laser pulse. This pulse generates charges within the device which are separated by the built in field, and create a capacitance voltage as they move towards their respective contacts. By increasing the internal circuit resistance, and thus the RC time constant, the removal of charges is slowed, and the buildup of voltage from charges collecting on the contacts can be measured directly [89]. This allows for accurate measurements of the transit time of both charge carriers simultaneously [90], which can be used to calculate the carrier mobilities in a fully functional device layout. Our RPV measurements found a hole mobility of $5.2 \times 10^{-5}$ cm$^2$/Vs and $9.7 \times 10^{-5}$ cm$^2$/Vs for PTB7 and PBDTTT-EFT respectively.

In each of these measurements the PBDTTT-EFT shows a two to three-fold hole mobility increase over PTB7 (see table 3.1). Electron mobility in the polymer blends was also measured for both materials as part of the RPV experiment. It showed a value of $2.3 \times 10^{-4}$ cm$^2$/Vs for the PBDTTT-EFT blend and $2.5 \times 10^{-4}$ cm$^2$/Vs for the PTB7 blend. The similarity of the measured electron mobilities indicates that the PCBM electron transport pathways are essentially unchanged.
Table 3.1: Hole mobility measurements for PTB7 and PBDTTT-EFT using three different device-like mobility measurements

between the two blends. The mobility measurements performed here are all bulk measurements made in device-like orientation and interfaces. As such, they are more closely indicative of charge behavior in functional photovoltaic devices than other methods of measuring carrier mobilities.

GIWAXS measurements were also performed on the polymers in BHJ with PCBM70 (see figure 3.3). For both polymers, these BHJ blends displayed significantly more disordered spacing compared with the neat films. The spreads ranged from a $q_z$ of roughly 1.3 to 1.8 ($d_{\pi-\pi}$ of 0.35 nm to 0.48 nm). Along with the disordered spreading, the peak $q_z$ values appear to decrease to 1.4 for PTB7 and 1.5 for PBDTTT-EFT. This corresponds to an increase in average spacing distance to 0.45 nm for PTB7 and to 0.42 nm for PBDTTT-EFT.

3.3 Discussion

The charge carrier mobility in polymers is highly dependent on the microstructure and crystal packing of the material[70, 91, 71]. In organic materials the primary pathways for charge transport are along the polymer backbone and between chains through overlapping of the $\pi$ orbitals[29, 69, 67]. Over short distances, single chain backbone transport can dominate the mobility, but over the longer distances necessary in a bulk device, inter-chain hopping mobility becomes increasingly important. The identical polymer backbones of these two materials will not result in significant intra-chain transport differences, but by decreasing the $\pi-\pi$ stacking distance from
Figure 3.3: Grazing Incidence Wide Angle Scattering (GIWAXS) images of diffraction peaks in reciprocal space for A. PTB7:PC70BM blend, and B. PBDTTT-EFT:PC70BM blend on ZnO Substrates. Disorder and $\pi-\pi$ stacking distance are increased in both blends relative to the neat materials, however PBDTTT-EFT maintains smaller average stacking distance than PTB7. (Measurements performed by the Chabinyc group at UCSB.)

PTB7 to PBDTTT-EFT, the barrier to $\pi-\pi$ transfer is reduced, thereby increasing the inter-chain mobility, improving overall transport and device performance.

The change in molecular structure does create a small increase in the absorption shoulder of PCE10 compared to PTB7 (see Figure 3.4). However, this absorption increase has a relatively minor effect on device performance and is insufficient to account for the entirety of the efficiency increase. To verify this, device performance simulations were performed using simple parameter based calculations. These showed that the changes in the band gap and absorption profile between PTB7 and PBDTTT-EFT only account for a maximum efficiency increase of approximately 0.11 percentage points (a 1.5% improvement). This is far short of the measured 1.15 percentage point increase (a 12% improvement). Further simulated device performance calculations using a simple 0-dimensional kinetic model show that that
under device like condition, doubling the mobility while holding other parameters constant could cause an efficiency improvement of several percentage points, more than enough to account for the remainder of the measured efficiency increase.

In these calculations, the mobility lifetime product ($\mu\tau$) is used as the figure of merit. Mobility is predominantly dependent on the polymer spacing, but the carrier lifetime is more dependent on the bulk heterojunction blending, which largely controls the recombination rate in the device. However, in these two materials the BHJ morphology appears similar and CELIV recombination measurements\textsuperscript{57, 75} show that both materials exhibit Langevin recombination. Therefore, the carrier lifetime can be estimated as constant, and the mobility must be the dominant factor in the increased efficiency.

### 3.4 Conclusions

GIWAXS measurements show that PTB7 has a $\pi$–$\pi$ stacking distance 3-4 nm larger than that of PBDTTT-EFT. This decreased intermolecular spacing increases $\pi$–$\pi$ hole transfer and contributes to a measured three-fold increase in hole mobility.
from PTB7 to PBDTTT-EFT. This difference in mobility between the two materials is likely responsible for a large part of the increased performance of PBDTTT-EFT devices relative to devices made with PTB7.

