The Pennsylvania State University
The Graduate School
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EXAMINING CHARGE CARRIER TRAPPING AND RECOMBINATION
IN ORGANIC PHOTOVOLTAICS

A Thesis in
Chemistry
by
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ABSTRACT

The energy consumption of the planet is currently very high and expensive. With developing nations such as India and China increasing their need for energy, it has moved the energy issue to a front line topic. The high cost of energy has started to hit home to many people with the recent increase in the cost of fossil fuels, specifically gasoline. Gas prices have been steadily on the rise for the last decade. Recently the environmental repercussions of the use of fossil fuels have been headlined in the media. From the oil rig disaster in the Gulf of Mexico to the mine collapses across the world the danger of going after these natural resources has become evident. Global warming has also become an issue not only in the scientific community but also in the political. With these factors in mind a search for a renewable source of energy has begun in earnest. Renewable energy sources could help alleviate the world's thirst for energy and reduce the emissions that contribute to global warming.

Solar technology has been lauded as one of the renewable energy sources that has the most promise to contribute to the current energy crisis. Solar energy has the potential to produce all the energy the world needs, however there are many issues to overcome. Inorganic, primarily silicon, solar cells have been in use for decades at this time but are too expensive to effect the global market. A current area of research interest is in the area of organic photovoltaics (OPVs). OPVs show promise to have a lower cost than inorganic solar cells, however they currently suffer from very low efficiencies and
lifetimes. Current OPVs have too low efficiencies in order to be integrated into the energy production methods. Research is being done in order to improve solar technologies in hopes to provide a significant amount of energy for the world.

Two of the issues involved in OPVs are charge carrier mobility and recombination. This study focuses on these two issues using two complementary experiments. First being the Charge Carrier Extraction by Linear Increasing Voltage (CELIV) experiment that allows for the determination of the mobile charge carriers present in the sample. The complementary spectroscopic technique is a visible pump infrared probe transient experiment that allows for the determination of all the charge carriers present with a sample. By examining these two techniques information can be drawn about the charge trapping that takes place with the system. Understanding these issues are the first steps to overcoming them and bring forth OPVs as a viable energy source.
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<table>
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<th>Abbreviation</th>
<th>Full Form</th>
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<tr>
<td>OPV(s)</td>
<td>Organic Photovoltaic(s)</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk Hetero Junction</td>
</tr>
<tr>
<td>Vis-IR</td>
<td>Visible Pump Infrared Probe</td>
</tr>
<tr>
<td>TRIR</td>
<td>Transient Infrared Pump Probe Spectroscopy</td>
</tr>
<tr>
<td>2-D IR</td>
<td>Two-Dimensional Infrared</td>
</tr>
<tr>
<td>CELIV</td>
<td>Charge Carrier Extraction by Linear Increasing Voltage</td>
</tr>
<tr>
<td>PCBM</td>
<td>({6}-1-(3-(methoxycarbonyl)propyl)-{5}-1-phenyl-[6,6]-C61)</td>
</tr>
<tr>
<td>RR-P3HT</td>
<td>Regio-Regular poly(3-hexyl-thiophene-2,5-diy1)</td>
</tr>
<tr>
<td>RRa-P3HT</td>
<td>Regio-Random poly(3-hexyl-thiophene-2,5-diy1)</td>
</tr>
<tr>
<td>CN-MEH-PPV</td>
<td>Poly[2-methoxy-5-(2'-ethylhexloxy)-1,4-(1-cyanovinylene)phenylene]</td>
</tr>
<tr>
<td>MDMO-PPV</td>
<td>Poly[2-methoxy-5-(3',7'-dimethyloctloxy)-1,4-phenylenevinylene]</td>
</tr>
<tr>
<td>RPM</td>
<td>Revolutions per Minute</td>
</tr>
<tr>
<td>FTO</td>
<td>Flourine doped Tin Oxide</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium doped Tin Oxide</td>
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Lastly I would like to dedicate this in memory of Thelma Bell and Michael and Agnes Banyas who passed away before they could see me become who I am today.
Chapter 1

