Copyright

by

Marlene Gutierrez

2015

The Dissertation Committee for Marlene Gutierrez Certifies that this is the approved version of the following dissertation

Scanning Photocurrent Microscopy to Investigate Materials for Photovoltaics

Committee:

David Vanden Bout, Supervisor

Allen J. Bard

Bradley Holliday

Lauren Webb

Ananth Dodabalapur

Sean T. Roberts

Scanning Photocurrent Microscopy to Investigate Materials for Photovolatics

by

Marlene Gutierrez, B. S.

Dissertation

Presented to the Faculty of the Graduate School of

The University of Texas at Austin

in Partial Fulfillment

of the Requirements

for the Degree of

Doctor of Philosophy

The University of Texas at Austin December 2015

Dedication

Dedico este trabajo a mi mamá y mi hermano. Gracias por todo su amor y apoyo. Esto no habría sido possibel sin ustedes dos.

Acknowledgements

Firstly, I would like to acknowledge my advisor, Dr. David Vandenbout, this dissertation would not have been possible without your guidance, support, and most importantly funding. I would also like to thank my collaborators, Oleksiy Slobodyan (whose name I still cannot spell without looking up), Sara Moench, Doug Pernik, Tim Segler, and their respective advisors. Without your samples, materials, and substrates the work presented in this dissertation would have taken much longer to complete. I would like to thank all of my friends especially Leigh Kruger and Rebecca Anderson. You are fantastic women and I'm glad to call you my friends. Thank you Raluca Gearba, I look up to you and appreciate all of your guidance and help these past 5 years. I also thank Finn Gutierrez Dugger for always greeting me at the door with a smile after a long day.

Lastly, I would like to thank Jason Dugger. I cannot thank you enough for your constant love and support. If I thought graduate school was difficult with you, then it might have been impossible without you. Therefore, I expect you to read every page of this dissertation. Since you heard about all of the failed experiments, here are the ones that worked.

Scanning Photocurrent Microscopy to Investigate Materials for Photovoltaics

Marlene Gutierrez, Ph.D The University of Texas at Austin, 2015

Supervisor: David Vanden Bout

As the world becomes even more dependent on energy there is a dire need to find a clean and renewable energy source. Solar energy has the possibility to provide more then enough clean energy the world needs, yet, it is still not an option available to many due to production cost. New cheaper materials are investigated in hopes of building a low cost and efficient photovoltaic (PV). One method that can dramatically lower the cost of production is to use materials that can be deposited from solutions. Although many candidates fit the requirements needed to be solution processable, this technique consistently makes PVs with much lower efficiencies then their crystalline counter parts. Information about charge transfer and extraction processes of the charge carriers are necessary to optimize them. Scanning photocurrent microscopy (SPCM) is a technique that scans a sample across a focused laser beam and collects photocurrent as a function of position. Photoluminescence and reflectance are collected simultaneously providing information about the morphology and recombination. Information gathered from SPCM gives insight to intrinsic recombination and transport properties of the material. This dissertation will look at multiple systems used in PVs. First the space charge regions of a Langevin polymer with and without an additive are compared to see the effects of morphology on collection. A Langevin polymer is then compared to a non-Langevin to

find intrinsic differences between them. A perovskite solar is scanned using different polarized light. Finally, A new thin film and new device architecture was probed using SPCM.

Table of Contents

List of Tables	X
List of Figures	. xi
Chapter 1: Scanning Photocurrent Microscopy as a Tool to Investigate New Ma for Photovoltaics	aterials
1.1 Motivation	1
1.2 Organic Bulk Heterojunction	2
1.3 Lateral Bulk Heterojunctions	7
1.5 New systems and device architecture	.10
1.4 Scanning Photocurrent Microscopy	.11
Chapter 2: Using Lateral Bulk Heterojunctions to Study the Effects of Additive PTB7:PC ₆₁ BM Space Charge Regions	s on 14
2.1 Introduction	14
2.2 Materials and Methods	18
2.3 Results and Discussion	
2.4 Conclusion	
Chapter 3: Investigation of Long Drift Lengths in a non-Langevin Polymer PDTSiTzTz Using Scanning Photocurrent Microscopy	36
3.1 Introduction	.36
3.2 Experimental	.40
3.2 Results and discussion	.42
3.4 Conclusions	.56
Chapter 4: Scanning Photocurrent Microscopy of a Planar CH ₃ NH ₃ PbI ₃ Solar C	Cell58
4.1 Introduction	.58
4.2 Experimental	.62
4.3 Results and Discussion	.64
4.4 Conclusions	.75

Chapter 5: Probing New Device Structures with SPCM	76
5.1 Introduction	76
5.2 Experimental	78
5.2 Results and Discussion	80
5.3 Conclusions	87
Reference	90

List of Tables

able 2.1. Extracted space charge region length for samples with and without DI	0
	1
able 3.1: Extracted SCR lengths for all tested device lengths4	9

List of Figures

Figure 1.1. Schematic of a BHJ
Figure 1.2 The chemical structure for the non-Langevin polymer PDTSiTzTz and the
Langevin polymer PSBTBT5
Figure 1.3 Schematic of LBHJ7
Figure 1.4 carrier concentration, photocurrent, electric field, and voltage profile as a
function of position as a function of position within the LBHJ9
Figure 2.1 Schematic of experimental microscope and structure of lateral BHJ20
Figure 2.2 Example of photocurrent, reflectance image, and flourescence image 21
Figure 2.4 Averaged line scans for sample without DIO under dark and white light
bias conditions
Figure 2.6 Averaged line scans for sample with DIO under dark and white light bias
conditions
 conditions
conditions
 conditions. 29 Figure 3.1 The chemical structure of PDTSiTzTz and schematic of a lateral bulk heterojunction device 38 Figure 3.2 SPCM images for a 20 μm device with a -200 V applied bias under dark and light conditions. 43 Figure 3.3 SPCM images for a 8 μm device with a -200 V applied bias under dark and light conditions. 46 Figure 3.4 Voltage vs. extracted SCR length for SCR near the Au anode and the al
 conditions. 29 Figure 3.1 The chemical structure of PDTSiTzTz and schematic of a lateral bulk heterojunction device. 38 Figure 3.2 SPCM images for a 20 µm device with a -200 V applied bias under dark and light conditions. 43 Figure 3.3 SPCM images for a 8 µm device with a -200 V applied bias under dark and light conditions. 46 Figure 3.4 Voltage vs. extracted SCR length for SCR near the Au anode and the al cathode
conditions. .29 Figure 3.1 The chemical structure of PDTSiTzTz and schematic of a lateral bulk heterojunction device heterojunction device .38 Figure 3.2 SPCM images for a 20 µm device with a -200 V applied bias under dark .43 Figure 3.3 SPCM images for a 8 µm device with a -200 V applied bias under dark and .43 Figure 3.3 SPCM images for a 8 µm device with a -200 V applied bias under dark and .46 Figure 3.4 Voltage vs. extracted SCR length for SCR near the Au anode and the al .51 Figure 3.5. Averaged line scans for PTB7 and PDTSiTzTz under dark and white light .20

Figure 4.1. Device architecture of a planar CH ₃ NH ₃ PbI ₃ perovskite solar cell and
scanning microscope set-up61
Figure 4.2. Reflectanc and photocurrent images of perovskite solar cell
Figure 4.3. Photoluminescence and Photocurrent images taken using 0° and 90°
polarized excitation beams
Figure 4 Line scans from photocurrent and photoluminescence images using 0° and
90° polarized excitation beams
Figure 4.5. Original fluorescence image, original photocurrent image convolved
fluorescence image, and original photocurrent image modified scale.74
Figure 5.1. A schematic of the layers in the grooved device and SEM image of a
device with multiple grooves78
Figure 5.2 Reflectance image of single groove solar cell. Photocurrent image take
Figure 5.2 Reflectance image of single groove solar cell. Photocurrent image take under dark and white light biased
 Figure 5.2 Reflectance image of single groove solar cell. Photocurrent image take under dark and white light biased
 Figure 5.2 Reflectance image of single groove solar cell. Photocurrent image take under dark and white light biased. Figure 5.3 Reflectance image of single groove solar cell. Photocurrent image take under dark and white light biased conditions.
 Figure 5.2 Reflectance image of single groove solar cell. Photocurrent image take under dark and white light biased. Figure 5.3 Reflectance image of single groove solar cell. Photocurrent image take under dark and white light biased conditions. Figure 5.4 A line scan of the photocurrent image under dark and white light biased
 Figure 5.2 Reflectance image of single groove solar cell. Photocurrent image take under dark and white light biased. Figure 5.3 Reflectance image of single groove solar cell. Photocurrent image take under dark and white light biased conditions. 81 Figure 5.4 A line scan of the photocurrent image under dark and white light biased conditions.
 Figure 5.2 Reflectance image of single groove solar cell. Photocurrent image take under dark and white light biased. Figure 5.3 Reflectance image of single groove solar cell. Photocurrent image take under dark and white light biased conditions. Figure 5.4 A line scan of the photocurrent image under dark and white light biased conditions. Figure 5.5 Reflectance , dark , and white light biased photocurrent images of a 3-
 Figure 5.2 Reflectance image of single groove solar cell. Photocurrent image take under dark and white light biased. 80 Figure 5.3 Reflectance image of single groove solar cell. Photocurrent image take under dark and white light biased conditions. 81 Figure 5.4 A line scan of the photocurrent image under dark and white light biased conditions. 82 Figure 5.5 Reflectance , dark , and white light biased photocurrent images of a 3-channel device using a 633 nm excitation beam.

Figure 5.8 Line scans of the dark and white light bias photocurrent image 488nm .87

Chapter 1: Scanning Photocurrent Microscopy as a Tool to Investigate New Materials for Photovoltaics

1.1 MOTIVATION

The increase in consumption of energy has pushed researchers to look for new ways to meet the rising energy demands. Current forms of traditional energy, such as fossil fuels, are finite, and with the present climate change issues there is a need for a clean and renewable source of energy. Photovoltaic cells (PVs) have the potential to be a viable alternative source of energy, yet the cost of production has limited the wide spread use of this technology.^{1,2} The materials and processing techniques needed to make an efficient cell quickly drive up the costs of production. Therefore researchers have focused on new PV materials and fabrication approaches that have the potential to lower these costs.

One potential path to dramatically decrease production costs is to deposit PV materials from solutions. While crystalline Si PVs require extreme processing conditions, PVs made from solution can be made at low temperatures. The production costs can further be driven down using solution-based techniques to deposit them such as inkjet, screen, or flexographic printing.³ Unlike traditional PVs, which can only be produced on rigid substrates, solution processed films have the capability to be applied on flexible substrates. This would allow for integration into consumer products. Yet many solution-processed PVs suffer from low efficiencies due to current incomplete understanding of the complex morphology of the film, which results in losses of conversion of energy from light.^{4,5} Thus, there is a need for a basic understanding of carrier physics in order to further improve charge generation, transport, and extraction.

This dissertation will use scanning photocurrent microscopy (SPCM) to study the recombination and transport properties of different PV materials using different device architectures. Photocurrent images can be produced using SPCM, allowing researches to visualize the transport of free carriers in a PV device. Additionally, reflectance and photoluminescence are simultaneously collected, providing information about radioactive recombination and the morphology of the device. Correlations between the acquired data can provide insight into the basic photophysics that governs the production of photocurrent in the probed PV devices.

1.2 ORGANIC BULK HETEROJUNCTION

Organic materials have been an area of great interest in PV research due to the ability to easily chemically tailor and deposit then from solution.⁶ A structure that has great potential for success is the bulk heterojunction (BHJ). The BHJ consists of two, or more, photoactive materials mixed together and deposited as a thin film to form the photoactive layer.^{4,7} high photovoltaic efficiencies for organic based cells have been achieved by using a blend of polymer acceptor and fullerene donor materials.⁸ The processes necessary to generate power in a cell are described in figure 1.1 from a kinetics point of view. The beginning step (i) shows the absorption of a photon to create a coulombically bound electron hole pair, or an exciton. (ii) Then the diffusion of the exciton to an interface where (iii) charges separate, and charge transport of the electron (iv). Finally, (v) transport of the separated charges through their corresponding materials and (vi) charge collection at the electrodes.



Figure 1.1. Schematic of a BHJ showing the generation of an exciton (i), its diffusion to an interface (ii), subsequent splitting into free carriers (iii,iv), and traveling to the electrode for collection (v, vi).⁹

This simplified model is the starting point to understanding the issues facing BHJ photovoltaic cells. Though these cells have been studied for many years there is still debate about the basic photophysics driving the charge carriers and therefore governing the efficiency of light conversion to electricity.^{10–13}

These types of cells typically have an optimal device thickness of 100 nm with only 60% of the incident light absorbed.¹⁴ A way to increase the efficiency of a BHJ is to increase the thickness, which will allow for more absorption of photons leading to the creation of more charge to be collected However, the efficiency in these cells tends to decrease even though there is an increase in absorption. This has been attributed to the increase in bimolecular recombination, or the recombination of two free carriers, due to the greater distance the carriers must travel towards the electrodes. ^{15,16}

Such thickness dependence of the BHJ materials is detrimental not only to the photoconversion efficiency, but also to the ability to mass produce PVs. The current methods for making films that are 100 nm thick can only be used for small area devices.

In order to feasibly mass-produce these cells, printing techniques would be preferential, but these techniques cannot produce submicron films.¹⁷ There have been significant efforts to understand how to control the bimolecular recombination in these materials.

Bimolecular recombination in organic semiconductors has been shown to follow the Langevin expression. Therefore the rate of recombination is equal to the sum of the mobilities of both carriers.¹⁸ The rate of recombination is given by,

$$R = \gamma(np - n_{int}p_{int}) \qquad \qquad Equation \ 1.1$$

where Υ is the Langevin recombination constant, n (p) is the free electron (hole density, and n_{int} (p_{int}) is the intrinsic electron (hole) density. For a defect free material the Langevin recombination constant, Υ , is given by,

$$\gamma = \frac{q}{\varepsilon} (\mu_n + \mu_p) \qquad \qquad Equation \ 1.2$$

where q is the elementary charge, ε is the dielectric constant, $\mu_n(\mu_p)$ is the mobility of the electron (hole).¹⁹ In a BHJ the carriers are confined to different phases so this equation accurately represents the Langevin recombination. Karl and Sommer found that the Langevin expression does describe recombination in organic materials.²⁰ But there are some systems whose Langevin recombination constant deviates from that predicted value.

Suppressed bimolecular recombination results in a suppressed Langevin recombination constant and is a sought after property in a photovoltaic material. Materials with non-Langevain behavior have been found to have the ability to make cells with a thicker active area than those whose recombination follows Langevin statistics.²¹ A thicker active layer would allow for the absorption of more photons and the creation of more carriers, therefore increasing the efficiency. Additionally, more fabrication processes are available to mass-produce devices with a thicker active layer.

The nature of a reduced bimolecular recombination in these materials is still under investigation, and few known BHJ exhibit it. Annealed poly (3-hexylthiophene-2, 5-diyl) (P3HT) was found to exhibit a reduced recombination rate constant in 2005 and since then many theories as to how this occurs have been developed.²² Blom et. al. argued that the recombination constant is limited by the slower carrier and does not depend on the mobility of the faster carrier.²³ Deibel et. al. used a model that considered local changes in charge carrier concentrations, which lead to a variety of recombination rates that overall produced a reduced recombination rate.²⁴ Unannealed P3HT does not have this reduction bimolecular recombination constant, Juška et. al. attributed the reduction due to lamellar structures formed after annealing.²⁵



Figure 1.2 The chemical structure for the non-Langevin polymer PDTSiTzTz (black) and the Langevin polymer PSBTBT (green)

Non-Langevin behavior is frequently attributed to the morphology of the active layer, like that seen in annealed P3HT. ²⁶ In 2011 another polymer was synthesized that also showed a reduced bimolecular recombination rate, being called poly [(4,4'-bis (2-

ethylhexyl) dithieno [3,2-b: 2', 3'-d] silole)-2,6-diyl-alt- (2,5-bis 3-tetradecylthiophen-2yl thiazolo 5,4-d thiazole)-2,5diyl] (PDTSiTzTz). The chemical structure of PDTSiTzTz figure 1.2a.²⁷ The efficiency of the device with a PDTSiTzTz as a function of thickness is compared to that of poly[(4,4'-bis(2-ethylhexyl)dithieno [3, 2-b:2',3'-d]silole)-2, 6diyl-alt-(2,1,3-benzothiadiazole)- 4,7-diyl] (PSBTBT), the chemical structure shown in figure 1.2b. For an efficient device a high fill factor is desirable, and the fill factor vs thickness of a device based on either PSBTBT or PDTSiTzTz was studied by Peet et al.²⁸ The fill factor for PSBTBT drops quickly after about 100nm while PDTSiTzTz has a high fill factor up to 400nm, therefore indicating non-Lagevin recombination.