In general, this highlights the importance of improved mobility of polymer photovoltaic devices and shows that intermolecular spacing should be considered an important part of the design criteria for new polymers, with closer π–π spacing being a potential pathway to improved hole mobility, as long as the BHJ morphology is preserved.

### 3.5 Experimental

Solutions of PTB7 and PBDTTT-EFT were prepared as follows: Blended polymer fullerene solutions were prepared with one part polymer to two parts fullerene in a solution of orthodichlorobenzene (ODCB) at a concentration of 36 mg per ml. The solutions were left stirring overnight at 70° C. Two hours before deposition, 1,8-Diiodooctane (DIO) was added in an amount equal to 2.5% of the ODCB volume. The active layers were then spun cast at 850 rpm for 20 seconds, yielding a thickness of ∼130 nm. For the neat films, the polymers were dissolved in chlorobenzene at a ratio of 20 mg per ml. DIO was added to the solution at 3% per volume. The films were spin deposited at 1000 rpm for 30 seconds, yielding a thickness of ∼110 nm.

Devices were made with ITO and zinc oxide (prepared from a diethylzinc solution) as the bottom contact, and vacuum deposited molybdenum oxide (MoOx) and silver as the top contact. For MIS-CELIV measurements a 50 nm thick layer of Silicon Monoxide, SiO, was vacuum deposited on top of the active layer to serve as the insulator. No top contact was deposited on the samples for GIWAXS, but they were otherwise prepared in the same manner.
Photo-CELIV measurements were ramped 2 volts over 20 µs with a 4 µs delay. MIS-CELIV measurements were ramped 2 volts over 20 µs with a 5 V offset. RPV measurements were taken over a resistance sweep from 10 Ω – 1 MΩ.
Chapter 4

Morphological Effects of Solubility Group and Tail Length on Novel Fullerenes

4.1 Introduction

Although recent improvements in organic photovoltaic active layer materials have significantly increased device efficiencies, the vast majority of these changes have been made to the polymer electron donor. Many of these devices still rely on (6,6)-phenyl-C61-butyric acid methyl ester, (PCBM). However, there are several other C60 buckeyball based electron acceptors which have the potential for higher Voc than PCBM and thus could potentially be used to create more efficient solar cells. One such fullerene, synthesized by the Hummelen group from the Stratingh Institute for Chemistry and Technology in the Netherlands, is 9,9-dialkyl-9H-fluoren-2-yl-C61-butyric-acid methyl ester, or FCBM [92]. FCBM is similar in structure to PCBM but has a fluorene group replacing the benzene ring on the tail and two carbon tails of varying length attached to the fluorene (see figure 4.1). The molecules
created of FCBMs with 6 carbon, 8 carbon and 10 carbon tail lengths are referred to as F6CBM, F8CBM, and F10CBM respectively.

Figure 4.1: Molecular structure diagrams of F6CBM, F8CBM, F10CBM, and PCBM

The LUMO level of these FCBMs is quite similar to that of PCBM, and therefore, they should be expected to yield about the same Voc in a device. However, instead these FCBMs yield a Voc more than 30 mV greater than PCBM when in a blend with P3HT (see Table 4.1) and can show an even greater increase with other donor polymers (up to 120 mV).

Table 4.1: Device performance characteristics of PCBM and FCBMs in a bulk heterojunction with P3HT, demonstrating the FCBMs increased Voc.

<table>
<thead>
<tr>
<th>Material</th>
<th>Voc (mV)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT:F6CBM</td>
<td>606 +/- 2</td>
<td>5.7 +/- 0.4</td>
<td>55.7 +/- 2.6</td>
<td>2.0 +/- 0.1</td>
</tr>
<tr>
<td>P3HT:F8CBM</td>
<td>620 +/- 1</td>
<td>6.0 +/- 0.2</td>
<td>53.0 +/- 0.4</td>
<td>2.0 +/- 0.1</td>
</tr>
<tr>
<td>P3HT:F10CBM</td>
<td>604 +/- 3</td>
<td>7.2 +/- 0.1</td>
<td>42.9 +/- 0.7</td>
<td>1.8 +/- 0.1</td>
</tr>
<tr>
<td>P3HT:PCBM</td>
<td>574 +/- 7</td>
<td>7.4 +/- 0.2</td>
<td>63.2 +/- 1.1</td>
<td>2.8 +/- 0.1</td>
</tr>
</tbody>
</table>

The origin of this increased Voc in FCBMs relative to PCBM is not entirely clear. However, UV-Vis measurements of these blends show a significant enhancement in the low energy peak (see figure 4.2) which could indicate a change in the charge transfer energy ($E_{CT}$) which would significantly affect the Voc.
natively, the increased alkyl chain length of the FCBMs could potentially diminish the ground state interaction by forcing a spatial separation between the polymer and fullerene. This would reduce the overlap of the wavefunction between the lowest unoccupied molecular orbital (LUMO) of the acceptor and the highest occupied molecular orbital (HOMO) of the donor. This increase in steric hindrance could reduce the recombination current, $J_0$, thereby increasing the Voc in accordance with the detailed balance relationship\cite{94, 95} (equation 4.1), where $k$ is the Boltzmann constant, $T$ is the temperature, and $q$ is the charge of an electron.