Introduction

1.1 Global Energy Issues

The key issue in alternative energy has become an interest in the scientific, economic, and political worlds. The search for a clean renewable source of energy has played an increasing role in recent political elections.\textsuperscript{1} Today's energy is mainly based on the use of fossil fuel which is not a renewable resource.\textsuperscript{1,2} Fossil fuels have become increasing dangerous to obtain as is evident in the recent events in the Gulf of Mexico. Oil rig and mine disasters have also become increasingly prevalent in today's news. Current estimates show that petroleum and natural gas supplies could run dry within 100 years.\textsuperscript{1,3,4} Since the sources of fossil fuels will run out, a search for an alternative energy has begun in earnest in the scientific community. A variety of renewable energy technologies have already been implemented around the world. These include wind, hydroelectric, and solar technologies. These technologies are the first steps in getting away from our dependency on fossil fuels. However, these renewable technologies are being implemented at a slow rate and thus far are unable to match fossil fuels in their energy output.\textsuperscript{1,5,6}

Another worldwide issue that has become a topic of great interest over recent years is global warming. It is believed that emissions from fossil fuel combustion, mainly carbon dioxide, is having an increasing effect on the planet.\textsuperscript{3,4,7} It has been shown
that there has been a steady rise in the production of carbon dioxide since the start of the industrial revolution beginning in the mid 1800s. If these emissions are allowed to increase at their current rate it is possible that various unforeseen and disastrous consequences could occur. Since fossil fuels are our main source of energy and currently developing countries such as India and China have become larger users of these fuels it can only be expected that the current emission rate will rise in coming years. If something is to be done to counteract the effect on the planet an alternative source of energy is required that will allow for at least the maintaining of the current emission levels or better yet, a reduction in these levels.

Currently solar energy has been lauded as one of the solutions to the energy issues. The solar energy that strikes the planet everyday could be harnessed and used it could potentially provide all the energy that is needed by today's society. Inorganic photovoltaics, most commonly silicon, are too expensive to replace fossil fuels. Therefore a newer technology is being researched, organic photovoltaics (OPVs). OPVs have shown an increase in efficiency over the past several years, as well as a lower cost of materials than their silicon based counterparts. Based upon these two considerations OPV devices show promise in becoming large contributor in the effort to reduce dependency on fossil fuels.

1.2 History of Organic Photovoltaic Materials

Organic photovoltaic materials were first discovered in 1959 when single crystal anthracene was placed between two electrodes and illuminated. However, it was not
until the late 1980s that the field of OPVs became an active area of interest.\textsuperscript{8,10,11} There is a major difference between the inorganic solar cells and the organic solar cells. In inorganic solar cells the charge carriers are generated in the bulk of the material. These charge carriers have a long life time and can freely migrate to the electrodes whereas in organic solar cells the charge carriers are generated in the donor material and consist of a tightly bound pair of an electron and a hole, which is known as an exciton.\textsuperscript{16} This exciton has a large barrier of separation and can only be separated at an interface of the donor and acceptor material. Early experiments were done with a heterojunction cell where the donor and acceptor are layered on top of one another.\textsuperscript{11} These devices produced a low efficiency of approximately 1%. In the early 1990s a bulk heterojunction design was introduced. This design has both the donor and acceptor material combined in solution and deposited on a substrate.\textsuperscript{8,11} This creates a active layer with the donor material surrounding the acceptor material which is confined to small domains. The bulk heterojunction (BHJ) design has allowed for an increase in efficiency to about 5.8%.\textsuperscript{11} This stands as a significant improvement over past designs but further progress is needed to compete with inorganic devices.

1.3 Current Limitations of OPV Materials

There are a number of issues that are known to limit the efficiency of OPV devices, one of which is the charge carrier separation of the exciton.\textsuperscript{15} The bound electron-hole pair has a large potential barrier of separation. This barrier can be overcome at the interface of the donor and acceptor material. The difference in energy
between these two materials allows for the electron and hole to separate and then migrate toward the electrodes.\textsuperscript{12,17} Charge carriers in OPVs can undergo two processes of recombination, they are geminate and bimolecular recombination. Geminate recombination is when an exciton, a bound electron hole pair, relaxes back to its ground state. Bimolecular recombination is when an electron and hole that are not bound to one another combine to relax back to the ground state. The process of recombination gives the charge carriers a lifetime in which they can be extracted from OPV cells. Since the charge carriers in OPVs have a short lifetime this separation has to occur quickly before the charge carriers recombine. This short lifetime means that the exciton has a limited distance it can migrate to each an interface before it relaxes back to its ground state.\textsuperscript{18,19}