Unlike annealed P3HT, PDTSiTzTz does not have large morphological features. Therefore, there is a need to better understand how this reduction of the bimolecular recombination constant occurs. Understanding of the inherent differences between Langevin and non-Langevin polymers is critical to the design of these polymers. Yet, there are not obvious differences in their chemical structures to imply reduced recombination rates. This dissertation will invrestigate a Langevin and non-Langevin polymer using a lateral bulk heterojunction (LBHJ) to directly probe the active area of the device.

1.3 LATERAL BULK HETEROJUNCTIONS

Multiple techniques have been implemented in order to study transport and recombination in A BHJ. Some of these techniques include ambipolar thin film transistors^{29–31}, time-resolved microwave conductivity^{32,33}, photocurrent charge extracting in a linear increasing voltage (photo-CELIV)³⁴, and transient photocurrents.^{35,36} These experiments are done on a vertical device similar or identical to working solar cells and require interpretation of a transient response A lateral bulk heterojunction (LBHJ) structure has recently been implemented in order to directly probe the photoactive layer using microscopy and spectroscopy techniques.^{37–40} A schematic of a LBHJ device structure is show in figure 1.3.



Figure 1.3 Schematic of LBHJ

Unlike in a vertical device that has the active area buried between two electrodes, in a LBHJ the electrodes are found in the same plane as the active material deposited on to the

substrate. This makes it is possible to directly probe the active material and scan in the direction of transport under steady state conditions. Although the direction of transport is different from that in a vertical cell, we can still gather valuable information about the transport and recombination that complement studies on vertical cells.

Ooi et. al. performed simulations to formulate the device physics within the LBHJ.⁴¹ The device has three distinct regions when under operation, two regions of high photocurrent near the electrodes, referred to as space charge regions (SCR), and a central region of little to no photocurrent, referred to as the recombination zone. The formation of these three regions is a direct result of having a channel length longer than drift length of the photogenerated charge carriers. The drift length is a product of the carrier's mobility, lifetime, and the applied electric field. The drift length will dictate the extent to which the photocurrent may be collected from the electrode. The photocurrent in the SCR is described by,

$$J = (4\varepsilon\mu)^{1/4} (eG)^{3/4} V^{1/2}$$
 Equation 1.3

where ε is the dielectric constant, μ is the mobility of the slower carrier, e is the elementary charge, G is the generation rate and V is the applied voltage. In the central zone the carriers are too far to be collated at the electrodes, therefore, there is little photocurrent.

Figure 1.4a shows the simulations of a 20 μ m channel length device under uniform illumination and probed with a laser spot with a 0.5 μ m FWHM. The asymmetric carrier concentrations near the electrode lead to the formation of an SCR, and correspond to high photocurrent generation in the SPCM image scan. This accumulation of carriers at the electrodes occurs because the carriers generated there are transported quicker then they can be extracted leading to a build-up of charge.⁴²



Figure 1.4 (a) Numerically simulated carrier concentration and photocurrent as a function of position within the LBHJ under uniform illumination and probed with a laser spot 0.5 μ m FWHM. The anode is located at 0 μ m and the cathode is located at 20 μ m. (b)Simulated electric field and voltage profile as a function of position

The equal concentration in the center of the LBHJ device leads to high recombination of the carriers and little or no photocurrent. Figure 1.4b shows that at a SCR there is an increase in electric field near each electrode and a voltage drop in the applied potential. The recombination zone has a constant electric field and potential profile. The signal of the photocurrent can be used to determine the length of the SCRs and information about the mobility of the carriers.

The actual size of the SCR is dependent on the generation rate, applied electric field, and mobility. The relative size is related to the mobility through a relation derived from the continuity equations. In the recombination zone the electron current extracted is,

$$J_n = q\mu_n E_r n_{equi} \qquad \qquad Equation \ 1.4$$

Where E_r is the electric field in the recombination zone, and p_{equi} is the equilibrium electron concentration. The electron current is give by,

$$J_n = -qGL_C \qquad \qquad Equation \ 1.5$$

where L_C is the length of the SCR at the cathode.⁴¹ Similarly, equations for the SCR near the anode and the hole concentrations in the recombination zone can be expressed. Under ideal conditions, these equations can then be combined since the electron and hole concentrations are equal in the recombination zone, from the charge continuity equations, $\frac{-qGL_C}{-qGL_A} = \frac{q\mu_p E_r p_{equi}}{q\mu_n E_r n_{equi}} \rightarrow \frac{L_C}{L_A} = \frac{\mu_p}{\mu_n} \qquad Euqation 1.6$

The slower carrier will accumulate near the electrode due to imbalanced mobilities and by measuring the SCR the slower carrier can be determined. This will be discussed in chapter 3.

1.5 NEW SYSTEMS AND DEVICE ARCHITECTURE

The lateral device structure is not an efficient PV device and is only used to study the active area directly in the direction of transport, but SPCM has also been used with vertical devices by focusing through the transparent electrode.^{43,44} Information about the photocurrent and photoluminescence have provided insight into the effects of morphology on transport. Information about recombination and morphology of new materials is vital for optimizing the PV active layer. One such material is the organometallic perovskite thin film, which will be investigated in chapter 4.

Just as it is important to optimize the material in the active area it is also necessary to optimize the device architecture to the material chosen for the PV. As mentioned before the lateral device structure is not a structure that will make efficient cells. Yet, a grooved structure has been developed to take advantage of some of the properties of nano crystal materials. The grooved device has multiple 1 um channels on a substrate, with contacts inside each channel, therefore the transport here is similar to that in the LBHJ. One advantage of the grooved structure is that it is possible to join them easily in series. This device structure will be studied in chapter 5.

1.4 SCANNING PHOTOCURRENT MICROSCOPY

Scanning techniques have been implemented to study many materials used in PVs. The need for high resolution information about the morphology of the active layer has led to the use of atomic force microscopy (AFM)^{45,46}, conducting AFM^{47,48}, electrostatic force microscopy (EFM)⁴⁷, scanning kelvin probe microscopy (SKPM)^{49,50}, near field scanning optical microscopy (NSOM)^{51,52}, and tunneling luminescence AFM⁵³. SPCM is closely related to laser induced photocurrent (LBIC), which was previously used to investigate multiple PV systems such as, cadmium telluride⁵⁴, copper indium gallium diselenide⁵⁵, and organic BHJs⁵⁶. All of these techniques are powerful tools to study the intrinsic electrical properties of PV materials.

This work investigates photovoltaic materials using SPCM. This technique scans a PV device across a focused laser beam to produce photocurrent, reflectance, and photoluminescence images pixel-by-pixel. Photocurrent is collected via lock-in detection and the reflectance and photoluminescence are collected via photodiodes. Many photovoltaic materials are sensitive to oxygen or water; therefore, the homebuilt SPCM system is enclosed in a nitrogen glove box to ensure that there is no degradation of the active layer due to oxygen or water. The laser is focused onto a single-mode fiber optic that transfers the laser into the nitrogen glove box.

This set-up has successfully been use to investigate both lateral and vertical photovoltaic devices. 37,38,43,44 Information from this technique has been used to study vertical device composed of Cu(In_{1- x}Ga_x)Se₂ (CIGS) nano-crystals and correlate the photoluminescence and photocurrent. Different morphological features in both images were compared to see the effects on the photocurrent.⁴³ This technique was also successfully used in conjunction with a LBHJ to estimate the carrier mobility in a poly[(4,40-bis- (2-ethylhexyl)dithieno[3,2-b:20,30-d]silole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl]) (PSBTBT) BHJ active layer.³⁷ In the present work the system was rebuilt in a glovebox in order to successfully obtain data on oxygen and water sensitive systems.

Chapters 2 and 3 will couple this system with a LBHJ device structure to investigate the SCRs of a Langevin and non-Langevin polymer and compare inherent differences between the SCRs. Additionally, effects of an additive used to control morphology will be compared to the untreated polymer in chapter 2. SPCM will be used to look at the high photoluminescence and long transport lengths of a new emerging material used in photovoltaics, organometallic pervoskite thin films, in chapter 4. Lastly

Chapter 5 will use SPCM to investigate the photocurrent in a new channel device architecture.

Chapter 2: Using Lateral Bulk Heterojunctions to Study the Effects of Additives on PTB7:PC₆₁BM Space Charge Regions ¹

¹Previously Published

2.1 INTRODUCTION

Photovoltaics have been at the forefront of alternative energy research for some time, promising to become an efficient, clean, and economical option. Increasingly, the importance of economical and environmental factors in device implementation has driven research towards the development of organic photovoltaics (OPVs). OPVs have the potential to be very affordable due to low-cost starting materials and processing conditions. They also have the additional advantage of being printable on flexible substrates, which would provide an opportunity for integration into consumer electronics, among other uses.^{3,5} Though OPVs have the potential to be less expensive than their inorganic counterparts; poor device efficiencies are a significant issue. Thus far, OPV efficiencies of up to 10% have been achieved through a combination of improvements in processing techniques that yield better control of nanoscale morphology, and molecular engineering developments, which have led to development of push-pull polymers with tunable band gaps. ^{4,5,57} Despite these advances, a gap in the fundamental understanding of charge separation and transport in these devices hinders OPV research from attaining higher efficiencies. Charge separation and transport theories for common silicon solar cells have assisted researchers in making advances in traditional photovoltaic efficiencies. It stands to reason that a similar fundamental understanding of these

¹Gutierrez, M.; Slobodyan, O.; Dodabalapur, A.; Vanden Bout, D. A. Using Lateral Bulk Heterojunctions to Study the Effects of Additives on PTB7:PC61BM Space Charge Regions. *Synth. Met.* **2015**, *209*, 158–163. Gutierrez preformed experiments. Slobodyan made substrates. Dodabalapur and Vanden Bout provided expertise and guidance for the work.

processes in OPVs would likewise accelerate the development of truly competitive organic alternatives to silicon solar cells.

A promising OPV device active layer structure is a bulk heterojunction (BHJ), made from a mixture of an electron donating polymer and an electron accepting material. This structure leads to nanoscale phase separation and interconnected networks of its components enabling separation and transport of photogenerated carriers. Two types of recombination primarily interrupt charge transport. Due to the low dielectric constant of BHJ materials, absorption of a photon leads to the formation of an exciton (a bound electron-hole pair) rather than free carriers. The separation of an exciton into free carriers is a crucial step in OPV transport and current generation. As most organic materials are unable to easily separate excitons into free carries, geminate recombination (recombination of the coulombically bound electron and hole) significantly limits the photocurrent.⁵⁸ The phase separation and interconnected networks in the active layer of a BHJ structure limit germinate recombination and allow for the separation and transport of these carriers. Once an exciton is successfully separated into free carriers, the internal electric field drives the carriers to be collected at electrodes. This leaves bimolecular recombination (recombination of a free electron and free hole) as the main loss of photocurrent in these devices.⁵⁹

Researchers have found that the morphology of the active layer is crucial to device efficiency. A complication that typically arises in the BHJ active layer is the presence of a large amount of phase segregation, which leads to isolated fullerene and polymer domains with little intermixing. In order to separate into free carriers the exciton must reach a donor/acceptor interface, which provides the driving force to separate electron-hole pairs, before recombination occurs.^{60,61} Films with sufficient mixing of the fullerene and polymer have been shown to create free carriers almost instantaneously,

and it provides a good pathway to nanoscale pure domains, which are necessary for efficient collection.^{33,62} Large domains of pure polymer or fullerene lead to an enhancement of geminate recombination, since an exciton will decay back to the ground state before being separated into free carriers or free carriers may be trapped in a isolated domain. Furthermore polymers have numerous degrees of freedom that lead to a complex energetic landscape that may limit the transport of carriers due to trap assisted recombination.^{4,58}

In order to further study these systems there is a need to understand the transport dynamics within the device active layer. Unfortunately few methods allow for directly probing the active layer of a working device. Instead inferences must be made from techniques that employ vertical cells such as transient photocurrent measurements, time-resolved microwave conductivity, and photo-generated charge extraction in a linearly increasing voltage (photo-CELIV).^{27,32,35} While extremely valuable, these transient measurements rely on complex data interpretation and are generally not preformed under a steady state condition. In addition, unlike other scanning photocurrent techniques, implementing a lateral device structure with the scanning confocal microscope allows for decoupling of the transit length from device thickness and also allows for uniform charge generation. A similar technique used to look at the local photocurrent is photoconductive atomic force microscopy (pcAFM). This technique use the AFM tip as the back contact of the device. Images must be collected in contact mode and samples are limited to very smooth surfaces.^{63,64} In contrast, scanning photocurrent microscopy (SPCM) is a complementary tool that can be used to examine a wide array of samples.

In this chapter we directly measure the steady state photocurrent generated within the active layer of a lateral bulk heterojunction (LBHJ) device using SPCM. In a LBHJ device the two electrodes are defined on the same plane and the active material is deposited on top of these electrodes. This allows us to interrogate the active material inbetween two electrodes of different work function by illuminating with a focused laser beam from below. LBHJ devices allow the electrode distance to be varied from 2-100 μ m, permitting scanning along the charge transport direction as a function of position from the electrode. Previous experiments have shown that lateral devices are a useful platform for interrogating BHJ materials and can provide valuable information about the size of the space-charge region, mobility, and lifetime of carriers.^{37,39} Although transport in a vertical cell is dominated by charges moving vertically through the film, it is also useful to study these parameters in the lateral direction. Experimentally derived quantities such as carrier densities and recombination coefficient depend on charge flow during the experiment, it is therefore important to measure such parameters along multiple directions. Multiple studies implementing a LBHJ have been able to compare their results to vertical cells.^{65,66}

There has been wide interest in the low band gap polymer [(2-ethylhexyl) oxy] benzo [1,2-b: 4,5-b'] dithiophene-2, 6-diyl} {[3-fluoro-2- [(2-ethylhexyl) carbonyl] thieno [3,4-b] thiophenediyl}) (PTB7), which has reached device efficiencies up to 9% by implementing an inverted structure while also using the additive 1,8-diiodooctane (DIO).⁶⁷ It has been previously shown when the additive, DIO, is added to a chlorobenzene solution, the solubility of the fullerene increases and yields smaller domains of PC₆₁BM when films are made.⁶⁸ Transmission electron images of films without DIO show that there are round aggregates, which are attributed to PCB₆₁M domains. This study by Foster et al found that adding DIO leads to better intercalation of the PCB₆₁M and PTB7.⁶⁹ An explanation for the enhanced solubility of PCB₆₁M when DIO is added to the solutions is the interaction between the iodine atom with a partial negative charge and electron deficient PCB₆₁M.⁷⁰ Poly (3-hexylthiophene-2, 5-diyl)

(P3HT) is considered the standard polymer for OPV research, though its recombination dynamics may differ from most other polymers. Therefore PTB7 may give a broader insight into recombination in OPV systems. In the present study we examine the effects of DIO on the space charge region (SCR) of PTB7: PC61BM and demonstrate that measurable changes of the SCR can be seen experimentally.

2.2 MATERIALS AND METHODS

Lateral devices were fabricated using photolithography onto a glass substrate with a thickness of 150 μ m. 50 nm of aluminum (Al) and gold (Au) electrodes were deposited via thermal (Denton thermal deposition chamber) and E-beam deposition (Cooke E-beam/sputter deposition). These metals were chosen as the electrodes to suppress reverse bias carrier injection. Prior to deposition of the BHJ active material, the glass substrate was cleaned with phosphoric acid to remove any oxide that may be present on the Al electrode. A solution of PTB7 and PC₆₀BM (1:1.5) in dichlorobenzene was heated for at least 6 hours at 120 °C. The same process was followed for blends with 3-v/v% 1,8-diiodooctane (DIO). The solution was then spun-cast on to cleaned substrates at 1000 rpm for 60 s. The sample was then annealed at 120 °C for 10 min followed by encapsulation in nitrogen atmosphere.

SPCM measurements were acquired using 20 μ m active area LBHJ devices; biases of -100 V, -150 V, and -200 V, which correspond to respective electric field strengths of -5×10⁴ V cm⁻¹, - 7.5×10⁴ V cm⁻¹, -10×10⁴ V cm⁻¹, were applied during photocurrent collection. These field strengths are consistent with fields for a working 100 nm device. ^{37,71} The negative bias was applied to the Au electrode, and the Al was grounded. A negative base was applied via a Keithley sourcemeter and the photocurrent was collected via a Lock-in amplifier. The incident light was chopped at 141 Hz. The active area was excited using a 633.8 nm laser beam (Melles Griot) focused though an oil immersion objective (Ziss) with a 1.25 numerical aperture and 100x magnification. The focused laser spot is 350 nm diameter for the wavelength used in the experiment. Laser power did not exceed 75 nW, which resulted in an incident power density of 78 W/cm². Even at these high power densities the sample was stable and showed no signs of degradation during scanning. There is a potential for phase segregation issues that could lead to a substantially different entrenchment in PCB₆₁M aggregation at the air-surface interface.^{72,73} However the current experiment will only minimally probe these regions, as we illuminate from the bottom. Since the electrodes are 50 nm thick and the film is 100 nm thick, the photocurrent will originate in the first 50 nm. The sample was raster scanned across the objective using a piezoelectric stage (Queensgate), and photocurrent, reflectance and fluorescence were collected simultaneously. A white light bias of 80 W/cm² was applied. This experimental setup in this work is similar to previously described set-ups.^{43,44} AFM measurements we made using an Asylum AFM (MFP-3D) in tapping mode.