$$V_{oc} = \frac{kT}{q} \ln \left( \frac{J_{sc}}{J_0} + 1 \right) \quad (4.1)$$

![Graph](image)

Figure 4.2: UV-Vis measurements of PCBM, F6CBM, F8CBM, and F10CBM in blends with P3HT showing slightly more ordering and an enhanced charge transfer peak in the FCBMs.
4.2 Results

4.2.1 AFM Study

To further explore the potential spatial separation and other behaviors of FCBM relative to PCBM, we performed measurements using the atomic force microscope (AFM). The AFM is a powerful tool to probe the properties of materials on the nanometer scale. The instrument consists of a very small tip on a cantilever which is moved over a sample’s surface. A laser is reflected off the back of the tip and on to a photodiode which records the deflection of the cantilever due to atomic force interactions between the sample material and the tip. One particularly illuminating AFM method is conductive AFM (c-AFM). In c-AFM, a voltage is applied between the tip and the sample. The current produced through the material due to this applied voltage is measured as the tip moves across the sample. This allows for the conductive properties of the material to be measured and mapped on scales as small as half a micrometer.

In order to probe how the various tail lengths of FCBMs effected the morphology, we created and measured samples of the fullerenes blended with the well-studied polymer poly(2-methoxy-5-(30,70-dimethyloctyloxy)-1,4-phenylene vinylene) (MDMO-PPV). MDMO-PPV was selected as a donor polymer due to its stability in air and ease of AFM imaging. AFM scans were then made over several 5 micron by 5 micron locations for each of the samples and the current characteristics probed under a 3 volt bias.

There was a direct correlation of the roughness of the current map to the length of the carbon tail on the FCBM:MDMO-PPV bulk heterojunctions. The smoothest sample was F6CBM:MDMO with an average RMS value of 1.6 pA. The F8CBM blend was the next smoothest with an average RMS value of 3.48 pA, followed by
F10CBM at 4.37 pA. PCBM:MDMO-PPV fell between F8CBM and F10CBM with a RMS value of 4.05 pA. (See table 4.2)

There was no discernible correlation between average current flow and tail length. F8CBM had the highest average current flow with 44.25 pA, followed by F10CBM with 40.75 pA. PCBM had and average value of 37.25 pA and F6CBM had a value of 32.5 pA. The scans did reveal what appeared to be domain like features of high current spots (see figure 4.3). The size of these high current spots also appear to show a dependence on the length of the FCBM carbon tail. F10CBM had the smallest spots with an average area of 3300 pixels. F8CBM’s average size was 5649 pixels with PCBM falling between them at 3509 pixels. The initial analysis of F6CBM spots however showed a smaller pixel size on average than F8CBM, although not as small as PCBM. This is believed to be an error in our data analysis, as it is clearly evident with a visual inspection that the size of the F6CBM spots is larger than the other samples. We believe that this is due to the smoothness of the F6CBM:MDMO-PPV samples having a higher contrast which caused the particle analysis program to pick up several smaller areas of variation which brought the average size down.

<table>
<thead>
<tr>
<th>AFM data</th>
<th>F6CBM</th>
<th>F8CBM</th>
<th>F10CBM</th>
<th>PCBM</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMS (nm)</td>
<td>1.6</td>
<td>3.48</td>
<td>4.37</td>
<td>4.05</td>
</tr>
<tr>
<td>Average Current (pA)</td>
<td>32.5</td>
<td>44.25</td>
<td>40.75</td>
<td>37.25</td>
</tr>
<tr>
<td>Current Spot Size (pixels)</td>
<td>4912*</td>
<td>5649</td>
<td>3300</td>
<td>3509</td>
</tr>
</tbody>
</table>

Table 4.2: AFM measurements of PCBM and FCBMs in a bulk heterojunction with P3HT, showing film roughness (nm), average current (pA), and average current spot size (pixels) for each blend.

It should be noted these current features are on the order of a hundred nanometers. This is greater in scale than would be expected for individual domains of the two materials. The currents spots are therefore likely an average over several domains which are interconnected to form charge carrier conductance pathways.
Figure 4.3: 5 µm by 5 µm AFM scans of A. F6CBM:MDMO-PPV, B. F8CBM:MDMO-PPV, C. F10CBM:MDMO-PPV, D. PCBM:MDMO-PPV. Height scans are shown on the left in dark brown and current scans are shown on the right in red.
through the BHJ. Additionally, the height variations of the samples are on a significantly larger scale than the current irregularity and are thus discredited as the source of the current distribution.

### 4.2.2 TEM Study

While the AFM measurements were able to probe the larger scale microstructure effects of the FCBM fullerenes, the resolution of the equipment as well as its restriction to only surface scans limits the information that can be obtained about the nanostructure in a bulk heterojunction. To better probe this nanostructure, transmission electron microscopy (TEM) was used.