Another common issue in OPVs is the charge carrier mobility.\textsuperscript{20} The charge carriers have a limited lifetime and therefore a limited distance that they can travel before recombining. These limitations affect the thickness of the device. However, this thickness can have an inverse effect on the mobility of the charge carriers. A thick active area means that the charge carriers have to migrate further to reach an electrode, the electrodes being on the top and bottom on the cell (Figure 5). Since the diffusion length of charge carriers is limited in OPVs, the likelihood of charge recombination increases as the device thickness increases. This requires the OPV device layer to be very thin in order to maximize charge carrier extraction.

The materials used in the making of OPV devices have a tendency to degrade with time and exposure, primarily among these is exposure to oxygen and light.\textsuperscript{21} Many of the donor materials used are polymers with vinylene bonds that react readily in the presence of oxygen due to oxygen's tendency to form a long lived singlet state. These
materials can also be further degraded by the presence of water. However there are other
issues that can degrade these devices. The electrodes of OPV devices are commonly
vapor deposited metals. These metals can cause the surface of the devices to be damaged
by contact with the metal atoms during deposition.

Lastly, relating to the issue of degradation, is the issue of charge trapping.22 Even
after the exciton has dissociated at the interface of the donor and acceptor the charge
carriers still may be unable to be extracted and are therefore trapped within the materials.
Charge carriers that are trapped cannot be extracted and therefore lead to a decrease in

efficiency. One major trapping site present in OPVs are areas that are damaged by photo-
oxidation. These damaged areas can form low energy states that the charge carriers can
occupy causing them to become trapped. These areas have a large activation energy
barrier that cannot be overcome.

1.4 Charge Carrier Trapping and Recombination

My contribution to the continued study of OPV materials is in the area of charge
trapping and recombination dynamics. Recombination in OPV materials has been
reported in the literature to behave by Langevin recombination. Langevin recombination
is described by a theory developed by P. Langevin that relates the rate of bimolecular
recombination to the underlying dielectric permittivity and carrier mobility of the
material. There are four key assumptions for Langevin recombination, charge density is
uniform throughout, dielectric permittivity is uniform throughout, the charge carrier
mobility is uniform and time independent, charge carriers undergo immediate
recombination. A key prediction of Langevin's theory is that the charge carrier mobility and recombination lifetime should be inversely proportional to each other. A further breakdown of the equations is shown later in chapter 4. However, using a transient Vis-IR experiment it has been shown that the recombination kinetics deviate from the behavior predicted by Langevin's theory. My work suggests that it is the presence of charge traps within the material itself that causes the appearance of Langevin recombination. Some of the experiments that have lead to this conclusion involved the work of Ryan Pensack including ultrafast and 2-D IR experiments.

The main focus of the Asbury group is time-resolved spectroscopy that provides information about all carriers present with a system independent of the mobility of those carriers. In order to gain information on the mobile carriers that are present in the system an electrical method of measurement was implemented. This technique is called Charge Carrier Extraction by Linear Increasing Voltage (CELIV). The CELIV project was started in conjunction with initial help from Larry W. Barbour, a former Asbury group member.
Chapter 2

Experimental Techniques

2.1 Materials

All the materials used in these experiments are commercially available. The majority of the materials were purchased from Sigma-Aldrich and/or American Dye Source. The RR-P3HT that was used in these experiments was obtained from Rieke Metals.