Figure 2.1 (a) Schematic of experimental microscope, (b) structure of lateral BHJ illuminated from below.

2.3 RESULTS AND DISCUSSION

SPCM measurement allow for the simultaneous collection of induced photocurrent, fluorescence, and reflectance images. Figure 2.1a shows a schematic of the experimental microscope set-up. Figure 2.1b shows a diagram of the device scanned; here the electrodes are in the same plane as the active material. A focused laser beam illuminates the device from below, and the sample is scanned across the objective. Photocurrent, florescence, and reflectance images are collected pixel-by-pixel. Induced photocurrent is collected via a lock-in amplifier (Figure 2.2a) while the reflectance is measured (Figure 2.2b) via an avalanche photodiode. Although fluorescence (Figure 2.2c) was collected there were no apparent features that could be distinguished, or they were beyond our resolution. There was a constant fluorescence signal across the entirety of the channel. This is not surprising since it is a common radiative recombination pathway in OPV systems. Using the reflectance image we distinguish between the electrodes and determine orientation of the device. SPCM measurements were taken on 20 μ m devices with applied bias of -100 V, -150 V, and -200 V, which correspond to a potential per unit length of -5×10⁴ V cm⁻¹,



Figure 2.2 Example of photocurrent image (a), example of reflectance image (b), and example of fluorescence image (c).

 -7.5×10^4 V cm⁻¹, -10×10^4 V cm⁻¹. For simplicity the potential per unit length will be referred to as the electric field, but it is important to realize that the true electric field within lateral devices is not uniform. These fields are similar to those found in vertical cells due to the vast difference in device length when compared to that of a typical vertical cell where the active layer is usually around 100 nm.

The result of combining the lateral geometry of the device and the operational mode is the manifestation of space-charge-limited (SCL) photocurrent. SCL photocurrent device physics has been reported both in vertical and lateral structures.^{37,39,42} Photocurrent images were used to create averaged line scans for PTB7: PC61BM samples (Figure 2.3). Figure 2.3a shows the averaged line scans for induced photocurrent under dark conditions (no white light bias) exhibiting two current peaks near the electrodes that decay as the beam moves away from the electrode. Peaks are located near the edge of the electrode representing where most of the photocurrent is being collected. In the center of the device there is a large recombination zone, an area of little to no photocurrent since the free carriers must travel farther to reach the electrodes, hence the chances of recombination before being collected are much higher. The left electrode corresponds to the electron-collecting cathode, and the right electrode corresponds to the hole-collecting anode; thus, the current near each electrode is due to the accumulation of carriers which it is collecting.⁴²

An empirical model was used to fit the space charge regions (SCR) near the electrodes in lateral bulk heterojunctions (LBH). The photocurrent is modeled as falling off exponentially with distance away from the electrode. The data are fit by convolving and Gaussian instrument response function with an exponential decay the starts at the edge of the electrode. The width of the Gaussian and the edge of the electrode can be determined independently from the reflectance data. Two independent decays are used



Figure 2.3. (a) A gaussian insttrument response function and (b) decaying exponential convolved to produce a fit for the SCR (c).

for each electode and convovled with the same Gaussian response. Figure 2.3 shows the individual Gaussian response function and individual decay that are convolved to yield the final fits shown in Figure 2.3c. Figure 2.3c shows the fits at the left electrode in a 20 μ m device with a -200 V bias under white light conditions. By convoluting the functions in figure 2.3a and 2.3b we can get a more accurate fit for the data then with just an exponential and will prevent from overestimating the SCR lengths due to instrument broadening

The length of the SCR is taken to be the length associated with the exponential decay in the fit. Fitting the PTB7: PC61BM data using this method resulted in the following space charge lengths near the cathode: 625 nm, 875 nm, and 1050 nm for -100 V, -150 V, and -200 V respectively. The length of the SCR near the anode were found to be; 750 nm, 925 nm, and 1000 nm for -100 V, -150 V, and -200 V respectively. The increase in bias causes an increase in the intensity of the photocurrent peaks as well as a small increase in the size of the SCR (Table 2.1), which is consistent with previous results.³⁷ Under dark conditions there is a feature that is not accounted for in the fitting scheme used. It is important to note that it is not in the scans with a white light bias.


Figure 2.4 Averaged line scans for sample without DIO under dark (a) and white light bias (b) conditions. All samples were scanned with -100 V, -150 V, and -200 V bias. The dash line represents the electrode edge.

In order to study the effects of light on a working device the sample was exposed to a constant white light bias. Exposing a device to a white light bias will increase the carrier concentration, filling energetic traps. The carriers that are created using the white light bias are not represented in the current scans because measurements were taken via lock-in detection to only measure the AC current induced by the laser probe. Due to the increase in carrier concentration there are less carriers to be excited by our laser probe, therefore there is a decrease in the photocurrent when under a white light bias. Figure 2.4b shows averaged line scans for the device under white light bias conditions. When the PTB7: PC60BM is illuminated with a white light bias there is an increase in the SCR length for both the cathode (675 nm, 900 nm, 1150 nm) and anode (700 nm, 1150 nm, and 1200 nm) for applied biases of -100V, -150V, and -200V, respectively. These increases are expected and can be attributed to trap filling which allows collection of free carriers farther from the electrodes by allowing more trap free pathways to the electrodes.

The effects of morphology on the SCR were studied by using the additive DIO, which selectively dissolves $PC_{61}BM$ in the solution before spin casting. Figure 2.5 shows AFM height (a and b) and phase (c and d) images of films without (a and c) and with (b and d) DIO. The sample without DIO has round isolated $PC_{61}BM$ domains, which have been circled in white in Figure 2.5a. The height images that these aggregates are protruding above the rest of the film, which range between 500nm and 10nmn in size. In the phase image we see a slightly different composition for the aggregates then that of the rest of the film. The top of these aggregates have similar composition to that around the aggregates due to the polymer that if formed on top of these aggregates at the surface/air interface.⁷³ Figure 2.5b and d shows that with the addition of the DIO the round features



Figure 2.5 AFM height (a, b) and phase (c, d) images show the morphology differences for samples without (a, c) and with (b, d) DIO.

in the height and phase are no longer apparent. We theorize that the absence of these large round features indicates a larger amount of intermixing between the $PC_{61}BM$ and the PTB7. Pervious reports have also shown round $PCB_{61}M$ domains in transmission electron images of PTB7: $PC_{61}BM$ of similar size in devices made without DIO.⁷⁴ Large isolated domains of $PC_{61}BM$ have the potential to trap many free carriers and leads to trap limited recombination, this effect has been seen in PTB7 devices without the use of an additive.^{75–77} Using SPCM we can detect the effects that morphology has on the space charge region in PTB7 devices.

Figure 2.6 shows averaged line scans for a device with 3% v/v DIO under dark (Figure 2.6a) and illuminated (Figure 2.6b) conditions. All SCR lengths are reported in Table 2.1. The magnitude of the photocurrent for devices with DIO is smaller then that for devices without DIO. The magnitude of the photocurrent is dependent on multiple processes including the generation rate and mobility as shown by Ooi et al. in addition, it also depends on the extraction at the contacts.⁴¹ The lower photocurrent in the sample with DIO is most likely due to less efficient collection at the electrodes. It is important to note that the main concern for these experiments is the special dependence of the SCR region. The devices with DIO have larger space charge regions under both the dark and light conditions than a device without DIO, indicating that we are able to collect charges generated farther from the electrodes with the addition of DIO. The average increase of the SCR for the sample without DIO when comparing the dark conditions and the white light biased conditions was 6% and 9% for the cathode and anode, respectively. The sample with DIO showed a SCR growth of 21% for near the cathode and 16% near the anode. We can conclude that there is a stronger dependence on carrier concentration; evidently filling traps will increase the efficiency of collection for a sample with DIO



Figure 2.6 Averaged line scans for sample with DIO under dark (a) and white light bias (b) conditions. All samples were scanned with -100 V, -150 V, and -200 V bias. The dash line represents the electrode edge.

while having a smaller effect on a sample without. When you compare the SCR size under illumination for a sample without and with DIO reveals a significant increase in the SCR for the sample with DIO, with an average increase of 52% and 31% for the cathode and anode, respectively. As DIO incorporation changed the cathode SCR length more, its effect is greater on collection of electrons rather than holes. This can be confirmed by analyzing the ratio of the size of the SCR since it is proportional to the mobility ratio by,

$$\frac{L_C}{L_A} = \frac{\mu_p}{\mu_n} \qquad (1)$$

	Dark					Light				
	W/O DIO			W/ DIO		W/O DIO		_	W/ DIO	
Applied Bias (V)	Left (nm)	Right (nm)	-	Left (nm)	Right (nm)	Left (nm)	Right (nm)		Left (nm)	Right (nm)
-100	625	750		1000	1000	675	700		1200	1150
-150	875	925		1050	1050	900	1150		1250	1250
-200	1050	1000		1125	1025	1150	1200		1625	1450

 Table 2.1. Extracted space charge region length for samples with and without DIO

where L_C and L_A are the lengths of the SCR at the cathode and the anode respectively, and μ_p and μ_n are the mobilities for the hole and electron respectively.⁷⁸ The mobility ratio for the line scans without DIO are averaged for all voltages and are greater than one for both dark (1.1) and light (1.09) conditions. Indicating that the hole is the faster mobility carrier. When DIO is added the mobility ratio is slightly less than one for dark (0.97) and light (0.95) conditions. Therefore, from the changes in SCR length we conclude that the addition of DIO increases the mobility of the electron due to the decrease of PC₆₁BM electron traps.

DIO has previously been shown to dramatically increase the efficiency of PTB7 solar cells by increasing the solubility of $PC_{61}BM$ into solution, therefore promoting strong intermixing of the acceptor and donor materials.^{79,80} The nanoscale morphology of the acceptor and donor provides a bicontinuous pathway to the electrodes, which leads to better transport and collection of the free carriers. Hedley et al found that by using DIO in BHJ films results in fiber-like fullerene- and polymer-rich domains that lead to extremely fast dissociation of excitons and high extraction efficiency when compared to that without DIO.⁷⁷ The current profiles show that there is a dramatic increase in the SCR length of samples with DIO compared to those without, as samples that contain DIO allow collection of carriers farther from the electrodes due to fewer isolated domains, which could trap carriers. In addition, based on the current profiles this morphology has a larger effect on the collection of electrons than holes, which has a larger growth in the cathode SCR under a white light bias. Since the $PC_{61}BM$ is the electron acceptor, isolated domains leave the electrons no pathway to the electrode, leading them to recombine with free carriers near the polymer/fullerene interface. The large growth in the SCR with DIO implies that we are able to collect carriers farther from the electrode, confirming the consequences of trapping and a lack of pathways to the electrode due to morphology.

Studies have found that the use of additives suppresses trap-limited recombination. Li et al reported transient photocurrent measurements which demonstrated that there is less-trap assisted recombination in a PTB7 sample with DIO compared to those without, and directly connected device efficiency to charge trapping.⁸¹ Lambardo et al demonstrated through transient photovoltage, voltage dependent charge extraction, and timed delayed collection field measurements that devices processed without DIO show photocurrent losses from both geminate and nongeminate recombination, while nongeminate recombination is more important in devices processed with DIO.²⁹ Additionally, a study on the thickness dependence of PTB7 devices showed that efficient charge collection in thick devices could be improved via increase of $PC_{61}BM$ phase connectivity, although this was done by increasing $PC_{61}BM$ content. Our findings support that DIO does improve charge extraction as well.⁸² Due to the lack of mixed phase in samples without DIO it is difficult to create free carriers in just the pure polymer or fullerene regions, which in turn leads to an increase in geminate recombination. In addition the mixed phase can provide a vital pathwayto the pure phase, which serves as the pathway to the appropriate electrode.

The results herein demonstrate that SPCM is a valuable technique for quantifying and visualizing the effects that additives have on the SCR of LBHJs. Although this technique can only measure free carriers, it is evident that the small increase of the SCR length in samples without DIO (6% and 9% for cathode and anode, respectively) is due to the absence of an efficient pathway to the electrodes. Addition of DIO results in significant growth of the SCR when comparing between dark and illuminated conditions (21% and 16% for cathode and anode, respectively). We attribute this to an increase in mixed phase within the film morphology, allowing for more efficient separation of the free carriers, and more importantly better transport conditions.

2.4 CONCLUSION

We have demonstrated that SPCM is a useful tool for probing a device under working solar cell conditions. A LBHJ structure was used to probe the active layer of a PTB7: PC61BM with and without DIO. Using SPCM we found that the space charge region increased when using the additive DIO. It has previously been seen that DIO increases the efficiency of devices containing PTB7 in the BHJ and by using techniques such as transient photovoltage, voltage dependent charge extraction, and timed delayed collection field measurements researchers have found that DIO reduces trap assisted recombination and geminate recombination. SPCM measurements show that DIO has a larger effective SCR near the cathode, which is a measure of how far electrons may be collected from the electrode. This growth can be attributed to a better mixing of the acceptor and donor phases that allow for less charge trapping and, more importantly a better network for charge transport, leading to a better efficiency of collecting charges further from the electrodes.

The lack of growth in the SCR for samples without DIO demonstrates the crippling effect that poor morphology has on the collection efficiency. Hence we conclude that filling traps has little effect on the collection of free carriers for samples without DIO and the efficiency deteriorates because of poor pathways for charges traveling to the electrodes. The growth of the SCR in samples with DIO can be attributed to improved pathways to electrodes, therefore other recombination pathways become of greater importance for device charge extraction, leading to the larger change under white light bias.

SPCM is a relatively new technique that can distinguish small changes in the SCR for a device under working conditions. As these are direct rather than indirect measurements, there is no need to make inferences about the active layer since we can directly probe it using a lateral bulk heterojunction structure. This type of scanning microscopy could be useful not only for bulk heterojunctions but other photovoltaic materials as well. It is important to note that there are still differences between lateral and vertical cells, such as the direction of transport and the direction of phase separations. However, using SPCM would allow researchers to make direct correlations between morphology, processing techniques, and space charge current, providing answers to vital questions that previously could not be directly probed.

Chapter 3: Investigation of Long Drift Lengths in a non-Langevin Polymer PDTSiTzTz Using Scanning Photocurrent Microscopy

3.1 INTRODUCTION

Organic photovoltaics (OPVs) have been of interest to the energy community for years due to a number of favorable properties these materials possess. The low cost and flexibility of the materials would make it feasible to quickly incorporate into affordable commercial products.⁴ As such, there has been much research devoted to this subgroup of photovoltaic, yet they still lack the efficiency to compete with their crystalline counterparts. The energetic landscape in organic solar cells is complicated by the different intramolecular and intermolecular interactions, presence of both crystalline and amorphous regions, and structural disorder from the flexible polymer. ^{1,83} These effects lead to increased recombination of free carriers and thus lower photoconversion efficiency, inefficient charge collection, and material degradation.⁵ To overcome these obstacles, a greater understanding of the electron dynamics is still necessary to make organic photovoltaics a viable consumer product.

A bulk heterojunction (BHJ) is a common device structure used for OPV materials. BHJs consist of a mixed polymer and fullerene active layer. Due to the low dielectric constant of the materials, a bound electron-hole pair is produced upon photo-excitation, which must then be separated into free carriers and collected at their respective electrodes.¹⁸ The active layer of these cells produced in a lab is commonly around 70-90 nm thick and slightly transparent.²⁷ One way to increase the cell efficiency is to produce more excitons by absorbing more of the incident light, and can easily be done by increasing the thickness of the active layer. Increasing the active layer would

also allows for a wider verity of processing techniques to be used, such as inkjet printing, which is only possible to do at larger thicknesses.¹⁷

In most polymer: fullerene systems increasing the thickness of the active layer leads to an increase in bimolecular recombination: the recombination of two free carriers. Bimolecular recombination is the most common recombination mechanism in OPVs.¹⁶ Once an exciton dissociates into a free electron and hole, each charge must travel to its respective electrode in order to be collected. Increasing the thickness of the active layer leads to a competition between extraction of the free carriers and their recombination.^{84,85} The thickness of the BHJ is therefore, limited by the diffusion length of the free carriers that is on the order of 10-100 nm. The diffusion limited recombination is referred to as Langevin-type recombination.⁸⁶ There are few examples of material systems that do not follow Langevin recombination, among them is the well-studied annealed regioregular poly (3-hexylthiophene-2, 5-diyl) (P3HT): phenyl-C61-butyric acid methyl ester (PC₆₀BM), where high fill factors in devices up to 200 nm have been noted. ⁸⁷

Annealed P3HT has been found to have a bimolecular recombination coefficient lower than predicted from Langevin theory, leading it to be referred to as a non-Langevin polymer. ²² Unannealed and regiorandom P3HT do not exhibit Langevin type behavior, therefore the reduction in bimolecular recombination is attributed to the increase in polymer crystallinity and phase segregation present after annealing. ^{86,88,89} Although this may seem like a viable hypothesis that would result in a decreased bimolecular recombination, there are other polymers that have a reduced bimolecular recombination without any increase in crystallinity.^{7,15} It is still unclear how to modify and construct a BHJ material system that would have this desired characteristic, thus motivating further research into the intrinsic properties of these complex materials.