Transmission electron microscopy is an imaging technique which uses electrons instead of photons to probe a sample. In TEM, a beam of electrons are transmitted through a sample, interacting with it before being focused onto an imaging screen. This allows for resolution down to less than a nanometer\[96\], which is significantly beyond what is capable with a light microscope, and allows the entirety of the films volume to be probed.

TEM requires an ultra-thin (\(\sim 80 \text{ nm}\)) sample without a substrate or contacts. To prepare this sample we first deposited a layer of highly diluted liquinox soap on a cleaned glass substrate and allowed the coating to dry. We then deposited a P3HT fullerene BHJ blend on top of this layer. This technique causes the BHJ active layer to lift off when the sample is placed in a water bath, allowing it to be easily transferred to a TEM screen.

These samples were sent to Aram Amassian at the King Abdullah University of Science and Technology (KAUST). He performed TEM measurements and generated a 2D projection image for each sample, as well as an energy filtered sulfur map highlighting the location of the sulfur containing P3HT molecules (see figure 4.4).
Figure 4.4: TEM images of A. F6CBM:P3HT, B. F8CBM:P3HT, C. F10CBM:P3HT, and D. PCBM:P3HT. On the left are unfiltered scans with a 30 \( \mu \text{m} \) objective aperture, on the right are scans energy filtered to map sulfur content, showing P3HT domains in white. The Scale bars are 200 nm long.
The scan of the F6CBM blend shows some minor phase separation between polymer and donor, but only shows minimal P3HT fibrillar crystals\textsuperscript{[97]} in the unfiltered image. The F8CBM and F10CBM blends show no clear phase separation, however the unfiltered images do show more clear P3HT fibrillas. In the PCBM:P3HT scans a clear phase separation is evident. Additionally, the unfiltered scan shows significantly more crystalline P3HT fibers than the in the FCBM blends. None of the scans showed the presence of fullerene nanocrystals\textsuperscript{[98]} but this may be due to their small size, as the samples had not undergone the annealing process which encourages crystal growth. All samples also appear to show bright aggregates that we believe are contaminates. The contaminates are potentially from the marker used to label the samples, or from liquonox residue that was not completely dissolved in the lift-off bath.

4.3 Conclusions

Overall, an increased tail length of the FCBM BHJ blends caused the samples to have greater surface roughness. Additionally, it resulted in greater roughness in the current flow, and smaller average spot areas of high current, however, it did not appear to have a direct correlation with overall conductivity of the samples. In all cases the PCBM:MDMO-PPV control fell between the F8CBM:MDMO-PPV samples and the F10CBM:MDMO-PPV samples.

Perhaps the more interesting result of the AFM study was the general inhomogeneity of the current samples themselves. We expected the samples to have much greater uniformity in current distribution with the entirety of each sample ideally at the high current level. Variation of current implies variation of conductivity across the cell and therefore variation in charge transportation. This heterogeneity is large enough to cause inefficiencies in these solar cells, potentially decreasing macroscopic
device performance. Removing these irregularities in current flow could help improve the performance of organic photovoltaic devices.

In contrast with the AFM scans where PCBM appeared to mix similarly to F8CBM and F10CBM, the TEM scans indicate that there is better phase separation and P3HT crystallization in the samples with PCBM compared to the samples with FCBMs. This may be due to the change in polymer causing different packing and morphologies, or it could be indicative of the difference between the bulk and surface morphologies.

The changes in polymer-fullerene intermixing shown in the TEM scans supports the idea that changes in polymer-fullerene spacing in FCBM blends could be increasing the steric hindrance and thereby increase the Voc. However, the complexity of the images taken from TEM makes it difficult to obtain quantifiable data. This is further complicated by the complexities of bulk heterojunction microstructure. The change of the function group and tail lengths does appear to affect the polymer-fullerene packing to some extent, but also modifies the solubility of the fullerenes and thus influences the bulk morphology. Distilling these two effects to determine the nature of the relationships between molecular structure and bulk microstructure is difficult and requires further study.

4.4 Experimental

To prepare our samples for AFM measurement, PCBM, F6CBM, F8CBM, and F10CBM were mixed in a 4:1 ratio by weight with MDMO-PPV. We then dissolved the samples in a chlorobenzene at a ratio of 1 ml of chlorobenzene for 12 mg of active layer material. We let these solutions stir for several days at 600 rpm and at 60 degrees Celsius. For the conductive substrates we used 1” by 1” unpatterned Indium Tin Oxide (ITO) slides. ITO is crystalline and has a large domain size, in order to negate the effect of these domains on the polymer layout, we coated the ITO
with a layer of normal conductivity PEDOT-PSS (NC-PEDOT). The NC-PEDOT was thinned with isopropyl alcohol (IPA) at 10% by volume and brought to room temperature. It was then spin-coated on to a cleaned ITO substrate at 2000 rpm for 60 s. After spin coating, the PEDOT coated ITO was annealed at 200 degrees Celsius for 10 minutes. Once the substrates were prepared and the active layers fully mixed, the mixture was spun onto the substrate at 1000 rpm for 60 seconds, producing an active layer approximately 200 nm thick. The samples were then stored in a nitrogen environment until they were ready to be measured.