2.2 Charge Carrier Extraction by Linear Increasing Voltage (CELIV)

The CELIV experiment allows for the determination of the mobility and the lifetime of charge carriers simultaneously. However, the technique only measures mobile carriers and so is incapable of determining whether long-lived charge carriers are mobile enough to move to the outer electrodes. Some of the charge carriers can become so deeply trapped in the system that they are not capable of producing photocurrent. The system for this experiment is a small solar cell. The extraction of charge carriers is done using a voltage ramp that is applied at a specific delay after the laser pulse strikes the cell (Figure 1). The ability to measure the population of the mobile charge carrier has wide ranging application in all organic-based electronic devices. The lifetime of the charge carriers can be determined by varying the time delay between when the laser pulse hits the cell and the start of the extraction ramp (Figure 2). As the delay increases between
when the laser pulse hits the system and the start of the voltage ramp the amount of photocurrent will decrease. The reduction in the density of charge carriers can be attributed to either charge recombination or charge trapping. The mobile carrier density kinetics, \( q(t) \), are obtained by integrating the CELIV transients for each time delay, \( t \), according to the equation \( q(t) = \int j(t, \tau) d\tau \), where \( j(t, \tau) \) is the preliminary photocurrent transients. The density of the mobile charge carrier lifetime is well described by a power law with a 300 microsecond recombination lifetime. The power law was chosen to describe the kinetic decay because this function form is derived from bimolecular charge recombination kinetics.

**Figure 1.** Diagram of the CELIV experimental setup
Figure 2. Example of how the CELIV experiment works. The dark trace is when no laser pulse is used to excite the polymer. The light trace is when the laser pulse excited the polymer and the mobile carriers are extracted. \( t_{\text{del}} \) is the time delay between when the laser pulse hits the sample and the start of the voltage ramp. \( j(0) \) and \( \Delta j \) are the current before charge carrier formation and the increase in current due to charge carriers respectively.

2.3 Linear/Transient Vis-IR Spectroscopy (Linear/TR-IR)

To measure all potential charge carriers present in the sample a pump/probe spectroscopic setup is used (Figure 3). The Yag-IR setup consists of a visible laser that excites the polymer without exciting PCBM and an IR beam that probes the carbonyl stretch on the PCBM electron acceptor. A shift in the carbonyl stretch results from an electron transferring to the PCBM molecule from the polymer. The electron transfer results in a reduced absorption of the neutral ground state of the carbonyl on PCBM. This reduced absorption of the neutral ground state of PCBM is referred to as a bleach. This bleach is proportional to the number of all charge carriers in the system. The recombination of the charge carriers can be obtained from observing the area of the bleach as a function of time (Figure 4). The difference in the charge carrier density as a
function of time of both the mobile carriers and all available carriers can be examined using a MCT detector to determine the role of charge trapping within the system.

Figure 3. Experimental setup for the YAG-IR studies. This setup been enclosed in a purgable dry air box to eliminate noise from water lines present in air. The sample has varying setups, it can be simply placed on a mirror or can be enclosed within the cryostat to be held under vacuum for the experiment.

2.4 Sample Preparation

Samples for these experiments were spin cast and airbrushed on the surface of aluminum mirrors or Fluorine-doped tin oxide (FTO) coated glass substrates. The solutions were composed of various polymers of different molecular orders with the electron acceptor PCBM (American Dye Source). Polymers include RR-P3HT (Rieke Metals), CN-MEH-PPV (H.W. Sands), RRa-P3HT (American Dye Source), MDMO-PPV (Sigma Aldrich), the structure for these materials can be found in Figure 4. The ratio of polymer to PCBM was generally 1:1, however in the case of MDMO-PPV a ratio of
1:4 (polymer to PCBM). The ratios of polymer to acceptor stated previously were used to be consistent with current research being done in the area of OPVs.

Figure 4. Structures of the different polymers used and the electron acceptor PCBM.

Solutions for the BHJ films were prepared by dissolving the solids in chlorobenzene (Sigma Aldrich), all the listed polymers and PCBM are soluble in chlorobenzene. Solutions were made to an approximate 1.0% mass ratio of solute to solvent, meaning that 1:1, polymer to acceptor, solutions would contain 50% polymer and 50% PCBM giving a 1.0% solution overall. Solutions for airbrushing were made to an approximate 2.0% mass ratio. The higher ratio was shown to yield more even coverage of the substrate. Solutions were then deposited on the appropriate substrate and spun cast at approximately 80 rpm until the solvent completely evaporated. Film thickness was on the order of three or more microns. Before experiments were
performed on the samples a linear IR spectrum was measured to characterize the carbonyl stretching mode of PCBM.