Figure 3.1 The chemical structure of PDTSiTzTz (a). A schematic of a lateral bulk heterojunction device (b).

A polymer:fullerene system that displays no increase in crystallinity yet low bimolecular recombinaiton is poly [(4,4'-bis (2-ethylhexyl) dithieno [3,2-b: 2', 3'-d] silole)-2,6-diyl-alt- (2,5-bis 3-tetradecylthiophen-2-yl thiazolo 5,4-d thiazole)-2,5diyl] (PDTSiTzTz) blended with [6,6]-phenyl C61-butyric acid methyl ester (PC₆₀BM) has also been found to be a non-Langevin polymers with a bimolecular recombination coefficient of 2.2×10^{-12} cm⁻³ s⁻¹, much smaller than predicted by Langevin theory.^{7,90} The

chemical structure for PDTSiTzTz is shown in Figure 3.1a. This polymer has no indication of crystallization in films that can be correlated to the recombination kinetics; therefore other explanations for the reduced bimolecular recombination must be investigated. ²⁷ In this paper we will use scanning photocurrent microscopy (SPCM) to investigate the space charge regions (SCR) in a PDTSiTzTz:PC₆₀BM lateral bulk heterojunction (LBHJ).

In order to directly probe the photocurrent of a working cell we will implement a LBHJ device structure. Figure 3.1b. shows the device structure of a LBHJ. This device structure allows for use of microscopic and spectroscopic tools to directly probe along the lateral transport direction that is not accessible in a vertical device. By scanning across the length of the device a special photocurrent map can be created as a function of distance from the electrodes. This method enables direct measurement of a device under steady state conditions. The direct spatial information provides complementary information to other methods such as time-resolved microwave conductivity, photogenerated charge extraction in a linearly increasing voltage (photo-CELIV), and transient photocurrent, which depend on analyzing a transient response.^{58,86,91}

Using SPCM along with LBHJ allows us to investigate the device while in the space charge limited regime. Modeling of this device structure predicts three distinct regimes that occur when the transport length of the device is much larger then than the device length. Near the electrodes will be a large SCR where most of the free carriers created are extracted. In between the two SCRs will be a region with no photocurrent where the carriers are too far from the electrodes to be collected, which we refer to as the recombination zone.^{37,41} In addition to the photocurrent map, reflectance and fluorescence images can also be collected simultaneously. Here in we present the results of SPCM on the non-Langevin polymer PDTSiTzTz, showing how it differs dramatically from the

non-Langevin polymer poly ({4,8-bis [(2-ethylhexyl) oxy] benzo [1,2-b: 4,5-b'] dithiophene-2, 6-diyl} {3-fluoro-2- [(2-ethylhexyl) carbonyl] thieno [3,4-b] thiophenediyl}) (PTB7).

3.2 EXPERIMENTAL

The known non-Langevin polymer PDTSiTzTz was synthesized according to modified procedures.92-94 literature The synthesis of the stannylated dithenylthiazolothiazole (DTZ) unit began with a Kumada coupling between 3bromothiophene and tetradecylmagnesium bromide. Subsequent bromination at the 2position using N-bromosuccinimide (NBS) yielded 2-bromo-3-tetradecylthiophene. This was treated with magnesium to form a Grignard reagent, which was reacted in situ with dimethylformamide via a Bouvealt aldehyde synthesis to give the desired aldehyde upon Condensation with dithiooxamide hydrolysis. vield the unsubstituted dithienylthiazolo[5,4-d]thiazole. Subsequent bromination with NBS was followed by treatment with n-BuLi to achieve lithium halogen exchange of the bromines, and then treated with a solution of chlorotrimethylstannane to give the stannylated monomer.

The stannylated silolodithiophene (SDT) unit was prepared by treating silicon tetrachloride with one equivalent of (2-ethylhexyl)magnesium bromide. The resulting mono-alkylated trichlorosilane was isolated and treated with a second equivalent of (2ethylhexyl)magnesium bromide to achieve dichlorobis(2-ethylhexyl)silane. This was then reacted with the trimethylsilyl-protected dibromothiophene to give the silolodithiophene. The trimethylsilyl groups were replaced with bromines through electrophilic isposubstitution to afford the halogenated Stille coupling partner. The DTZ and SDT monomers were copolymerized through a Stille polymerization reaction using tetrakis(triphenylphosphine)palladium(0) as the catalyst and tri(o-tolyl)phosphine as the ancillary co-ligand. The resulting polymer was purified through successive soxhlet extractions and characterized by gel permeation chromatography (GPC) and photophysical methods.

Lateral devices were fabricated by photolithography on a glass substrate with a thickness of 210 μ m. 100 nm electrodes of aluminum (Al) and gold (Au) were deposited via thermal (Denton thermal deposition chamber) evaporation. These metals were chosen as the electrodes for their work functions to suppress reverse bias carrier injection. Prior to deposition of the BHJ active material, the glass substrate was cleaned with phosphoric acid to remove any oxide that maybe present on the Al electrode. A solution of PDTSiTzTz and PC₆₀BM (1:2) in dichlorobenzene was heated for at least 6 hours at 120°C. The solution was then spun-cast on to cleaned substrates at 1000 rpm for 60 s. The sample was then annealed at 70°C for 120min.

SPCM measurements were acquired using 20 μ m, 15 μ m, 10 μ m and 8 μ m channel length LBHJ devices; at biases of -100 V, -150 V, and -200 V. These field strengths are consistent with fields for a working 100 nm device. In order to prevent degradation all scans were done in a nitrogen glove box. The negative bias was applied to the Au electrode, and the Al was grounded. A negative bais was applied via a Keithley sourcemeter and the photocurrent induced by the laser beam was collected via a Lock-in amplifier. The incident light was chopped at 141 Hz. The active area was excited using a 514 nm laser beam (Melles Griot) focused though an oil immersion objective (Zeiss) with a 1.25 numerical aperture and 100x magnification. The focused laser spot is 350 nm diameter for the wavelength used in the experiment. Laser power did not exceed 1.5 μ W, which resulted in an incident power density of 2.53 kW/cm². Even at these high power

densities the sample was stable and showed no signs of degradation during scanning. The sample was raster scanned across the objective using a piezoelectric stage (Queensgate), and induced photocurrent, reflectance and fluorescence were collected simultaneously. A white light bias of 80 W/cm² was applied. This experimental setup in this work is similar to previously described set-ups.^{43,44}

3.2 RESULTS AND DISCUSSION

We used SPCM to investigate the spatial photocurrent within the active region of a PDTSiTzTz:PC₆₀BM LBHJ. Figures 3.2a. and 3.2b. show the photocurrent response for a 20 μ m device with a -200 V applied bias under dark (figure 3.2a.) and white light (figure 3.2b.) conditions. These images were used to construct averaged lines scans like those shown in figure 3.2c. and 3.2d. Figure 3.2c. shows the averaged line scans at three different applied biases under dark conditions, and figure 3.2d. shows the averaged line scans for the device under a white light bias. The dotted vertical line indicates the electrode edge that are clearly visible in the reflection image. The left Al electrode is the grounded cathode that corresponds to the collection of electrons. The right Au electrode is the negatively biased electrode that corresponds to the collection of holes. By using an empirical fit program that convoluted a Gaussian instrument response function to model the size of the laser beam with and a decaying exponential to model the SCR.³⁸ From the fit of the photocurrent at each electrode we are able to extract an exponential decay constant that corresponds to the drift length at each electrode.



Figure 3.2 SPCM images for a 20 μm device with a -200 V applied bias under dark (a) and light (b) conditions. Averaged line scans for the device at all applied bias, under dark (c) and light (d) conditions.

The solid lines in figure 3.2c and 3.2d are the averaged line scans and the dotted lines are fits as described above. Under dark conditions only the scan biased at -200 V showed a SCR near the Al electrode. The measured peak at -200 V has a decay length of 1.6 µm. In contrast, the Au electrode has a clear SCR near it under all tested conditions. The decay lengths for the SCR near the Au electrode in figure 3.2c. are 1 µm, 1.1 µm, 1.8 µm for -100 V, -150 V, and -200 V respectively. As the bias voltage is increased both the peak height and the decay length of the SCR increases. Samples were exposed to a white light bias to see the effect of an increased carrier concentration. Figure 3.2d. shows the averaged lines scans for the same device under a white light bias. Due to the lock-in detection only carriers excited by our chopped laser beam are represented in these scans. Under light conditions the -150 V and -200 V biased scans show an apparent peak near the Al electrode. The decay lengths were 1.6 μ m and 1.8 μ m for -150 V and -200 V respectively. As with the dark scan, the SCR near the Au under light conditions has a larger peak then that near the Al and all peaks can be fit. The SCR decay lengths near the Au under light conditions are 1.6 μ m, 1.8 μ m, 1.8 μ m for -100 V, -150 V, and -200 V respectively. The extracted lengths of the space charge region give us insight to the collection ability of the device. Under dark and light conditions this device is able to collect free carries from about 1.5 µm away from the edge of the electrode. This is much larger then a previously tested Langevin polymer, PTB7, where space charge regions are on the submicron length scale.³⁸

The magnitude of the photocurrent peak depends on a combination of material properties. Mihailetchi et al. have previously described conditions, which would cause increased photocurrent near an electrode is due to accumulation of a carrier at that electrode.⁴² The mean electron and hole drift lengths depend on the mobility, lifetime and the electric field as seen in equation 1, ⁹⁵

$$w_{n(p)} = \mu_{n(p)} \tau_{n(p)} E$$

Where $\mu_{n(p)}$ is the electron or hole mobility, $\tau_{n(p)}$ is the electron or hole lifetime, and E is the electric field applied by the electrodes. In the case where $w_p \ll w_n$ and $w_p < L$, where L is the length of the device, the holes will accumulate much more near the anode then the electron will near the cathode. This accumulation then leads to an enhanced electric field at that electrode and as a consequence, better hole extraction. As a result of the enhanced electric field at the Au, the electric field near the Al decreases, which leads to worse electron extraction then that compared to the hole.⁴² This is seen in the photocurrent line scans in figure 3.2, where there is a large SCR near the holecollecting Au electrode and almost no peak near the electron-collecting Al electrode. The 20 µm device length provides conditions where collection is limited by the mean drift length of the hole, that is seen in the large difference in magnitude of the peaks. As it is difficult to interpret the magnitude of the photocurrent, we will focus on the length of the SCR in order to characterize this system.

The dark and white light conditions can be compared to see how increased carrier concentration affects the SCRs and charge collection. When the device is scanned under a white light bias there is an increase in the carrier concentration compared to that of the dark conditions. As noted previously, due to lock-in detection, the line scans only represent the photognerated carriers excited by the beam. Therefore, the excess carriers created under white light bias are not represented in the line scans. The addition of these photogenerated carriers can fill vacant traps to allow for collection farther from the electrodes. If this were occurring it should lead to an increase in the SCRs length near that electrode. For Al electrode SCR this comparison can only be made when the LBHJ is biased at -200 V, as this is the only bias that provides a peak. The electron SCR exhibits a small increase in the drift length under light conditions, however the change is



Figure 3.3 SPCM images for a 8 µm device with a -200 V applied bias under dark (a) and light (b) conditions. Averaged line scans for the device at all applied bias, under dark (c) and light (d) conditions.

sufficiently small (approximately 200 nm) that it seems the electron drift length is essentially independent of carrier concentration. There are measurable SCR near the Au at all applied biases. Here we also see little change in the decay lengths with white light, and conclude that the holes drift lengths are carrier concentration independent under these conditions as well.

The lateral structure of the device leads to the active material being in the same plane as the electrodes, consequently changing the channel length can give insight to carrier dynamics. The method used to test and analyze the 20 μ m channel length device was used on 15 μ m, 10 μ m, and 8 μ m long devices. In order to highlight the differences between the longer channel lengths (20 μ m and 15 μ m) and the shorter channel lengths (10 μ m and 8 μ m) Figure 3.3 shows the SPCM images and line scans for a 8 μ m device. Figure 3.3a. and 3.3b. show the SPCM image under dark and light conditions, respectively. There are two clear differences between the SPCM images from the 8 μ m device and those from the 20 μ m device. The first is the presence of a large SCR near the Al electrode with a magnitude comparable to the SCR near the Au. The second difference is the lack of a recombination zone. The 20 μ m device had little current in the center of the device, while the 8 μ m channel length has a considerable amount located within the center of the channel.

Figures 3.3c. and 3.3d. shows the average line scans for the 8 μ m device under dark and light conditions, respectively. Unlike the 20 μ m device, the 8 μ m device has a peak near the Al electrode at all applied biases. The extracted decay lengths for these SCRs are 0.9 μ m, 1 μ m and 1.1 μ m for -100 V, -150 V and -200 V respectively. The extracted decay lengths for the SCR near the Au electrode under dark conditions are 1.4 μ m, 1.4 μ m, and 1.4 μ m for -100 V, -150 V, and -200 V respectively. Like the 20 μ m device there is an increase in the magnitude of the photocurrent peak, but small change in the decay length with increasing bias. A key difference between the 20 μ m and the 8 μ m device is that there is no longer an extensive difference between the peak heights of the two SCRs.

For 8 μ m channel lengths under white light conditions there were also SCRs near both electrodes at all applied biases. The extracted decay lengths for SCR under light conditions near the Al are 3.1 μ m, 3.2 μ m, and 3.7 μ m for -100 V, -150 V, and -200 V respectively. The extracted decay lengths for the SCR lengths near the Au under light conditions are 1.5 μ m, 1.6 μ m, and 1.6 μ m for -100 V, -150 V, and -200 V respectively. When the dark and light decay lengths are compared we see a large increase in the SCR decay lengths, unlike the lengths of the 20 μ m device, which showed almost no change. Extracted decay lengths for all channel lengths tested can be found in Table 3.1. The increase in SCR length for the electron-collecting cathode under illumination is much larger than of the longer devices that were tested (20 μ m and 15 μ m), and we take this to signify that the recombination dynamics differ.

Table 3.1 shows the extracted SCR for each electrode for all devices at all voltages tested. The 20 μ m and the 15 μ m device have similar extracted SCR lengths and behavior. In these devices the length of the SCR is approximately 1.5 μ m with some changes in the length due to an increasing applied bias or white light bias. Once the channel length is decreased to 10 μ m there is a more predominate SCR at the Al electrode, as well as a different photocurrent response. Devices with channel length less than 10 μ m have SCR lengths comparable to those with a larger channel length under dark conditions. When these same devices are exposed to a white light bias there is a growth in the SCR near the electron collecting Al electrode, while the SCR near the Au

Extracted SCR lengths								
	Li	ght	Dark					
Voltage	Al	Au	Al	Au				
(V)	(µm)	(µm)	(µm)	(µm)				
-100	3.1	1.5	0.9	1.4				
-150	3.2	1.6	1	1.4				
-200	3.7	1.6	1.1	1.4				
10 (μm)								
-100	1.95	1.65	0.6	1.2				
-150	1.95	2.1	0.75	1.5				
-200	1.5	2.25	0.75	1.575				
15 (μm)								
-100	-	1.8	-	1.5				
-150	1.5	1.95	1.2	1.8				
-200	1.95	2.1	1.5	2.1				
20 (μm)								
-100	-	1.6	-	1				
-150	1.6	1.8	-	1.1				
-200	1.8	1.8	1.6	1.8				

Table 3.1: Extracted SCR lengths for all tested device lengths.

stays about the same. Previous reports have attributed this growth to trap filling, and allowing the free carrier to be collected farther from the electrode. ^{37,78}

It has previously been noted that P3HT field effect transistors display changes in mobility with increasing thickness due to changes in morphology and the disordered nature of the polymer. 96,97 In our lateral devices decreasing the channel length has a similar effect to decreasing the thickness of the device in a vertical cell. Carriers in devices of a smaller channel length will be exposed to a different energetic landscape then those in large devices. Therefore, as we decrease the length of the device we see a difference in the magnitude of the electron peak, or better electron extraction. In addition, channel lengths less than 10 µm have SCR that increase when a white light bias is applied. Because there are more carriers when the white light is applied it can be used to see if there is carrier concentration dependence on the SCR. We see that the 10 µm and 8 μ m SCR lengths are increased by the addition of a white light bias. For the 15 μ m and 20 µm device there is almost no increase in the SCR when a white light bias is applied. This is consistent with other measurements that show this increase is trap filling at the shorter lengths has more of an effect on the carrier mobility then at larger device lengths.³⁴ Furthermore, there is a more dramatic change in the SCR associated with the electrons, and electron traps have been seen in multiple polymer: fullerene systems due to the fullerene molecules.⁹⁸ Decreasing the device length allows for a more uniform field leading to better extraction of the electrons and trap filling is now a relevant recombination pathway and effects the SCR.