AFM measurements were made on an Asylum Research MFP-3D AFM. The image analysis was done on IGOR Pro software from Wavemetrics. To determine the average current spot size, a particle analysis was performed by first flattening the image to an average value, smoothing it to remove irregularities, then maximizing the contrast and exporting it to the included particle analysis package using the midpoint value as a cutoff.

P3HT:Fullerene blends for UV-Vis and TEM measurements were prepared with a 1:1 weight ratio and dissolved in ODCB. For the UV-Vis, Films were deposited by spin coating and slow drying on quartz substrates. For the TEM study, the substrates were prepared by first mixing 1 part liquinox with 40 parts DI-H20. Once fully mixed, the solution was spun at 5000 rpm for 60 seconds on a cleaned glass substrate. The substrates were then allowed to dry before depositing sample on top. The active layer was spun on top at 600 rpm for a film thickness of 80 nm. This allowed the freestanding active layer to be lifted off as follows: First place the sample in Di-water and wait 10 minutes. Next carefully lift the substrate out of water and then dip back in. The surface tension of water should lift off and float the active layer.
Chapter 5

Resistance Photovoltage Measurements of Mobility in Hybrid Organometallic Perovskites

5.1 Introduction

Organometallic halide perovskites have recently come in to prominence as a highly promising thin film solution processed photovoltaic material. This interest has been driven by the rapid power conversion efficiency growth of these materials, particularly methylammonium lead triiodide (CH$_3$NH$_3$PbI$_3$), which has improved from 3.8% efficiency in 2009 to over 20% by 2015[18, 28]. These perovskite materials blend the solution processability and structure of organic photovoltaics with the polycrystallinity of more traditional solar cells. As such they have the potential to combine ease of manufacture and high performance to revolutionize the solar industry.
Despite their rapid performance growth, the mechanisms governing the intricacies of charge carrier behavior are still not fully understood. Of particular curiosity is the presence of hysteresis in the current-voltage measurements of perovskite devices, with higher current and voltage recorded when the photocurrent sweep originates from the forward bias direction as opposed to the reverse bias direction. There are several competing theories as to the cause of this hysteresis, such as ionic transport\cite{19} or the presence of surface and grain boundary trap states\cite{46}. Additionally, there is evidence that the recombination rate in perovskites is better than expected, while the carrier mobilities are lower than expected given their respective effective masses\cite{41, 52, 27}.

In order to better probe the origin of these issues and to more easily evaluate new or modified perovskite materials, full device charge transport measurements are important. Charge Extraction via Linearly Increasing Voltage (CELIV) has been previously attempted on perovskite devices\cite{99, 100}, however, the resulting transients are of poor quality. CELIV was developed for measurements on amorphous materials and as such, the mobilities of polycrystalline perovskites are at the upper limit of its experimental capabilities. Additionally, the variable applied voltage required for CELIV measurements may cause hysteresis-like effects in the perovskite materials, which could affect the measurement of charge transport properties. To combat these issues, we propose the use of a modified Resistance Photovoltage (RPV) experiment to measure the full device mobility of perovskites.

\subsection*{5.2 Results}

In RPV measurements, charge carriers are excited with a laser pulse and a high internal resistance is used to slow the charge collection, allowing for measurement of transit times. Unlike CELIV, this technique does not require an applied voltage and as such, should work for the perovskite devices. However, our initial attempts
at perovskite RPV were met with failure. The preliminary transit times measured by PRV turned out to only show the resolution limit of our experimental setup.

To overcome this, we took a two fronted approach: decrease the system response time, and increase the transit time. To decrease the system response time, we first shortened all our coaxial cables. The velocity factor of a coaxial cable is around 66, so a meter of cable delays the signal by approximately 5 ns. Next we ensured that we were using an oscilloscope with a high bandwidth, and that sampling mode and bandwidth were maximized, as the response time is proportional to the inverse of the bandwidth. With these adjustments, we were able to reduce the minimum system response time from 75 ns down to \( \sim 30 \) ns.

To decrease the transit time of the carrier, we increased the sample thickness. This is effective as the transit time is proportional to the square of the film thickness (see equation 5.1), where \( t_{tr} \) is the transit time, \( d \) is the the film thickness, \( \mu \) is the mobility, and \( V \) is the built in voltage.

\[
t_{tr} = \frac{d^2}{\mu V}
\]  

(5.1)

However, care has to be taken to ensure that this active layer increase does not affect the mobility of the film. As a polycrystalline material, charge transport in perovskites is best through individual crystals and is hindered at grain boundaries. With grain sizes ranging from \( \sim 75 \) nm - \( \sim 1 \) \( \mu m \)\[101, 25, 102\] depending on the fabrication technique, the maximum functional thickness will vary. We found that in our devices, the performance began to falter in devices with active layers greater than 800 nm.