Solutions for the bilayer films were prepared using orthogonal solvents. The polymer, RR-P3HT, was purified in a Soxhlet extractor. The solvent used to purify the polymer was dichloromethane. The low molecular weight portions of RR-P3HT are soluble in dichloromethane, while the high molecular weight portion is insoluble. After refluxing for approximately 24 hours the remaining polymer was extracted from the thimble using methanol and weighed. The approximate yield for the extraction was 50%. After the polymer was isolated it was then dissolved in chlorobenzene and deposited on an aluminum mirror. The PCBM was dissolved in dichloromethane and then spin cast on the RR-P3HT layer at 500-800 rpm.

Solutions for the CELIV experiment were prepared in a similar fashion to those used for the spectroscopic measurements. The substrate for this experiment was FTO or Indium-doped tin oxide (ITO) coated glass which serves as a transparent electrode. Initially samples were prepared to a similar thickness to those mentioned above. After these samples were determined to be too thick, spin casting was increased to 800-1000 rpm. Samples were also prepared in conjunction with the Xu group, at Penn State University's Engineering Science and Mechanics, in a nitrogen glove box. The back electrodes for these samples were a 80 nm thick layer of aluminum deposited using electron beam (e⁻ beam) and thermal deposition. A diagram of the CELIV cell can be seen in Figure 5.
Figure 5. Diagram of a CELIV cell.
Chapter 3

Challenges in the Charge Carrier Extraction by Linear Increasing Voltage Experiment

The CELIV experiment lead to a number of challenges, the first of these to come to light was the thickness dependence of the sample films. Initially the samples were prepared in the same method as the samples for the spectroscopic experiments. These thick samples lead to very slow charge extraction as seen in Figure 6. When the samples were prepared to be very thin layers as has been studied in the literature, a number of the samples suffered from electrical shorts due to contact between the two electrodes. This was most likely attributed to small pinholes present in the film or the deposition of the aluminum electrode caused surface perturbation. However, the samples that did function showed very fast kinetics in relation to the thick films (Figure 7). It should be noted that the CELIV traces reported here do not exactly match the diagram in Figure 2 because RR-P3HT has a residual metal catalyst, primarily nickel, left behind by its synthesis. The residual metal catalyst cause the curves to appear more conductive than the capacitive curve shown in figure 2. The thick films that were analyzed with the CELIV technique shows that not all charge carriers were extracted since the traces do not go to zero (Figure 6). This observation shows that films for a CELIV experiment need to be thin in order to completely extract the charge carriers.
Figure 6. CELIV trace using thick films similar to those used for spectroscopic studies. This sample shows slow charge carrier extraction within sample. $T$ = the time delay between the laser pulse and the start of the voltage ramp.

Figure 7. CELIV trace using thin films similar to those that are currently being researched. These thin samples show a marked increase in extraction speed.
A comparison of deposition methods was also conducted. A nitrogen purged box was built in order to limit exposure of the CELIV samples to oxygen. The CELIV samples were prepared both under atmospheric conditions and within the nitrogen purged box, referred to as minimal oxygen exposure. This comparison also tested the two methods of deposition, airbrushing, and spin casting. The airbrush samples were much thicker because with the airbrush it is possible to control the coverage of the surface. The spun cast films were very thin and often shorted, most likely due to incomplete coverage of the surface. Figure 8 show the comparison of the transient photocurrent traces measured from samples deposited using the different deposition methods.

![Figure 8. Comparison of the different deposition methods used in the CELIV experiments. This comparison shows that the presence of oxygen has a high effect on the sample traces.](image)

The traces in Figure 8 show that oxygen plays a crucial in the CELIV experiments. Since oxygen has been determined to play an important role in the mobile
charge carrier extraction in the CELIV experiment a collaboration with the Xu group was conducted. The Xu group has a nitrogen glove box which has the equipment in it to make the solution, deposit the samples, and evaporate the electrode. Working with Dr. Xu's students a sample was made in their glove box and tested on our CELIV setup (Figure 9). This sample was fabricated completely in the Xu group's glove box and then transported to our lab to be analyzed. The sample was only exposed to oxygen for the short period of time it was in transport. In the solid state the films is much less likely to absorb oxygen than the liquid. It is also known that RR-P3HT is relatively air stable in its solid form. The sample tested in collaboration with the Xu group showed much different behavior than that which was seen in pervious experiments. The Xu group's sample also exhibited a much different behavior than reported in the literature. However, further work with the Xu group produced cells that suffered from electrical shorting, or could not produce a stable photocurrent for the duration of the experiment.
Figure 9. CELIV sample made and tested in collaboration with the Xu group. This sample shows the expected behavior as previously seen in the literature.