One way to compare these devices can be to look at the applied voltage per unit length, but due to differences in the non-uniformity of the film this was not possible for these devices.³⁰ Smaller channel lengths have larger space charge regions as well as



Figure 3.4 Voltage vs. extracted SCR length for SCR near the Au anode (a) and the al cathode (b).

larger peak heights then devices with longer channel lengths even at similar applied voltage per unit length. Subsequently, in figure 3.4. we compare the applied bias to the SCR length under dark and light conditions for each device. Figure 3.4a. shows the applied bias vs. SCR drift length for the SCR near the Au electrode. All of the data points for this SCR drift length, which we attribute to hole accumulation, are within 1 μ m of each other, with almost no change under white light bias. The effect of a higher carrier concentration on the SCR length can be seen when under illumination. The lack of change in the SCR at the Au electrode under illumination indicates the drift length of the carriers remains unchanged even under conditions with higher carrier concentration.

Figure 3.4b. shows the SCR vs. applied bias for the Al electrode. Devices that have channel lengths less than 10 μ m show an increase in the SCR length when perturbed by a white light bias. We hypothesize that this increase is due to the change in carrier concentration, which directly affects the extraction of electrons. An increase in carrier

concentration can lead to the filling of traps that would allow for collection of the electrons farther from the electrode then under dark conditions. As previously seen in figure 3.4a. there is almost no change in the SCR near the Au, we interpret this to imply that predominate traps are electron traps. Deep electron traps have been found previously to be able to dominate over Langevin recombination and to cause deviation from Langevin behavior in P3HT.^{99,100} Deep traps have also previously been seen in this material after being exposed to white light and have been shown to affect the recombination characteristics.³⁴

The length of the SCR can give us insight into the mobility of the carriers in the material. The SCR length is proportional to the mobility ratio of their dominate carriers given by, $\frac{\mu_n}{\mu_p} = \frac{L_a}{L_c}$, where μ_n and μ_p are the mobilites for the electron and holes, respectively and L_a and L_c are the extracted SCR lengths for the anode and the cathode, respectively.⁶⁵ By analyzing the SCR region lengths we can draw conclusions on the changes in mobility. The mobility ratio was calculated at all possible applied voltages and averaged for each length, these are recorded in table 3.2. Under dark conditions. Under light conditions the 10 µm and 8 µm have a large change between the dark and the light conditions, and these are the two devices that display the most amount of photocurrent in the recombination zone. Only the 8 µm device provides conditions where the hole is the faster carrier. These findings are slightly contradictory to those form Slobodyan et al where the hole was the faster carrier in a 50 µm device.¹⁰¹ This may be due to oxidation at the Al electrode that would hinder electron extraction, because our devices are not exposed to oxygen this is not a factor in our measurements.⁴⁰

SCR length Ratio						
Length	Light	Dark				
8 um	0.47	1.40				
10 um	1.25	2.03				
15 um	1.19	1.45				
20 um	1.06	1.13				

Table 3.2: SCR length ratio

Comparing the mobility ratio of the long and the short channel can give us further insight into the mean drift length previously discussed. In the long channel the build up of positive charge near the anode (see figure 3.2.) implies a strong mismatch of mean drift length (equation 1.) where the hole is the carrier with the smaller drift length. The calculated mobility ratios in table 3.2. supports this as the holes have a smaller mobility compared to the electrons. As the length of the device is reduced an SCR near the Al emerges, hence electron collection is more efficient then before. The 8 μ m device in figure 3.3 shows no recombination zone in the device and the largest mismatch in mobility ratio.

The SCR drift lengths in the 10 µm and 8 µm devices are extremely high: on the order of the device lengths. This sought after behavior has been seen in some vertical devices, which allow for fabrication of devices with thicker active layers. ¹⁰² Instead of a recombination zone there is an over lap of the SCR regions, here electrons and holes are accelerated across this quasi- neutral region because of the increase in the field.⁷⁸ We have previously reported lengths on the order of a 100's of nanometers for the very efficient polymer PTB7; here we see lengths three times those reported for PTB7. Figure 3.5 shows the averaged line scans under dark (figure 3.5a. and 3.5c.) and white light (figure 3.5b. and 3.5d.) biased conditions for a device with a PTB7 (figure 3.5a. and 3.5b.) and PDTSiTzTz (figure 3.5c. and 3.5d.) BHJ. While PTB7 has the capacity to produce efficient OPVs, it's optimal efficiency is still very limited by the thickness of the

active layer.⁸⁰ The device made with PDTSiTzTz has the capacity to collect charges much farther from the electrodes then PTB7.



Figure 3.5. Averaged line scans for PTB7 and PDTSiTzTz under dark (a,c) and white light bias (b,d) conditions

3.4 CONCLUSIONS

A LBHJ device made of a non-Langeivn polymer PDTSiTzTz and PC₆₀BM was used to look and carrier dynamics in the active layer. Photocurrent images were constructed as a function of position within the channel, and three distinct regions were found; two SCR and a recombination zone. Devices with channel lengths of 20 μ m, 15 μ m, 10 μ m, and 8 μ m were tested. There were apparent differences between the regions probed for devices that were 20 μ m and 15 μ m when compared to those that were 10 μ m and 8 μ m. Shorter lengths displayed SCR peaks near both electrodes and had a lack of recombination zone. Additionally, these devices also showed an increase in SCR length when a white light bias was applied, which we attribute to carrier concentration dependent mobility. The larger devices do no display this behavior due to large difference in mean drift length causing a uniform electric field in the device.

The SCR lengths are related to the mobility and were used to find the mobility ratio. We found that devices with a channel length of 20 μ m, 15 um, and 10 μ m the hole was the faster carrier. The 20 μ m and 15 μ m devices were severely limited by the large mismatch in mean drift length of the carriers, leading to poor electron extraction and a carrier concentration independent mobility. The 10 μ m had no recombination zone and two distinct peaks near both electrodes. In the 8 μ m device we saw the most dramatic shift in dynamics. There was no recombination zone and the SCR was most affected by the increase in carrier concentration. This device had a mobility ratio less than 0.5, therefore at this point the hole mobility was greater then the electron mobility.

PTB7 is a Langevin polymer that has been found to make efficient BHJ devices, yet it is highly limited by the thickness of the device. The SPCM line scans for PTB7 were used to compare those form PDTSiTzTz. We found that in a PDTSiTzTz: PC₆₀BM LBHJ it is possible to collect carries much further from the electrodes then it is from a device with a PTB7: $PC_{60}BM$ active layer. Both LBHJ devices tested that were tested had a 10 µm channel length, yet they exhibited very different recombination dynamics. PTB7 has no current in the center of the device, and PDTSiTzTz has a significant amount of current that could be generated in the center of the device. This leads to the conclusion that it maybe possible to use PDTSiTzTz as an active material in thicker BHJ devices. There few polymers that exhibit this non-langevian behavior, one being the polymer studied here PDTSiTzTz. Additional study of the non-Langevian behavior seen here can lead to better insight for designing polymers with this highly sought after property and further the evolution of thin film organic solar cells.

Chapter 4: Scanning Photocurrent Microscopy of a Planar CH₃NH₃PbI₃ Solar Cell

4.1 INTRODUCTION

Research in crystalline PVs have led to an increase in efficiency and a lowering of production cost of energy to levels similar to those obtained from fossil fuels.¹⁰³ There is still a drive to further lower the costs by using new materials. One new class of materials that has been a major focus of research in recent years are is organometallic halide perovskites, owing to their extremely high efficiency and low cost.¹⁰⁴ Along with their high solar-to-electrical power conversion efficiencies, these materials also possess the added benefit of being solution processable.^{104–106} There has been extensive research on methylammonium lead halide perovskites, such as, CH₃NH₃PbI₃, CH₃NH₃PbBr₃, and CH₃NH₃PbCl₃ due to their large optical absorption range and excellent electronic properties.^{107–109} Efficiencies of these cells have been steadily rising and have reached 20% for a very small area cells (0.1cm²).¹ Although great increases in efficiency have been made, the underlying photophysics are still not well understood.

Processing techniques to increase grain size and control morphology have been a major focus of research in this field, but the overall impact of these characteristics is not yet fully understood. Theoretical studies have shown that the grain boundaries do not introduce deep defect trap states, which maybe explain the long carrier diffusion lengths exhibited by these materials.¹¹⁰ However, large grains may still be favorable for device performance, due to a potential barrier for electron transport that has been found at the grain boundries.^{111,112} There is also debate whether control of the orientation of the polycrystalline phase of a solution-processed film is crucial to improving the efficiency of these cells.^{113,114} Molecular dynamic simulations have indicated that it would be possible to improve charge separation and extraction in lead iodide perovskites through

the careful control of the film surface orientation and crystallization.¹¹⁵ Yet, solutiondeposited films are composed of a mix of orientations of the polycrystalline phase and have exhibited long carrier life times despite this.¹¹⁶

Attempts to understand these materials have been undertaken by microscopists, spectroscopist, and theorists. Long range balanced electron and hole transport lengths have been found using femtosecond transient optical spectroscopy on films with different electron or hole transporting layers.¹⁰⁷ Additionally, photoluminescence quenching measurements found diffusion lengths greater than 1 µm in a solution processed perovskite thin films.¹¹⁷ Wen et al. studied the impact of morphology on carrier transport using one- and two- photon fluorescence microscopy, which allowed separation of surface and bulk effects on the carrier transport and recombination.¹¹² They found that the imperfect interface between the electron or hole transporting layer and the grain boundaries have a negative effect on charge extraction. Additionally high photoluminescence has been correlated with long carrier life times and better PV performance. ¹¹⁸ SPCM will be used to verify the correlation between high photoluminescence and increase photocurrent.

Although many works have focused on thin perovskite films, there is still no concise picture on transport of carriers and their recombination in a working device. The use of spectroscopic and microscopic techniques will be vital to answering basic questions about these devices. Descheler et al. found that free carriers are created within 1ps and showed very little non-radiative recombination by using transient absorption and transient photoluminescence on a film and a PV device.¹¹⁹ What is most interesting about this study is that these desirable properties were present in both the film and device.¹¹⁹ In order find the impact of morphology on transport and charge extraction in a device, this

study will use scanning photocurrent microscopy (SPCM) to look at carrier behavior on a mesoscale instead of using averaged device properties.

SPCM has been a valuable tool for looking at recombination and transport in multiple systems. It has been used to map the spatial heterogeneity in Cu (In_{1-x}Ga_x) Se₂ nanocrystals, and found that CdS aggregates were detrimental to the photocurrent.⁴³ SPCM has also been used in combination with a lateral bulk heterojunction structure to investigate space charge regions in organic photovoltaics.^{37,38} Here we investigate a planar CH₃NH₃PbI₃ perovskite, with a schematic of the device shown in figure 4.1a. The device structure includes a transparent fluorine-doped tin oxide (FTO) coated glass, coated with a compact layer of TiO₂ that acts as the hole-blocking layer. The perovskite is then solutions deposited on the TiO₂ using a two-step method, followed by a 2,2',7,7'-tetrakis- (N, N-di-p-methoxyphenylamine) 9,9'-spirobifluorene (spiro-OMeTAD) electron blocking layer and a gold (Au) top contact. This is a common device architecture, which has been extensively studied by other groups.^{120–123}


Figure 4.1. a) Device architecture of a planar CH₃NH₃PbI₃ perovskite solar cell and b) scanning microscope set-up.

A schematic of the scanning photocurrent microscope is shown in figure 4.1b where a laser beam is focused through an extra long working distance objective in order to focus through the glass on which the perovskite layer lies. By raster scanning the sample across the objective we can collect photocurrent, photoluminescence and reflectance information as a function of position. In addition to this information, the polarization of the laser beam can be changed from 0° to 90° that will provide information on the mesoscale orientation of the film, as well as the effects of the orientation on the photocurrent.

4.2 EXPERIMENTAL

All chemicals were procured from Sigma-Aldrich unless stated otherwise

Solar cells were made based off modified procedures reported on elsewhere.^{124,125} Cells were optimized for signal, not for efficiency, in this report. In a typical experiment, 1"x1" fluorine-doped tin oxide (FTO) substrates (Hartford Glass Co, TEC 15) were patterned with zinc powder (Fluka) and hydrochloric acid (37 wt%, Fisher Scientific). After rinsing thoroughly with water to remove residual acid and zinc, the substrates were washed with 2% Hellmanex in water, DI water, and then left to sonicate in ethanol for ~30 minutes. To remove residual organics, a 30 minute UV-Ozone treatment was also performed.

A compact layer of titanium dioxide was deposited by spin-coating a 0.2 M solution of titianium isopropoxide bis-acetylacetanoate (TAA) in 1-butanol, followed by treatment at 500 C for 1 hour. Lead iodide (Alfa Aesar, ultra dry, 99.999%) was dissolved 1 M in dimethylformamide (DMF) with 24 mg/mL methylammonium iodide (MAI, Solaronix) for 2 hours at 70 °C. In a separate vial, a 10 mg/mL solution of MAI in isopropyl alcohol (IPA) was mixed. The two-step perovskite deposition was performed

by spin-coating the lead iodide solution, post-filtering, at 6000 rpm for 15 seconds onto substrates and annealing for 5 minutes at 150 C, followed by spin-coating the pure MAI solution at 4000 rpm for 15 seconds and a one minute anneal at 150 C. A hole transporting material (HTM) layer was mixed by adding 72 mg/mL 2,2',7,7'-Tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene (spiro-OMeTAD, Luminescence Technology Corp) to anhydrous chlorobenzene with 28.8 μ L/mL 4-tert-butylpyradine (TBP), 26.5 μ L/mL bis-(trifluoromethane)sulfonimide lithium salt (LiTFSI) stock solution, and 17.5 μ L/mL FK 102 cobalt (III) TFSI stock solution (CoTFSI, Dyesol). The stock solutions of LiTFSI and CoTFSI were 520 mg/mL and 300 mg/mL, respectively, in anhydrous acetonitrile. This HTM solution was spun onto the substrate at 5000 rpm for 20 seconds and dried in a desiccator overnight. After this, 60 nm of gold was evaporated as a top contact, and external contact points were covered with silver paint for an improved contact interface.

SPCM measurements were acquired under short circuit conditions at zero volt bias and the resulting photocurrent was measured using a Keithley sourcemeter with the photocurrent induced by the laser beam was collected via a Lock-in amplifier. The incident light was chopped at 141 Hz. The active area was excited using a 514 nm laser beam (Melles Griot) focused though an extra long working distance objective (Nikon) with a 0.7 numerical aperture and 60x magnification. The focused laser spot is 350 nm diameter for the wavelength used in the experiment. Laser power did not exceed 5 μ W, which resulted in an incident power density of 5.2 kW/cm². Even at these high power densities the sample was stable and showed no signs of degradation during scanning. The sample was raster scanned across the objective using a piezoelectric stage (Queensgate), while induced photocurrent, reflectance and fluorescence were collected simultaneously. Fluorescence was collected using a long pass filter. The polarization was changed using a polarizer and a half waveplate.

4.3 RESULTS AND DISCUSSION

The reflectance and photocurrent images of an area with a large drying ring defect in the perovskite cell are shown in figure 4.2. Grain sizes in perovskite thin film can range from nanometer to micrometer in length.^{116,126} The two step method used to make this perovskite film produces grains that are about 50nm in size.¹⁰⁸ The reflectance image (figure 4.2a.) shows small round features with diameters of about 1.5 μ m, indicating that individual grains are beyond the resolution of this microscope set-up. Variation in the reflectance intensity is due to the variations in the thickness of the film. The drying ring causes great fluctuation in the reflectance due to the large and rapid changes in material thickness. Differences in transparency can be seen by eye when films are being made at this type of defect sites. The inconsistencies in film thickness cause the photocurrent to fluctuate as well.