Due to the strong optical absorption of perovskites (absorption coefficient of \( 9.9 \times 10^6 \) at the measurement wavelength of 550 nm) roughly 80% of the light is absorbed in the first 150 nm of the film (see figure 5.1). As such, the photo absorption in these thick films can be considered surface generation as opposed to bulk generation. This
means the RPV measurements will be limited to only measuring the mobility of the transiting carrier. In the case of our experiments, the samples use the standard perovskite geometry of Glass/ Transparent Conducting Oxide/ Electron Transport Layer/ Perovskite/ Hole Transport Material/ Metal Contact. In this configuration the measured transiting carriers are holes, however, electron mobilities can also be measured by using a devices with inverted geometry.

![Transmittance at 550nm](image)

Figure 5.1: Percent of 550 nm light absorbed as a function of film thickness for measured perovskite devices.

Using these adjustments we were able to get RPV data for perovskite materials, but not without a few other issues. The hysteresis present in perovskite devices did complicate data collection somewhat. Upon device illumination, the entire extraction curve began to offset, shifting upwards. This shift raises the baseline voltage and takes place over the course of several seconds, but does not appear to affect the shape or response time of the extracted curve. To account for this hysteresis-like shifting, we determined that at the beginning of each measurement the sample should be held in under illumination for one minute before data collection begins.
Additionally, all of the extraction curves were zeroed based on their preexcitation value.

In contrast to OPV devices, RPV measurements on perovskite devices displayed a very large amount of noise. This noise appeared in two forms: a periodic high frequency overlay, and as an apparent RC ringing. Some of this high frequency noise was mitigated by shortening the coaxial cables and improving the grounding on the circuit, but the remainder persisted. This noise may be caused, in part, by the different device layout used in perovskite fabrication compared to that used in OPV; The larger pixels and contact areas of the perovskite devices could be acting as antennae. The ringing noise, however, does not appear in RPV measurements made on organic photovoltaic devices of similar geometry. This indicates that cause of the ringing is inherent to the perovskite material itself. The period for this ringing is approximately 50 ns which is too long to be caused by any optical resonance in the device, but this ringing could potentially be the result of phonon resonance or a piezoelectric response in the perovskite active layer. The occurrence of this ringing suggests the presence of an interesting physical phenomenon and could be an area for future study, but for the time being it merely serves to blur the data, and thus is removed.

To remove this noise for data analysis, the raw data was first fed into a Fourier analysis to find the peak noise frequency. The data was then smoothed with boxcar smoothing, using the peak noise frequency as the smoothing interval. Next a high pass filter was applied and the results subtracted to remove the ringing. This results in a final smoothed curve that can more easily be analyzed (see figure 5.2), and the procedure can be applied uniformly to all the collected data.

To test this experimental measurement, two perovskite devices were prepared by Mengjin Yang in Kai Zhus group at NREL. Both devices had an architecture composed of a fluorine doped tin oxide (FTO) transparent conductor, a compact
Figure 5.2: Example of automated perovskite RPV smoothing. Zeroed raw data in red, smoothed data in black. Each RPV curve is a composite of scans made over several different time scales.

<table>
<thead>
<tr>
<th></th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>Fill Factor (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Device 1</td>
<td>21.1</td>
<td>1.03</td>
<td>69</td>
<td>15.1</td>
</tr>
<tr>
<td>Device 2</td>
<td>19.7</td>
<td>0.99</td>
<td>57</td>
<td>11.2</td>
</tr>
</tbody>
</table>

Table 5.1: Performance of perovskite Devices 1 and 2

titanium oxide baselayer, an electron transport modification layer, the perovskite active layer, a hole transport layer of Spiro-OMeTAD, and a silver top contact. The two active layers were both approximately 625nm thick but underwent different thermal annealing conditions. The first device shows improved device performance (see figure 5.3), increasing Jsc by 1.5 mA/cm², the Voc by 0.04 V, the fill factor by 12 percentage points, and the efficiency 4 percentage points (see table 5.1)

RPV measurements were performed on both devices (see figure 5.4) and the results over all pixels averaged. Device 1 shows an average transit time of 1.7 µs whereas device 2 shows a faster transit time of 0.92 µs. These transit times correspond to a mobility of 2.4 cm²/(Vs) for device 1 and 4.2 cm²/(Vs) for device
Figure 5.3: JV curves of perovskite devices 1 and 2. Scans were made from negative voltage to positive voltage and then from positive back to negative. Both devices exhibit significant hysteresis with the return curve showing improved performance.

2. Although this measurement does not appear to correspond to improved device performance, mobility itself is only part of the equation. For efficient charge carrier extraction from diffusion driven solar cells, the diffusion length must be less than the device thickness, $d$, as shown in equation 5.2 where $\mu$ is the mobility, $\tau$ is the carrier lifetime, $k$ is the Boltzmann constant, $T$ is the temperature, and $q$ is the charge of an electron.

$$\sqrt{\frac{6\mu kT}{q}} > d$$

As such, the figure of merit in determining the effect of charge carrier dynamics on device performance is the $\mu\tau$ product, where $\tau$ is dependent on the carrier recombination rate. An increase in carrier lifetime could result in improved device performance, even with a decrease in mobility.