Conclusions that can be drawn from this are that the experiments are very sensitive to the presence of oxygen and need to be done in a carefully controlled environment. In the literature these experiments are done completely within a nitrogen environment. When we were able to replicate an oxygen free environment, to the best of our ability, very different results from the literature were obtained. The time to decay by half was changed by a factor of ten. The charge carriers in the sample prepared in an oxygen-free environment contained carriers that showed a marked increase in speed. Since the cells often shorted, the deposition method of the electrode is also an issue being addressed. It has been reported in the literature that vapor deposition of metal can lead to
metal fibrils that pierce the OPV films and cause the two electrodes to come into contact with one another.\textsuperscript{40}
Chapter 4

Langevin Recombination

It has been reported in the literature that charge carriers undergo Langevin recombination in OPV materials.\textsuperscript{37,38} Langevin recombination describes bimolecular recombination of electrons and holes within the material. Two types of recombination in OPV materials are geminate and bimolecular recombination. When an exciton is created it is as a bound electron hole pair. The electron and hole are attracted to each other by Columbic force. An exciton is formed when a photon is absorbed by the polymer and the electron is excited. The excited electron leaves behind a localized positive charge referred to as a hole. The exciton is stabilized by the Columbic force between them. Geminate recombination is the relaxation of the associated electron and hole back to its ground state. Bimolecular recombination is a process where electrons and holes that have diffused apart and so are not correlated with each other recombine to eliminate their charge.

The rate law for Langevin recombination is as follows:

\[
\frac{dn}{dt} = -B_L n(t)^2 \quad \text{(Equation 1)}
\]

\[
B_L = \frac{4\pi e \mu}{\varepsilon \varepsilon_o} \quad \text{(Equation 2)}
\]

where \(B_L\) is the coefficient for Langevin recombination given by equation 2 and \(n(t)\) is the population of charge carriers at a given time. In equation 2, \(4\pi\) is a normalization constant that is the result of integration over all angles, \(e\) is the elementary charge, \(\mu\) is the charge carrier mobility, and \(\varepsilon \varepsilon_o\) is the dielectric permittivity. The rate law for
bimolecular recombination assumes that the number of electrons is equal to the number of holes. Solving equation 1 for \( n(t) \) gives the following:

\[
n(t) = \frac{n(0)}{1+t/\tau} \quad \text{(Equation 3)}
\]

\[
\tau = \frac{1}{n(0)B_L} \quad \text{(Equation 4)}
\]

Here \( \tau \) is defined as in equation 4 and is the effective recombination lifetime of the charge carriers. Knowing that \( B_L \) is equal to equation 2 and that \( 4\pi e/\varepsilon\varepsilon_0 \) is constant for a specific material the relationship between mobility (\( \mu \)) and lifetime (\( \tau \)) can be written (equation 5).

\[
\tau \propto \frac{1}{\mu} \quad \text{(Equation 5)}
\]

\[
l_D = \sqrt{\left(\frac{\tau D}{\varepsilon(\varepsilon+1)}\right)} \quad \text{(Equation 6)}
\]

\[
D = \frac{(kT/e)\mu}{\varepsilon(\varepsilon+1)} \quad \text{(Equation 7)}
\]

Equation 5 states that the lifetime of the charge carriers is inversely proportional to their mobility. Equation 6 is the diffusion length of a charge carrier which is dependent on the lifetime and diffusion constant described in equation 7. Since the lifetime and mobility are thought to be inversely proportional the product \( \mu\tau \) should be constant.