There are fewer variations in the photocurrent image (figure 4.2b) then in the reflectance. Unlike the reflectance image, which shows great detail about the film morphology, the photocurrent is more uniform. The photocurrent also has broader features compared to the reflectance image indicating long carrier diffusion lengths. Micrometer long diffusion lengths in solution processed films have been reported and partially explained by unusual defect physics in these materials.¹¹⁷ Yin et. al. applied first–principle calculations to show that shallow defects lead to increased carrier life time and diffusion.¹²⁷ The lack of detail in the photocurrent suggest that the individual grains do not hinder transport in the cell, and that nanoscale morphology may not have a large

effect on long range transport. High reflectance is indicative of lower absorbance as long as the



Figure 4.2. Reflectance (a) and photocurrent (b) images of perovskite solar cell.

reflectivity is constant through out the film. Yet, areas of high reflectance have little effect on the photocurrent of the film. Even in the presence of the large defect the photocurrent remains mostly constant suggesting that only the large drying feature has and effect on absorption.

This area of the device has a more homogenous morphology than that in figure 4.2, therefore the photocurrent is not as dependent on the thickness of the film as it was in the previous figure. In order to study the mesoscale organization of the film the polarization of the excitation beam was changed. Figure 4.3a. and 4.3c. are the photoluminescence and photocurrent images, respectively, acquired using an excitation beam with 0° polarization. Figure 4.3b. and 4.3d. shows the photoluminescence and photocurrent images are excitation beam with 90° polarization.

Mesoscopic variation in the photoluminescence will be due to changes in absorption of the polarized excitation beam due variations in to perovskite phase composition and orientation.¹²⁸ Ordered structures have a polarization dependent absorption, while a mixture of orientations will not. Some regions like this are detected and highlighted in figure 4.3a. and 4.3b., the areas labeled with an white circle have a low photoluminescence count in the 0° image (fig4.3a.), but a higher photoluminescence count in the 90° image (fig 4.3b.), thus indicating a predominantly highly ordered phase. The amount orientation of the polycrystalline phase in the film is highly dependent on the production process (annealing, deposition, treatments etc.), and multiple attempts by researchers have been made to control it.^{116,124} In contrast to these polarization dependent areas, there are other domains that do not depend on the polarization of the excitation beam. One such domain is labeled in figure 4.3a. and 4.3b. as black circle, where there are high photoluminescence counts in both images. These areas emerge due to the

presence of unorganized polycrystalline domains that have been found in solutionprocessed films.¹²⁹ Strong photocurrent response from these isotropic regions are outlined



Figure 4.3. Photoluminescence (a and b) and Photocurrent (c and d) images taken using 0° (a and c) and 90° (b and d) polarized excitation beams.

by the black circles in figure 4.3c and 4.3d, indicating that large-scale orientation may not be necessary to optimize these films.

The SPCM images can be used to determine if there is a correlation between high photoluminescence and high photocurrent. Areas of high photoluminescence do correlate with areas of high photocurrent and vice versa, this can be seen in the areas marked by black and white circles in figure 4.3a and 4.3c. This correlation can easily be seen in figure 4.4. Figure 4.4 is a line scan of the photocurrent and fluorescence images using a 0° (figure 4.4a) and 90° (figure 4.4b) polarized excitation beam, the dotted line in figure 4.3 shows where the line scan was taken. This increase of both the photoluminescence and the photocurrent is indicative of a decrease in non-radiative recombination.¹¹⁹ Though there are few points that deviate from this trend: the red dotted line in figure 4.4a. and 4.4b. is an example of a deviation. Along this line, an increase in photoluminescence does not correspond to an increase in photocurrent indicating that non-radiative recombination pathways or charge extraction barriers are present and affect the photocurrent.

In order to quantify the correlation between the fluorescence and the photocurrent a statistical linear correlation test was performed. This test calculates a linear correlation coefficient (r) between the two images. The r-value can range from -1, which would correspond to two images that were completely anti-correlated, to 1, which would indicate that the images were completely correlated. An r-value of $+0.6088\pm0.0039$ was calculated between 0° polarization photocurrent and photoluminescence. Considering the size of the image, both are strongly correlated. The 90° polarization also shows strong correlation, with a calculated r-value of $+0.5390\pm0.0042$. Perovskite films have demonstrated that efficient photoluminescence quantum yield correlates to high efficiency, and it has been shown that there are few non-radiative recombination pathways.¹¹⁹ The SPCM images show few instances where the photoluminescence and



Figure 4.. Line scans from photocurrent and photoluminescence images using 0° (a) and 90° (b) polarized excitation beams.

photocurrent do not correlate, but the increase in photoluminescence and decrease in photocurrent shown by the dotted red line in figure 4.4 is an instance where a non-radiative decay is present within the device.

Like figure 4.2, the photocurrent image in figure 4.5 has a broader photocurrent image when compared to the photoluminescence. An explanation for this broadening is that the photocurrent depends on how close it is to the bright photoluminescent features, and if the carriers are excited near these regions they can be extracted. Therefore, we can extract a diffusion length by comparing the two images. We are able to artificially recreate a fluorescence images with better correlation to photocurrent images by convolving each pixel in the image with a Gaussian using a convolution filter. Figure 4.5 the original photoluminescence (4.5a), photocurrent (4.5b), image after convolution (4.5c), and the photocurrent scaled to better visualize the fluctuations in photocurrent (4.5d). Figure 4.5 is 20µm x 20µm window of figure 4.3. Figure 4.5c was compared to the photocurrent using the statistical correlation test and the convolved image increased the r-value by 0.0979, therefore confirming that they are indeed better correlated. The width of the Gaussian used to convolve the image can be converted to find a diffusion length of 1.1 µm for free carriers. This length is larger then previously reported for this material.^{111,117} Stranks et. al. previously determined the diffusion for the electron and the hole exceeded a micrometer in a CH₃NH₃PbI_{3-x}Cl_x film using photoluminescence quenching measurements. The diffusion lengths for CH₃NH₃PbI_{3-x}Cl_x were found to be smaller, about 400 nm. The discrepancy between these numbers is most likely due the difference in experimental set-ups, as SPCM uses a working device while photoluminescence quenching methods require multiple films with either an electron- or hole-blocking layer.



Figure 4.5. a) Original fluorescence image, b) original photocurrent image ,c) convolved fluorescence image, and d) original photocurrent image modified scale.

4.4 CONCLUSIONS

As we find new materials for photovoltaics it is important to understand the basic photophysics of the material to best optimize the device based on these materials. By looking at an area with a large defect site using SPCM we found that the amount of light absorbed relative to the rest of the film has little effect on the photocurrent for this device. Other researchers have found that the non- radiative recombination pathway is strongly inhibited in organometallic perovskites, making them an excellent material for PVs. Unlike other PV materials where radiative recombination is detrimental to the photocurrent, the increased radiative recombination is correlated to high photocurrent.⁴⁴ SPCM allows for simultaneous mapping of both the fluorescence and photocurrent. SPCM images show that an increase in the radiative decay correlates with an increase in photocurrent in a working device, indicating that there is suppressed non-radiative decay.

SPCM images also indicate that the photocurrent is not hindered by the grain boundaries of the film as seen figure 4.2, and large-scale orientation may not necessary to optimize the PV device. The photocurrent images suggest that there is still enough nonradiative decay to have detrimental effects on the current produced in a solution deposited film. Owing to the decreased non-radiative recombination, few detrimental large-scale morphological and orientation effects, pervoskites are an ideal candidate for solution deposition. Efforts to increase the efficiency of these devices through integration of a mesoporous layer and quality of electron and hole blocking layers are still on going, and promising in such a new field.

Chapter 5: Probing New Device Structures with SPCM

5.1 INTRODUCTION

There have been significant improvements in the photoconversion efficiency of solar cells based on organic materials. Another factor that prevents these materials from being used in commercial cells is the operational lifetime of the cell. Many materials that are a focus of photovoltaic research suffer from significant degradation effects. Organic photovoltaics can degrade when exposed to air and long exposure to light. ^{8,40,130,131} Perovskite solar cells have been a popular research subject in the recent years, yet it they are unstable in the presence of water.¹³² Recently the effects of rain water on a perovskite cell were investigated and found that the rain would cause irreversible damage to the absorbing layer.¹³³ There is a need to find materials that are not only efficient, but also durable and retain integrity in the harsh conditions they will be subjected to.

Cu (In, Ga) Se2 (CIGS) based cells have proven their stability in long term out doors testing.^{134,135} These cells even show better stability under electron and proton radiation then conventional high efficiency Si and GaAs cells.^{136,137} However, they also suffer from similar drawbacks that conventional cells do, specifically they are costly to produce. In order to construct an efficient photovoltaic with a large functional area it is necessary to control the stoichiometry of the CIGS.¹³⁸ A way to produce CIGS layers with controlled stoichiometry and without high annealing temperature is to make nanocrystals then deposit them from solution to make the photoactive region of the solar cell.¹³⁹ Progress has been made in the nanocrystal synthesis of CuInSe₂ with hopes of producing an efficient solar cell that can be processed from solution.¹⁴⁰ Solution Additionally, this approach also allows for application on to flexible device structures, which is attractive due possible integration with a greater number of consumer products.

Yet so far the efficiency of the nanocrystal devices is not high enough to compete with their polycrystalline counter parts.

As with other materials deposited from solution the efficiency is not competitive against those that are made using more extreme conditions. An innovative way to improve the efficiency is through engineering of the device architecture. Inverted geometries have been implemented and have successfully made efficient PVs.¹⁴¹ A tandem architecture has been employed with a variety of materials.^{142–144} Patterning of substrates has been used to increase scattering and increasing absoption.¹⁴⁵ It is important to tailor the device architecture to the material in order to take advantage of its particular properties. Vahid et. al. demonstrated that CdInSe₂ nanocrystal are limited by the thickness of the active area to about 50 nm, therefore it is important to use a structure that can control the thickness of the active layer.

A grooved architecture has been developed in order to be able to construct small parallel devices with minimal processing. Figure 5.1a shows a schematic of the layers in the groove. The blue layer is a polymer composite that makes up the entirety of the substrate. The selective contacts in the groove are achieved via angled vacuum deposition of Al, Au, and CdS. The nanocrystals are then deposited on top of the entire device. In addition to limiting the thickness of the active area this structure has the added benefit of increasing absorption through photon scattering and multiple channels can easily be linked in series. A SEM image of multiple channels is shown in figure 5.1b. In order to find the bulk efficiency of a cell the active are should be know. Due to the architecture of the cell current produced outside of the cannel can lead to an overestimation of the efficiency. Electrical characterization gives insight to the efficiency of the bulk device, but there is a need to further characterize this device structure to fully understand where

the photocurrent is concentrated. Additionally, the lateral direction of transport makes this device structure an ideal sample to study the photocurrent using SPCM.



Figure 5.1.a) A schematic of the layers in the grooved device. b) SEM image of a device with multiple grooves.

5.2 EXPERIMENTAL

CuInSe₂ nanocrystals (NCs) were synthesized using oleylamine (OLAm, Aldrich), diphenylphosphine (DPP, Aldrich), and tributylphosphine (TBP, Aldrich) as coordinating ligands which has previously been reported.^{146,147}The following compounds were placed under vacuum at 115°C for 30 min, 2 mmol indium trichloride (InCl₃), 2 mmol copper chloride (CuCl), and 16 mL OLAm, and then storedin a nitrogen atmosphere. 4 mmol selenium powder (Se, Aldrich) was dissolved in a mixture of 2.5 mL TBP and 1.5 mL DPP at 60°C with. The CuCl, InCl₃, and OLAm mixture was raised to 180°C, and then the Se-DPP-TBP solution was added. This mixture was held at 180°C for 30 minutes and then the temperature was increased to 240°C and held constant for 10 mins. Substrates are made via sequential angled vacuum deposition.

Nanocrystals were purified using solvent/antisolvent precipitation. The product (20 mL) was collected in a centrifuge tube, and 14 mL ethanol was added. The mixture was centrifuged at 4500 rpm for 2 minutes. The supernatant was discarded and 10 mL toluene was added to redisperse the dry flocculate. 7.5 mL ethanol was added to this dispersion before centrifugation again at 4500 rpm for 2 minutes. This step was repeated twice more. The supernatant was kept and diluted to a concentration of 50 mg/mL for storage.

SPCM measurements were acquired under short circuit conditions at zero volt bias and the resulting photocurrent was measured using a Keithley sourcemeter and the photocurrent induced by the laser beam was collected via a Lock-in amplifier. The incident light was chopped at 141 Hz. The active area was excited using a 514 nm and 633 nm laser beam (Melles Griot) focused though an UMPlanFl objective (Olympus) with a 0.8 numerical aperture and 50x magnification. The focused laser spot is 490 nm and 604 nm in diameter for the wavelength used in the experiment. Laser power did not exceed 5 μ W, which resulted in an incident power density of about 2.65 kW/cm². Even at these high power densities the sample was stable and showed no signs of degradation The sample was raster scanned across the objective using a during scanning. piezoelectric stage (Queensgate), and induced photocurrent, and reflectance were collected simultaneously. A white light bias was applied to the sample using a broadband fiber optic illuminated (Thor Labs) and was calibrated to one sun (note. figure 5.2 was illuminated with less then one sun). The white light bias was applied from above, therefore in the opposite direction of the laser probe.

5.2 RESULTS AND DISCUSSION

Figure 5.2 shows reflectance (a) and photocurrent images under dark (b) and white (c) light biased conditions with a 514 nm excitation beam. The channel is millimeters in length and the scan size is 80 μ m x 80 μ m, therefore this is only partial, but representative, sample of the device area. The reflectance image shows features from the deposition and drying of the nanocrystal solutions. Under dark we see that the photocurrent is not limited to the 1 um channel as originally hypothesized. Instead the current is along the flat to the right. Electrons are the majority carrier for the CdS layer, which allows extraction of electrons not only in the channel but also the flat. Since the deposition of the nanocrystal is not limited to the channel this can allow for other areas along the CdS to collect. The majority carrier in the CIS nanocrystal is the hole that has a long diffusion length and can travel the long lengths necessary to be extracted at the gold.



Figure 5.2 a) reflectance image of single groove solar cell. Photocurrent image take under dark (b) and white light biased (c) conditions.

A white light bias was applied to the grooved sample and the result is shown in Figure 5.2c. The white light bias was applied from above the sample, opposite in the direction from the laser probe, therefore the power of the white light biased is much less

then expected due to absorption from the back layers. Applying a white light bias will still increase the amount of carriers in the device. As previously mentioned the carriers created by the white light bias are not represented in the photocurrent due to the lock-in detection. The white light biased photocurrent shows there is a drop in the distance that carriers can be collected from. The increase in carrier concentration also increases the probability of bimolecular recombination of the free carriers. Modeling of the grooved devices shows that the majority carrier in the CIS nanocrystal will limit the photocurrent. Due to the almost millimeter lengths, if the flat outside of the scan size is considered, that the hole must travel to be collected and increase in carrier concentration, there will be increase in the probability of recombination and decrease in the drift length. This effect when the white light bias is applied.



Figure 5.3 a) Reflectance image of single groove solar cell. Photocurrent image take under dark (b) and white light biased (c) conditions.

Although the single channel displayed a larger active area then anticipated the goal of the channel device is not to have one channel but many channels on a single substrate connected in series. Figure 5.3 shows the reflectance (a) and photocurrent images under dark (b) and white (c) light biased conditions with a 514 nm excitation beam of a three-channel device. The reflectance image in figure 5.3a. shows a similar

morphology to that of a single channel that is due to the method of sample preparation. The three-channel sample also develops photocurrent outside of the channel area similar to the single channel. Figure 5.3b. shows photocurrent well out ide of the channel. There is also a grain-like structure in the photocurrent that can be attributed to a rough substrate surface. In figure 5.3c. we see a similar decrease in current as with the single channel device due to the increase in carrier concentration under illumination. In order to look at the photocurrent in more detail a single line scan from the dark and white light biased photocurrent images are shown in figure 5.4. Note that the effects of the substrate surface results in very inconsistent photocurrent. Improvement in substrate processing maybe beneficial to improved solar cell performance.



Figure 5.4 A line scan of the photocurrent image under dark (a) and white light biased (b) conditions.