One explanation for why a lower mobility might still correspond to a high overall performance is the presence of charge masking. Density functional theory calcula-
Figure 5.4: Normalized sample RPV curves of perovskite devices 1 and 2 showing voltage response versus time. Black lines indicate the maximum transit time for each device (average transit times are faster and not marked here). Scans were made over multiple time scales to capture the full extraction curve.

Sections have shown[52] that the freedom of rotation of the CH$_3$NH$_3$ methylammonia (MA) units in the perovskite lattice allows the MA dipole to reorient itself around a charge carrier. This dipole reorientation causes the formation of large polaron quasiparticles which partially mask the charge and support charge carrier separation, reducing the recombination rate. These polarons, however, also increase the carriers effective mass, which will lower the charge carrier mobility. If a perovskite device has enhanced polaron creation, the mobility will be lowered, but the $\mu\tau$ product, and thereby overall device performance, may be increased.

### 5.3 Conclusion

In conclusion, RPV can be a powerful tool for comparing the mobilities of perovskites under full solar cell device conditions. This measurement will only measure the back contact extracting carrier, but inverting the geometry of the device can
allow for measurement of both carriers. These measurements can be a good way to
get information on the charge mobility of these exciting materials inside functional
devices, but should also be paired with a carrier recombination measurement to
obtain a more complete picture of device performance.
Bibliography


[14] Wenchao Huang, Eliot Gann, Lars Thomsen, Cunku Dong, Yi Bing Cheng, and Christopher R. McNeill. Unraveling the morphology of high efficiency


[41] Atsuhiko Miyata, Anatolie Mitioglu, Paulina Plochocka, Oliver Portugall, Jacob Tse-Wei Wang, Samuel D. Stranks, Henry J. Snaith, and Robin J.


[50] Jing Feng. Mechanical properties of hybrid organic-inorganic CH$_3$NH$_3$BX$_3$ (B = Sn, Pb; X = Br, I) perovskites for solar cell absorbers CH$_3$NH$_3$BX$_3$ (B = Sn, Pb; X = Br, I) perovskites for solar cell absorbers. 3(2014), 2014.


[99] Namyoung Ahn, Dae Yong Son, In Hyuk Jang, Seong Min Kang, Mansoo Choi, and Nam Gyu Park. Highly Reproducible Perovskite Solar Cells with Average Efficiency of 18.3% and Best Efficiency of 19.7% Fabricated via Lewis


Appendix A

Measurement Instructions and Tips

A.1 CELIV

An important part of setting up the CELIV is finding the right period and ramp amplitude. This can be tricky and will depend somewhat on the material and active layer thickness. A good starting point is 20 $\mu$s and 2 V. Start with the sample in the dark and make sure the dark curve is a good rectangle. If the front end of the rectangle is rounded off in a curve or the top of the rectangle does not flatten off, then the ramp time is likely too short. If the rectangle starts off good but curls up at the end, then the sample is experiencing a leakage current and the ramp amplitude should be lowered. Sometimes even at lower amplitudes, there will still be some leakage, this is either caused by a weak blocking layer or by the presence of pinhole shorts. Pinhole shorts can sometimes be removed by burning them off. To do this, increase the peak voltage substantially for a few seconds, then disconnect the device. Once reconnected, the shorts will hopefully be gone. We have found that 5 volts is usually sufficient, too much higher than that, there is a risk of permanently
damaging the blocking layer of that pixel. Once a clean dark CELIV rectangle (or a rectangle with a bump if your material has dark carriers) has been obtained, a photo-CELIV measurement can be attempted.

With Photo-CELIV, there should be a brief delay between the light signal and the beginning of your voltage ramp, we usually start with a 5 µs delay. This delay separates the initial laser current pulse from CELIV sweep pulse and allows for the determination of the CEILV pulse dimensions. Once the photo delay is in place, the scaling of the ramp rate can be finished. We have found that for best measurements, you want the CELIV bump peak to be in the first third of the ramp. This should allow time for the charges to be fully swept out of the device, with the tail of the bump returning to the dark $j_0$ value before the end of the sweep. If the ramp is too short and the tail does not make it all the way down, $Q_{ext}$ measurements will be unobtainable. However, if the ramp is too long, it can be difficult to determine the value of $t_{max}$. The ramp rate (and thus the bump extraction time) can be adjusted by changing either the ramp time or the peak voltage. In adjusting these parameters, it is important to be aware of leakage current at high ramp rates, and signal to noise issues at low ramp rates. If unsure, we will sometimes repeat the measurement at various ramp rates.

Once the ramp rate is set, it is time to set the offset. This is especially important in materials with high built in voltages. The goal of the offset is to keep enough carriers from the laser pulse in the device to measure their transit with the CELIV ramp. As such, the ideal offset is usually just a little under the device's Voc. To find this value, we usually do a sweep over a range of offsets. The optimal offset is one where the laser pulse current spike is diminished, but the general shape of the CELIV curve isn't distorted (see figure A.1).