### 4.1 Crystalline Variation of Polymers

In order to study the behavior of charge carriers in OPV systems, polymers of differing molecular order were used. A low molecular order polymer, CN-MEH-PPV, was compared to a highly ordered polymer, P3HT, to examine the effect trapping defects have on both the total and mobile carriers. Since some of the charge carriers can become
trapped the mobile and total charge carrier density may not be the same. The blue curve in figure 10 is a measure of the total carriers present in an OPV cell. This data was collected using the transient Vis-IR spectroscopic technique described above. This data is a result of convolving the bimolecular recombination kinetics for each sample with the corresponding photocurrent transient traces giving \( n(t) \). Convolving the recombination kinetics with the photocurrent transients ensures that the optical results are comparable to the mobile carrier density kinetics \( q(t) \). The black dots in figure 10 were data taken from a CELIV experiment. This technique measures the charge carriers as they leave the OPV cell. The mobile carrier density kinetics, \( q(t) \), also includes integrals over the photocurrent transients. Since it only measures charge carriers that are extracted from the cell, only the mobile carriers are measured in this experiment.

Previously in the literature it has been reported that recombination in OPVs follows Langevin recombination behavior.\(^{37,38}\) However, different behavior has been reported when the mobile carriers vs. the total carriers are measured (Figure 10). Figure 10 A shows that for the CN-MEH-PPV the blue curve, \( n(t) \) representing the recombination kinetics of all carriers regardless of their mobility, does not match with the black dots, \( q(t) \) representing the recombination kinetics of only the mobile carriers. However, the P3HT shows that the two curves overlay each other (Figure 10 B).\(^{39}\) The CN-MEH-PPV has been shown to exhibit Langevin recombination whereas the P3HT does not.\(^{37,38}\) The comparison of these two traces shows that in the low molecular order polymer, CN-MEH-PPV, the mobile carries do not match up with the total carriers in the OPV cell as they do in the high molecular ordered P3HT. This difference is believed to
arise from charge trapping in the CN-MEH-PPV due to its lower molecular order. The charge trapping is believed to be responsible for the apparent Langevin recombination.

The relationship between molecular order and charge trapping can also be seen in the TRIR vibrational spectra of the carbonyl stretch of PCBM. This technique allows for the direct observation of deeply trapped charge carriers in OPV materials. The TRIR vibrational of the carbonyl stretch of PCBM in a 1:1 blend with CN-PPV is shown in figure 11A. The four spectra present were normalized to their maximum signal for comparison. The positive going peak at 1740 cm\(^{-1}\) is the reduced absorption of neutral PCBM, referred to as a bleach, that is the result of electron transfer from the polymer. The negative going peak, labeled anion, appears at 1760 cm\(^{-1}\) on the microsecond time scale. Since the kinetics decay in figure 11B decay synchronously with the bleach peak it can be concluded that the new absorption is the result of the anion of PCBM. The appearance of this anion peak can then be interpreted as vibration evidence of deeply trapped charge carriers with the CN-PPV:PCBM blend. This interpretation is further supported by the TRIR vibrational spectra of the carbonyl of PCBM in a 1:1 blend with P3HT (Figure 11C). P3HT is a polymer with higher molecular order and does not show an anion peak like CN-PPV. Since P3HT is of higher molecular order it does not display the deep charge trapping characteristics that are seen in the low molecular order CN-PPV. Correspondingly, the new absorption arising from trapped carriers is missing in the transient spectra of the P3HT:PCBM blend.
Figure 10. Example of how bimolecular recombination differs when measuring the mobile carriers vs. all carriers in disordered polymers ex. CN-MEH-PPV vs. a higher order polymer ex. P3HT.

Figure 11. Vibrational signature of charge traps. The appearance of the anion peak in CN-PPV is direct observance of deeply trapped charge carriers with the OPV materials.36

4.2 Morphology Differences in OPVs

The deposition method of the OPV materials leads to different morphology. Two specific deposition methods were examined, the Bulk Heterojunction and Bilayer devices (Figure 12). The BHJ cells have large domains of PCBM that form when the donor/acceptor blend is deposited on the substrate from the same solution. Whereas the bilayer device has a very thin layer of PCBM spin-coated on the surface of the polymer from an orthogonal solvent. This allows the polymer to be deposited from one solution,
in the case chlorobenzene, and the PCBM from another, dichloromethane. The high molecular weight polymer left behind by the Soxhlet extraction is insoluble in the dichloromethane. The thin layer of PCBM is believed not to have the large domains formed as in the BHJ.