Figure 5.5 Reflectance (a), dark (b), and white (c) light biased photocurrent images of a 3-channel device using a 633 nm excitation beam

CdS thin films have and optical band gap of about 538nm. In order to confirm that the photocurrent was exclusively from the nanocrystals the sample was excited with a 633 nm excitation beam. Figure 5.5 shows the reflectance (a) and the photocurrent image under dark (b), white (c) light bias conditions. It is useful to note that the images in figure 5.3 and figure 5.5 are not the same device. Differences in the reflection between the two are due to changes in the wetting of the solution due to differences between the substrates. Variably in substrates is known to affect the efficiency between similarly prepared devices.^{148,149} Unlike illumination 12 512nm figure 5.3b, in figure 5.5b the photocurrent is smooth. Processing variability from substrate cleaning or thin film deposition may be the cause for the differences in the photocurrent between two substrates seen in figure 5.3b. and 5.5b. Additionally, there is a significant contribution to the photocurrent from the other



Figure 5.6 Line scans of the dark (a) and white light (b) bias photocurrent image.

two channels than there was in the devices shown in figure 5.3. This contribution is enhanced when the white light bias is applied, and can clearly be seen in figure 5.6. Figure 5.6 shows the line scan for the photocurrent image in figure 5.5 under dark (a) and white light biased (b) conditions. Once again we see that there is less contour in the photocurrent then that in figure 5.4, now the majority of the photocurrent is located near the channel. There is a much larger contrast between the dark and white light biased there was in figure 5.4. The line scans show much less photocurrent contribution from the flat area outside of the channel under a white light bias (fig 5.4b) then there was in the prior device. Under white light conditions there is more photocurrent in locations where it was expected then before. Due to these results we can conclude that the photocurrent in the flats is not only due to the CIS nanocrystals but also due to inhomogeneities in present in the substrate due to variations while layers are made.

To confirm that the decrease in photocurrent from the flat is due to inconsistencies between substrates and not due to the CdS layer, the same sample was probe with a 488nm excitation beam to ensure excitation of the CdS layer. Figure 5.7 shows the reflectance (a), photocurrent images with dark (b) and white (c) light biased photocurrent image. The reflectance image 5.7a shows a similar morphology to that in 5.5a. Figure 5.7b. shows a very sharp peak near the last channel and much smaller contribution to the flat photocurrent then that seen in figure 5.5a. confirming that the flat photocurrent is in fact from the CIS layer and a result of the substrate. The higher energy excitation caused an increase in photocurrent, but the photocurrent on the flat is still homogenous. The effects of the white light bias are seen in figure 5.7c. and just as in figure 5.5c there is a decrease in the amount of photocurrent that can be collected away from the channel



Figure 5.7. Reflectance (a), photocurrent under dark (b) and white (c) light biased conditions of a 3-channel device using a 488 nm excitation beam

Lines scan of the images in Figure 5.8 show that the decrease in the contributions form the flats under dark (a) and white light (b) biased samples is much more apparent. Contributions from the other channels are more dependent on the white light bias when excited by the 488 beam. Figure 5.8c is the only instance where the photocurrent broadens upon illumination. This is most likely an abnormality with in the cell. Due to the nature of the experiment, figures 5.5 and 5.7 are not taken at the same spot and therefore this may be a localized occurrence in this spot in the cell.



Figure 5.8 Line scans of the dark (a) and white light (b) bias photocurrent image.

5.3 CONCLUSIONS

SPCM was used to look at the effects of a new device architecture on the photocurrent. We have found that the photocurrent is not limited by the channel width and there are contributions from the flats. When another substrate was investigated to probe the contribution from the nanocrystals there was less photocurrent that occurred at the flats and decreased substantially when a white light bias was applied. This decrease in photocurrent was attributed to irregularities between substrates from processing. There is hope of making a device with an active area of 1um, but there is also a need to make a homogenous surface and decrease variability between substrates.

SPCM has been used to look at the effects of an additives effect on SCRs., a polymer with irregular properties, a new class of materials, and new device architecture to investigate the effects on the bulk performance of the cell. There is a need to not only focus on processes that occur on the nano-scale but also on the meso-scale. Using SPCM allows us to visualize of the photocurrent on a number of scales. Here we see that the inability to reliably reproduce the same substrate surface causes large change in the photocurrent. Efforts should focus first on the substrate in order to better be able to make conclusions about photocurrent produced by the nanocrystals.

This technique has been able to reproduce photocurrent data using air and water sensitive materials by setting up the microscope in a glove box. In order to further advance the technique it is critical use other techniques to complement the data. KPFM data would greatly benefit the photocurrent images. However just as this technique was limited before the use of n inert atmosphere is it essential to tailor the experimental set-up for the material in order to have reproducible results.

This dissertation has shown that photocurrent imaging along with photoluminescence information can provide information vital to understanding the transport properties of a number of photovoltaic materials. Using SPCM we can gain insight to the localized photocurrent instead of bulk properties. SPCM was used to study the SCRs in a Langevin and non-Langevin polymer, and found that the SCRs are much larger in the non-Langiven device. The photocurrent and photoluminescence of a perovskite solar cell were found to be correlated, and confirm prior research that suggested increase photoluminescence might increase the efficiency. Finally, a grooved device was found to have a larger active area. Visualizing the photocurrent in a device allows researchers to find the flaws within the device and ultimately find ways to limit them.

Reference

- (1) Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W.; Dunlop, E. D. Solar Cell Efficiency Tables (Version 45). *Prog. Photovoltaics Res. Appl.* **2015**, *23*, 1–9.
- (2) Ramanathan, K.; Contreras, M. A.; Perkins, C. L.; Asher, S.; Hasoon, F. S.; Keane, J.; Young, D.; Romero, M.; Metzger, W.; Noufi, R.; et al. Properties of 19.2% Efficiency ZnO/CdS/CuInGaSe2 Thin-Film Solar Cells. *Prog. Photovoltaics Res. Appl.* 2003, *11*, 225–230.
- (3) Shaheen, S. E.; Ginley, D. S.; Jabbour, G. E. Organic-Based Photovoltaics: Toward Low-Cost Power Generation. *MRS Bulletin*, 2005, *30*, 10–19.
- (4) Su, Y.-W.; Lan, S.-C.; Wei, K.-H. Organic Photovoltaics. *Mater. Today* **2012**, *15*, 554–562.
- (5) Darling, S. B.; You, F. The Case for Organic Photovoltaics. *RSC Adv.* **2013**, *3*, 17633.
- (6) Shrotriya, V. Organic Photovoltaics: Polymer Power. *Nat. Photonics* **2009**, *3*, 447–449.
- Peet, J.; Kim, J. Y.; Coates, N. E.; Ma, W. L.; Moses, D.; Heeger, a J.; Bazan, G. C. Efficiency Enhancement in Low-Bandgap Polymer Solar Cells by Processing with Alkane Dithiols. *Nat. Mater.* 2007, *6*, 497–500.
- (8) Scharber, M. C.; Sariciftci, N. S. Efficiency of Bulk-Heterojunction Organic Solar Cells. Prog. Polym. Sci. 2013, 38, 1929–1940.
- (9) Deibel, C.; Dyakonov, V. Polymer–fullerene Bulk Heterojunction Solar Cells. *Reports Prog. Phys.* **2010**, *73*, 096401.
- (10) Yang, Y.; Li, G. Progress in High-Efficient Solution Process Organic Photovoltaic Devices; Yang, Y.; Li, G., Eds.; Topics in Applied Physics; Springer Berlin Heidelberg: Berlin, Heidelberg, 2015; Vol. 130.

- (11) Grancini, G.; Fazzi, D.; Binda, M.; Maiuri, M.; Petrozza, A.; Criante, L.; Perissinotto, S.; Egelhaaf, H.-J.; Brida, D.; Cerullo, G.; et al. Ultrafast Exciton Dissociation at Donor/acceptor Interfaces. In *Proc. SPIE*; Banerji, N.; Silva, C., Eds.; 2013; Vol. 8811, p. 88111D – 88111D – 8.
- (12) Sheng, C.-X.; Tong, M.; Singh, S.; Vardeny, Z. V. Experimental Determination of the Charge/neutral Branching Ratio η Conjugated π-Polymers by Broadband Ultrafast Spectroscopy. *Phys. Rev. B* 2007, *75*, 085206.
- (13) Paquin, F.; Latini, G.; Sakowicz, M.; Karsenti, P.-L.; Wang, L.; Beljonne, D.; Stingelin, N.; Silva, C. Charge Separation in Semicrystalline Polymeric Semiconductors by Photoexcitation: Is the Mechanism Intrinsic or Extrinsic? *Phys. Rev. Lett.* **2011**, *106*, 197401.
- (14) Shaheen, S. E.; Radspinner, R.; Peyghambarian, N.; Jabbour, G. E. Fabrication of Bulk Heterojunction Plastic Solar Cells by Screen Printing. *Appl. Phys. Lett.* 2001, 79, 2996.
- (15) Adriaenssens, G. J.; Arkhipov, V. I. Non-Langevin Recombination in Disordered Materials with Random Potential Distributions. *Solid State Commun.* 1997, 103, 541–543.
- (16) Lenes, M.; Koster, L. J. a; Mihailetchi, V. D.; Blom, P. W. M. Thickness Dependence of the Efficiency of Polymer:fullerene Bulk Heterojunction Solar Cells. *Appl. Phys. Lett.* **2006**, *88*, 243502.
- (17) Krebs, F. C. Fabrication and Processing of Polymer Solar Cells: A Review of Printing and Coating Techniques. Sol. Energy Mater. Sol. Cells 2009, 93, 394– 412.
- (18) Koster, L. J. a; Mihailetchi, V. D.; Blom, P. W. M. Bimolecular Recombination in Polymer/fullerene Bulk Heterojunction Solar Cells. *Appl. Phys. Lett.* 2006, *88*, 1–3.
- (19) Langevin, P. Recombinaison et Mobilites Des Ions Dans Les Gaz. Ann. Chim. Phys. **1903**, 28, 122.

- (20) Karl, N.; Sommer, G. Field Dependent Losses of Electrons and Holes by Bimolecular Volume Recombination in the Excitation Layer of Anthracene Single Crystals Studied by Drift Current Pulses. *Phys. status solidi* **1971**, *6*, 231–241.
- (21) Mozer, A. J.; Clarke, T. M. Reduced Bimolecular Recombination in Conjugated Polymer Donor/Fullerene Acceptor Bulk Heterojunction Solar Cells. *Aust. J. Chem.* 2012, 65, 442.
- (22) Pivrikas, a.; Juška, G.; Mozer, a.; Scharber, M.; Arlauskas, K.; Sariciftci, N.; Stubb, H.; Österbacka, R. Bimolecular Recombination Coefficient as a Sensitive Testing Parameter for Low-Mobility Solar-Cell Materials. *Phys. Rev. Lett.* 2005, 94, 1–4.
- (23) Koster, L. J. a.; Mihailetchi, V. D.; Blom, P. W. M. Bimolecular Recombination in Polymer/fullerene Bulk Heterojunction Solar Cells. *Appl. Phys. Lett.* 2006, *88*, 052104.
- (24) Deibel, C.; Wagenpfahl, A.; Dyakonov, V. Origin of Reduced Polaron Recombination in Organic Semiconductor Devices. *Phys. Rev. B* 2009, *80*, 075203.
- (25) Juška, G.; Genevičius, K.; Nekrašas, N.; Sliaužys, G.; Österbacka, R. Two Dimensional Langevin Recombination in Regioregular poly(3- Hexylthiophene). *Appl. Phys. Lett.* **2009**, *95*, 8–11.
- (26) Pivrikas, A.; Sariciftci, N. S.; Juška, G.; Österbacka, R. A Review of Charge Transport and Recombination in Polymer/fullerene Organic Solar Cells. *Prog. Photovoltaics Res. Appl.* 2007, 15, 677–696.
- (27) Clarke, T. M.; Rodovsky, D. B.; Herzing, A. A.; Peet, J.; Dennler, G.; DeLongchamp, D.; Lungenschmied, C.; Mozer, A. J. Significantly Reduced Bimolecular Recombination in a Novel Silole-Based Polymer: Fullerene Blend. *Adv. Energy Mater.* 2011, *1*, 1062–1067.
- (28) Peet, J.; Wen, L.; Byrne, P.; Rodman, S.; Forberich, K.; Shao, Y.; Drolet, N.; Gaudiana, R.; Dennler, G.; Waller, D. Bulk Heterojunction Solar Cells with Thick

Active Layers and High Fill Factors Enabled by a Bithiophene-Co-Thiazolothiazole Push-Pull Copolymer. *Appl. Phys. Lett.* **2011**, *98*, 043301.

- (29) Lombardo, C.; Dodabalapur, A. Nongeminate Carrier Recombination Rates in Organic Solar Cells. *Appl. Phys. Lett.* **2010**, *97*, 233302.
- (30) Lombardo, C.; Danielson, E.; Ooi, Z.; Dodabalapur, A. Lateral Mobility Measurements in Organic Bulk Heterojunctions: Comparison of Field-Effect and Space Charge Mobilities. *J. Photonics Energy* 2012, *2*, 021007.
- Bronstein, H.; Chen, Z.; Ashraf, R. S.; Zhang, W.; Du, J.; Durrant, J. R.; Shakya Tuladhar, P.; Song, K.; Watkins, S. E.; Geerts, Y.; et al. Thieno[3,2-B] thiophene–Diketopyrrolopyrrole-Containing Polymers for High-Performance Organic Field-Effect Transistors and Organic Photovoltaic Devices. *J. Am. Chem. Soc.* 2011, *133*, 3272–3275.
- (32) Murthy, D. H. K.; Melianas, A.; Tang, Z.; Juška, G.; Arlauskas, K.; Zhang, F.; Siebbeles, L. D. a.; Inganäs, O.; Savenije, T. J. Origin of Reduced Bimolecular Recombination in Blends of Conjugated Polymers and Fullerenes. *Adv. Funct. Mater.* 2013, n/a – n/a.
- (33) Nardes, A. M.; Ferguson, A. J.; Wolfer, P.; Gui, K.; Burn, P. L.; Meredith, P.; Kopidakis, N. Free Carrier Generation in Organic Photovoltaic Bulk Heterojunctions of Conjugated Polymers with Molecular Acceptors: Planar versus Spherical Acceptors. *ChemPhysChem*, 2014, 15, 1539–1549.
- (34) Clarke, T. M.; Lungenschmied, C.; Peet, J.; Drolet, N.; Sunahara, K.; Furube, A.; Mozer, A. J. Photodegradation in Encapsulated Silole-Based Polymer: Pcbm Solar Cells Investigated Using Transient Absorption Spectroscopy and Charge Extraction Measurements. *Adv. Energy Mater.* 2013, *3*, 1473–1483.
- (35) MacKenzie, R. C. I.; Shuttle, C. G.; Chabinyc, M. L.; Nelson, J. Extracting Microscopic Device Parameters from Transient Photocurrent Measurements of P3HT:PCBM Solar Cells. *Adv. Energy Mater.* 2012, *2*, 662–669.
- (36) Tress, W.; Corvers, S.; Leo, K.; Riede, M. Investigation of Driving Forces for Charge Extraction in Organic Solar Cells: Transient Photocurrent Measurements

on Solar Cells Showing S-Shaped Current-Voltage Characteristics. *Adv. Energy Mater.* **2013**, n/a - n/a.

- (37) Lombardo, C. J.; Glaz, M. S.; Ooi, Z.-E.; Vanden Bout, D. a; Dodabalapur, A. Scanning Photocurrent Microscopy of Lateral Organic Bulk Heterojunctions. *Phys. Chem. Chem. Phys.* **2012**, *14*, 13199–13203.
- (38) Gutierrez, M.; Slobodyan, O.; Dodabalapur, A.; Vanden Bout, D. a. Using Lateral Bulk Heterojunctions to Study the Effects of Additives on PTB7:PC61BM Space Charge Regions. *Synth. Met.* 2015, 209, 158–163.
- (39) Lombardo, C. J.; Danielson, E. L.; Glaz, M. S.; Ooi, Z. E.; Vanden Bout, D. a; Dodabalapur, A. Device Physics and Operation of Lateral Bulk Heterojunction Devices. J. Phys. Chem. B 2013, 117, 4503–4509.
- (40) Morris, J. D.; Atallah, T. L.; Lombardo, C. J.; Park, H.; Dodabalapur, A.; Zhu, X.-Y. Mapping Electric Field Distributions in Biased Organic Bulk Heterojunctions under Illumination by Nonlinear Optical Microscopy. *Appl. Phys. Lett.* 2013, *102*, 033301.
- (41) Ooi, Z.-E.; Chan, K. L.; Lombardo, C. J.; Dodabalapur, A. Analysis of Photocurrents in Lateral-Geometry Organic Bulk Heterojunction Devices. *Appl. Phys. Lett.* 2012, 101, 053301.
- (42) Mihailetchi, V. D.; Wildeman, J.; Blom, P. W. M. Space-Charge Limited Photocurrent. *Phys. Rev. Lett.* **2005**, *94*, 126602.
- (43) Ostrowski, D. P.; Glaz, M. S.; Goodfellow, B. W.; Akhavan, V. a; Panthani, M. G.; Korgel, B. a; Vanden Bout, D. a. Mapping Spatial Heterogeneity in Cu(In1-xGax)Se2 Nanocrystal-Based Photovoltaics with Scanning Photocurrent and Fluorescence Microscopy. *Small* 2010, *6*, 2832–2836.
- (44) Ostrowski, D. P.; Vanden Bout, D. a. Correlation of Morphology with Photocurrent Generation in a Polymer Blend Photovoltaic Device. *Small* 2014, 9– 11.
- (45) Hoppe, H.; Niggemann, M.; Winder, C.; Kraut, J.; Hiesgen, R.; Hinsch, A.;

Meissner, D.; Sariciftci, N. S. Nanoscale Morphology of Conjugated Polymer/Fullerene-Based Bulk- Heterojunction Solar Cells. *Adv. Funct. Mater.* **2004**, *14*, 1005–1011.