With the ramp rate and the offset set, it is time to take some data! For a good signal to noise ratio, we usually have the system average over 1000 individual CELIV
ramps to get the final scan. While one of these scan is sufficient, we tend to take a couple data sweeps for good measure. We usually take one sweep over a range of offset voltages, and one sweep over different delay times, from 0 delay out to $\sim 20 \mu s$. By measuring the change in $Q_{ext}$ as the delay time increases, information can be found about the carrier recombination rate. Additionally, it is important to save a dark CELIV sweep with the final ramp rate for determination of $j_0$.

A.2 MIS-CELIV

The trickiest part of MIS-CELIV is finding a good insulator layer. For accurate mobility measurements the insulator must be less than half the thickness of the active layer, but also effectively block both holes and electrons under relatively high bias voltages. This is particularly difficult when attempting to measure device-like conditions for active layer materials which optimize at less than 100 nm thick. We tried using magnesium fluoride, MgF$_2$, as in the literature, but were still having leak-
age issues. We tried several polymer insulators like PMMA and PVP, but those did not work well either. We eventually settled on vacuum deposited silicon monoxide SiO, which was able to provide a good degree of insulation at just 50 nm thickness.

In order to get a strong signal, high reverse biases were necessary. Our function generator had a maximum output of 5 V, so a 10X amplifier was installed in the circuit. Once the ramp rate was set in a similar manner to photo-CELIV (see above) measurements were performed gradually sweeping the offset voltage. We recommend starting at 0 offset and stepping down to -8 V offset in increments of 0.5 V. Most devices begin to short-out at $\sim -7$ V offset. If the oscilloscope is monitored and the device is disconnected as soon as it starts to short (curve will begin to flicker), then the damage will be minimal and the device can be rescanned. However, if the device shorts under a high bias too long the pixels can become permanently damaged.

A.3 RPV

The key to RPV measurements is a rapid system response time. This can be obtained with short wires and a fast oscilloscope (bandwidths $> 1$ GHz). The oscilloscope must also have a high internal resistance (1 MΩ) setting. Triggering the oscilloscope in time with the laser pulse can also be difficult. After trying a couple different triggering methods, we ended up using a photossensor which triggered off scattering early in the lasers beam path.

With the internal resistance set to max, a full resistance RPV scan can be made without any external resistors. This scan is often sufficient to determine the mobility of the slower carrier, and sometimes the faster carrier as well. However, scanning over a full range of resistances makes finding the faster carrier transit time easier and allows for the saturation verification of the slower carrier. To obtain this sweep, we used an external variable resistor, hooked up in parallel to the oscilloscope. By adjusting the variable resistance $R_V$ we stepped the total resistance $R_T$ down
logarithmically from 1 MΩ to 10 Ω according to equation A.1.

\[ R_t = \frac{1}{\frac{1}{R_V} + \frac{1}{1MΩ}} \]  \hspace{1cm} (A.1)

Because the RPV measurement requires both high resolution for the initial rise and a fairly long extraction time, it was not possible to recorded the entire curve in a single scan. To get around this, each measurement was made with scans at five different scales; 50 ns, 500 ns, 5 µs, 50 µs, and 500 µs. These different scales were later overlaid and combined into a single logarithmic curve.
Appendix B

Igor Data Acquisitions and Analysis

B.1 Graphical User Interface

In order to facilitate the taking of CELIV measurements, we built a graphic user interface (GUI) for IGOR pro software package Version 6.3. While originally intended for photo-CELIV, the program expanded to enable i-CELIV measurements, MIS-CELIV measurements and RPV measurements (see figure B.1). This program creates a custom CELIV waveform for the function generator and allows the user to easily adjust the ramp time, ramp amplitude, delay time, and offset voltage for CLEIV measurements. The user can adjust the oscilloscopes time window and automatically zoom the scope in to maximize the extraction curve, as well as remotely change the resolution and number of averages. When connected to a cryostat, the program can control the sample temperature and set measurement sweeps at each temperature step, allowing for full temperature dependent measurements to be made without constant user supervision. The program is also set up to do data acquisition sweeps over a range of laser delays and voltage offsets.
Figure B.1: Image of the graphical user interface built for CELIV and RPV
We also built a program to automatically analyze CELIV data (see figure B.2). This program automatically finds the peak extraction time, the current peak, and the base current, and then calculates carrier mobility and relative recombination rate for the device.

Figure B.2: Image of the graphical user interface built for CELIV analysis

B.2 Code Sample

As a sample of code, the function used to reduce the noise for PRV measurements of perovskite devices is presented here. This code uses object oriented programming to take an extraction transient, find the period of high frequency noise by via Fourier transform, smooth the noise over that period, then run a high pass filter to isolate the RC ringing, align and subtract this ringing off, and return a fully smoothed extraction transient (see figure B.3). Contact the author for access to the complete data acquisition program and data analysis code.
Figure B.3: Code sample showing the RPV smoothing procedure.