![Diagram](image)

**Figure 12.** Difference between the BHJ and Bilayer cells.

Studying the two different deposition methods using the Linear IR and Transient Vis-IR spectroscopy lead to an appearance of a spectral shift of the carbonyl absorption at 1740 cm\(^{-1}\) (Figure 13). This shift is the result of a solvatochromatic shift.
Figure 13. Spectral shift of the Transient Vis-IR of P3HT at 1740 cm$^{-1}$. 

<table>
<thead>
<tr>
<th>Peak Shift of BiLayer P3HT</th>
</tr>
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<tbody>
<tr>
<td>Peak of Blend = 1738</td>
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<td>Peak of BiLayer = 1740</td>
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Chapter 5

Linear IR Temperature Study of CN-MEH-PPV:PCBM

The carbonyl stretch of PCBM was found to be slightly temperature dependent using the linear IR experiment. This stretch shows a small shift to a lower frequency at lower temperatures. This indicates that as the temperature decreases there is an increase of dipolar coupling between carbonyl groups of various PCBM molecules. Over the temperature range of 184 K to 390 K a shift of approximately 1.5 cm\(^{-1}\) was observed, one third of this shift occurring between 300 K and 390 K (Figure 14). The full width at half max of the carbonyl peak shifts only by 0.3 cm\(^{-1}\) over the entire temperature range. The peak appears to become slightly asymmetrical at lower temperatures due to a loss of absorption around 1760 cm\(^{-1}\).
The relative insensitivity to temperature of this system differs from other chemical systems. Other chemical systems show a significant shift as temperature changes due to strong coupling with their environment. Examples of strong coupling environments are, when hydrogen bonding is present within a system, having high concentrations, close proximately, and/or high molecular order present. Strong coupling environments are especially true of protein systems where their structure is highly dependent on temperature. For example the amide-I vibration of proteins is significantly dependent on temperature because of the high concentrations and strong interactions with their environment. Since amide bonds exist on every protein residue they exist in high concentrations. The close proximity of the amide bonds couples with a high intermolecular order present in alpha-helices and beta-sheets gives rise to collective vibrations that extend over large regions of the proteins. The thermal induced randomization of the comformations of amide groups reduce their coupling and gives rise to the temperature dependence. As they become more closely packed the influence of the intermolecular forces increases.

Since the peak shift of the carbonyl group on PCBM is essentially independent of temperature it can then be assumed that the methyl ester group of PCBM is in low concentration and has weak interactions with its environment in a BHJ CN-MEH-PPV:PCBM film. This is confirmed in that the density of pure PCBM is 1.5 g/cm$^3$ (1.0 molecules/nm$^3$) which puts the average distance between methyl ester groups at approximately 1 nm. At a distance of 1 nm there is weak coupling between the methyl
ester groups on PCBM, since there is no hydrogen bonding and the molecule is relatively non-polar. The small shift to a lower frequency can then be attributed to an increase of intermolecular order as the molecules decrease in temperature. As the temperature decrease the intermolecular forces between the methyl ester groups of PCBM become more influential on the spectra. This effect can also be seen in other systems, for example semicrystalline nylon II shows similar behavior when studied at varying temperatures.25

The concluded temperature independence of the vibrational line width of the carbonyl on PCBM then suggests the vibrational dynamics are insensitive to temperature. The temperature independence was confirmed by studying the effects of temperature on excited state relaxation, orientational diffusion, and spectral diffusion using ultrafast polarization resolved IR pump probe spectroscopy and 2D IR spectroscopy.33-36 The ultrafast experiments mentioned here were done by Ryan D. Pensack. These results suggest that the carbonyl stretch of PCBM molecules are well described as dilute weakly coupled local modes that experience a static solvent environment. The conclusion drawn from these experiments shows that the carbonyl group of PCBM is an ideal vibrational probe to study the charge carrier dynamics in OPV films.
References


25. Skrovanek, D.J.; Painter, P. C.; Coleman, M. M.