- (46) Moulé, A. J.; Meerholz, K. Controlling Morphology in Polymer–Fullerene Mixtures. Adv. Mater. 2008, 20, 240–245.
- (47) Douhéret, O.; Swinnen, A.; Breselge, M.; Van Severen, I.; Lutsen, L.; Vanderzande, D.; Manca, J. High Resolution Electrical Characterisation of Organic Photovoltaic Blends. *Microelectron. Eng.* 2007, *84*, 431–436.
- Leever, B. J.; Durstock, M. F.; Irwin, M. D.; Hains, a. W.; Marks, T. J.; Pingree, L. S. C.; Hersam, M. C. Spatially Resolved Photocurrent Mapping of Operating Organic Photovoltaic Devices Using Atomic Force Photovoltaic Microscopy. *Appl. Phys. Lett.* 2008, *92*, 5–7.
- (49) Hoppe, H.; Glatzel, T.; Niggemann, M.; Hinsch, a; Lux-Steiner, M. C.; Sariciftci, N. S. Kelvin Probe Force Microscopy Study on Conjugated Polymer/fullerene Bulk Heterojunction Organic Solar Cells. *Nano Lett.* 2005, *5*, 269–274.
- (50) Palermo, V.; Palma, M.; Samorì, P. Electronic Characterization of Organic Thin Films by Kelvin Probe Force Microscopy. *Adv. Mater.* **2006**, *18*, 145–164.
- (51) Higgins, D. a; Kerimo, J.; Vanden Bout, D. A.; Barbara, P. F. A Molecular Yarn: Near-Field Optical Studies of Self-Assembled, Flexible, Fluorescent Fibers. *J. Am. Chem. Soc.* **1996**, *118*, 4049–4058.
- (52) Riehn, R.; Stevenson, R.; Richards, D.; Kang, D. J.; Blamire, M.; Downes, A.; Cacialli, F. Local Probing of Photocurrent and Photoluminescence in a Phase-Separated Conjugated-Polymer Blend by Means of near-Field Excitation. *Adv. Funct. Mater.* 2006, *16*, 469–476.
- (53) Romero, M. J.; Morfa, A. J.; Reilly, T. H.; Van De Lagemaat, J.; Al-Jassim, M. Nanoscale Imaging of Exciton Transport in Organic Photovoltaic Semiconductors by Tip-Enhanced Tunneling Luminescence. *Nano Lett.* **2009**, *9*, 3904–3908.
- (54) Potlog, T.; Ghimpu, L.; Gashin, P.; Pudov, a.; Nagle, T.; Sites, J. Influence of

Annealing in Different Chlorides on the Photovoltaic Parameters of CdS/CdTe Solar Cells. *Sol. Energy Mater. Sol. Cells* **2003**, *80*, 327–334.

- (55) Dyk, E. E. van; Radue, C.; Gxasheka, A. R. Characterization of Cu(In,Ga)Se2 Photovoltaic Modules. *Thin Solid Films* **2007**, *515*, 6196–6199.
- (56) Bull, T. a.; Pingree, L. S. C.; Jenekhe, S. a.; Ginger, D. S.; Luscombe, C. K. The Role of Mesoscopic PCBM Crystallites in Solvent Vapor Annealed Copolymer Solar Cells. ACS Nano 2009, 3, 627–636.
- (57) Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W.; Dunlop, E. D. Solar Cell Efficiency Tables (version 43). *Prog. Photovoltaics Res. Appl.* **2014**, *22*, 1–9.
- (58) Street, R. A.; Cowan, S.; Heeger, A. J. Experimental Test for Geminate Recombination Applied to Organic Solar Cells. *Phys. Rev. B* **2010**, *82*, 121301.
- (59) Shuttle, C. G.; Hamilton, R.; O'Regan, B. C.; Nelson, J.; Durrant, J. R. Charge-Density-Based Analysis of the Current-Voltage Response of Polythiophene/fullerene Photovoltaic Devices. *Proc. Natl. Acad. Sci. U. S. A.* 2010, *107*, 16448–16452.
- (60) Zhu, X. Y.; Yang, Q.; Muntwiler, M. Charge-Transfer Excitons at Organic Semiconductor Surfaces and Interfaces. *Acc. Chem. Res.* **2009**, *42*, 1779–1787.
- (61) Proctor, C. M.; Kuik, M.; Nguyen, T.-Q. Charge Carrier Recombination in Organic Solar Cells. *Prog. Polym. Sci.* 2013, 38, 1941–1960.
- (62) Gélinas, S.; Rao, A.; Kumar, A.; Smith, S. L.; Chin, A. W.; Clark, J.; van der Poll, T. S.; Bazan, G. C.; Friend, R. H. Ultrafast Long-Range Charge Separation in Organic Semiconductor Photovoltaic Diodes. *Science* 2014, *343*, 512–516.
- (63) Berger, R.; Domanski, A. L.; Weber, S. a. L. Electrical Characterization of Organic Solar Cell Materials Based on Scanning Force Microscopy. *Eur. Polym. J.* 2013, 49, 1907–1915.
- (64) Groves, C.; Reid, O. G.; Ginger, D. S. Heterogeneity in Polymer Solar Cells: Local
Morphology and Performance in Organic Photovoltaics Studied with Scanning Probe Microscopy. *Acc. Chem. Res.* **2010**, *43*, 612–620.

- (65) Danielson, E.; Ooi, Z.; Liang, K.; Morris, J.; Lombardo, C.; Dodabalapur, A. Analysis of Bulk Heterojunction Material Parameters Using Lateral Device Structures. J. Photonics Energy 2014.
- (66) Lombardo, B. C. J.; Glaz, M. S.; Ooi, Z. E.; Bout, D. A. Vanden; Dodabalapur, A. Submitted to DOI: 10.1002/adma.((please Add Manuscript Number)) Scanning Photocurrent Microscopy of Lateral Organic Bulk Heterojunctions By. *Adv. Mater.* 2011.
- (67) He, Z.; Zhong, C.; Su, S.; Xu, M.; Wu, H.; Cao, Y. Enhanced Power-Conversion Efficiency in Polymer Solar Cells Using an Inverted Device Structure. *Nature Photonics*, 2012, 6, 593–597.
- (68) Lu, L.; Yu, L. Understanding Low Bandgap Polymer PTB7 and Optimizing Polymer Solar Cells Based on It. *Adv. Mater.* **2014**, 4413–4430.
- (69) Foster, S.; Deledalle, F.; Mitani, A.; Kimura, T.; Kim, K.-B.; Okachi, T.; Kirchartz, T.; Oguma, J.; Miyake, K.; Durrant, J. R.; et al. Electron Collection as a Limit to Polymer:PCBM Solar Cell Efficiency: Effect of Blend Microstructure on Carrier Mobility and Device Performance in PTB7:PCBM. *Adv. Energy Mater*. 2014, n/a – n/a.
- (70) Lou, S. J.; Szarko, J. M.; Xu, T.; Yu, L.; Marks, T. J.; Chen, L. X. Effects of Additives on the Morphology of Solution Phase Aggregates Formed by Active Layer Components of High-Efficiency Organic Solar Cells. J. Am. Chem. Soc. 2011, 133, 20661–20663.
- (71) Marsh, R. A.; Hodgkiss, J. M.; Friend, R. H. Direct Measurement of Electric Field-Assisted Charge Separation in Polymer: Fullerene Photovoltaic Diodes. *Adv. Mater.* 2010, *22*, 3672–3676.
- (72) Troshin, P. a; Sariciftci, N. S. Supramolecular Chemistry for Organic SE; 2012.
- (73) Hoppe, H.; Glatzel, T.; Niggemann, M.; Schwinger, W.; Schaeffler, F.; Hinsch, a.;

Lux-Steiner, M. C.; Sariciftci, N. S. Efficiency Limiting Morphological Factors of MDMO-PPV:PCBM Plastic Solar Cells. *Thin Solid Films* **2006**, *511-512*, 587–592.

- (74) Foster, S.; Deledalle, F.; Mitani, A.; Kimura, T.; Kim, K.; Okachi, T.; Kirchartz, T.; Oguma, J.; Miyake, K.; Durrant, J. R.; et al. Electron Collection as a Limit to Polymer : PCBM Solar Cell Effi Ciency : Effect of Blend Microstructure on Carrier Mobility and Device Performance in PTB7 : PCBM. 2014, 1–12.
- (75) Rauh, D.; Deibel, C.; Dyakonov, V. Charge Density Dependent Nongeminate Recombination in Organic Bulk Heterojunction Solar Cells. *Adv. Funct. Mater.* 2012, *22*, 3371–3377.
- (76) Foertig, A.; Kniepert, J.; Gluecker, M.; Brenner, T.; Dyakonov, V.; Neher, D.; Deibel, C. Nongeminate and Geminate Recombination in PTB7:PCBM Solar Cells. *Adv. Funct. Mater.* **2014**, *24*, 1306–1311.
- (77) Hedley, G. J.; Ward, A. J.; Alekseev, A.; Howells, C. T.; Martins, E. R.; Serrano, L. A.; Cooke, G.; Ruseckas, A.; Samuel, I. D. W. Determining the Optimum Morphology in High-Performance Polymer-Fullerene Organic Photovoltaic Cells. *Nat. Commun.* 2013, *4*, 1–10.
- (78) Lombardo, C.; Ooi, Z. E.; Danielson, E.; Dodabalapur, A. Electrical Characteristics of Lateral Organic Bulk Heterojunction Device Structures. *Org. Electron.* 2012, 13, 1185–1191.
- (79) Liang, Y.; Xu, Z.; Xia, J.; Tsai, S.-T.; Wu, Y.; Li, G.; Ray, C.; Yu, L. For the Bright Future-Bulk Heterojunction Polymer Solar Cells with Power Conversion Efficiency of 7.4%. *Adv. Mater.* 2010, *22*, E135–E138.
- (80) Guerrero, A.; Montcada, N. F.; Ajuria, J.; Etxebarria, I.; Pacios, R.; Garcia-Belmonte, G.; Palomares, E. Charge Carrier Transport and Contact Selectivity Limit the Operation of PTB7-Based Organic Solar Cells of Varying Active Layer Thickness. J. Mater. Chem. A 2013, 1, 12345.
- (81) Li, Z.; Lakhwani, G.; Greenham, N. C.; McNeill, C. R. Voltage-Dependent Photocurrent Transients of PTB7:PC70BM Solar Cells: Experiment and Numerical

Simulation. J. Appl. Phys. 2013, 114, 034502.

- (82) Collins, B. a.; Li, Z.; Tumbleston, J. R.; Gann, E.; McNeill, C. R.; Ade, H. Absolute Measurement of Domain Composition and Nanoscale Size Distribution Explains Performance in PTB7:PC 71 BM Solar Cells. *Adv. Energy Mater.* 2013, 3, 65–74.
- (83) Wohrle, D.; Meissner, D. Organic Solar Cells. Adv. Mater. 1991, 3, 129–138.
- (84) Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. J. Thermally Stable, Efficient Polymer Solar Cells with Nanoscale Control of the Interpenetrating Network Morphology. *Adv. Funct. Mater.* 2005, 15, 1617–1622.
- (85) Bartesaghi, D.; Pérez, I. D. C.; Kniepert, J.; Roland, S.; Turbiez, M.; Neher, D.; Koster, L. J. A. Competition between Recombination and Extraction of Free Charges Determines the Fill Factor of Organic Solar Cells. *Nat. Commun.* 2015, 6, 7083.
- (86) Pivrikas, A.; Juška, G.; Österbacka, R.; Westerling, M.; Viliūnas, M.; Arlauskas, K.; Stubb, H. Langevin Recombination and Space-Charge-Perturbed Current Transients in Regiorandom poly(3-Hexylthiophene). *Phys. Rev. B* 2005, *71*, 125205.
- (87) Deibel, C. Charge Carrier Dissociation and Recombination in Polymer Solar Cells. *Phys. status solidi* **2009**, *206*, NA NA.
- (88) Yang, X.; Loos, J.; Veenstra, S. C.; Verhees, W. J. H.; Wienk, M. M.; Kroon, J. M.; Michels, M. a J.; Janssen, R. a J. Nanoscale Morphology of High-Performance Polymer Solar Cells. *Nano Lett.* **2005**, *5*, 579–583.
- (89) Hamilton, R.; Shuttle, C. G.; O'Regan, B.; Hammant, T. C.; Nelson, J.; Durrant, J. R. Recombination in Annealed and Nonannealed Polythiophene/Fullerene Solar Cells: Transient Photovoltage Studies versus Numerical Modeling. *J. Phys. Chem. Lett.* 2010, *1*, 1432–1436.
- (90) Clarke, T. M.; Peet, J.; Denk, P.; Dennler, G.; Lungenschmied, C.; Mozer, A. J. Non-Langevin Bimolecular Recombination in a Silole-Based polymer:PCBM

Solar Cell Measured by Time-Resolved Charge Extraction and Resistance-Dependent Time-of-Flight Techniques. *Energy Environ. Sci.* **2012**, *5*, 5241–5245.

- (91) Österbacka, R.; Pivrikas, A.; Juška, G.; Genevičius, K.; Arlauskas, K.; Stubb, H. Mobility and Density Relaxation of Photogenerated Charge Carriers in Organic Materials. *Curr. Appl. Phys.* 2004, *4*, 534–538.
- (92) Osaka, I.; Sauvé, G.; Zhang, R.; Kowalewski, T.; McCullough, R. D. Novel Thiophene-Thiazolothiazole Copolymers for Organic Field-Effect Transistors. *Adv. Mater.* 2007, 19, 4160–4165.
- (93) Hou, J.; Chen, H.-Y.; Zhang, S.; Li, G.; Yang, Y. Synthesis, Characterization, and Photovoltaic Properties of a Low Band Gap Polymer Based on Silole-Containing Polythiophenes and 2,1,3-Benzothiadiazole. J. Am. Chem. Soc. 2008, 130, 16144– 16145.
- (94) Byrne, P.; Cheon, K.-S.; Dennler, G.; Drolet, N.; Thompson, S.; Waller, D.; Wen, L. Photovolatic Cell with Benzodithiophene-Containing Polymer. 020,227, 2011.
- (95) Goodman, A. M. Double Extraction of Uniformly Generated Electron-Hole Pairs from Insulators with Noninjecting Contacts. J. Appl. Phys. **1971**, 42, 2823.
- (96) Xue-Yan, T.; Zheng, X.; Su-Ling, Z.; Fu-Jun, Z.; Guang-Cai, Y.; Jing, L.; Qin-Jun, S.; Yun, W.; Xu-Rong, X. Thickness Dependence of Surface Morphology and Charge Carrier Mobility in Organic Field-Effect Transistors. *Chinese Phys. B* 2010, *19*, 018103–018107.
- (97) Groves, C.; Greenham, N. C. Bimolecular Recombination in Polymer Electronic Devices. *Phys. Rev. B Condens. Matter Mater. Phys.* **2008**, *78*, 1–8.
- (98) Guerrero, A.; Ripolles-Sanchis, T.; Boix, P. P.; Garcia-Belmonte, G. Series Resistance in Organic Bulk-Heterojunction Solar Devices: Modulating Carrier Transport with Fullerene Electron Traps. Org. Electron. physics, Mater. Appl. 2012, 13, 2326–2332.
- (99) Ferguson, A. J.; Kopidakis, N.; Shaheen, S. E.; Rumbles, G. Dark Carriers, Trapping, and Activation Control of Carrier Recombination in Neat P3HT and

P3HT:PCBM Blends. J. Phys. Chem. C 2011, 115, 23134–23148.

- (100) Mandoc, M. M.; Kooistra, F. B.; Hummelen, J. C.; De Boer, B.; Blom, P. W. M. Effect of Traps on the Performance of Bulk Heterojunction Organic Solar Cells. *Appl. Phys. Lett.* **2007**, *91*, 2007–2009.
- (101) Slobodyan, O. V; Danielson, E. L.; Moench, S. J.; Dinser, J. a; Gutierrez, M.; Vanden Bout, D. a; Holliday, B. J.; Dodabalapur, A. Unusual Charge Transport and Reduced Bimolecular Recombination in PDTSiTzTz:PC 71 BM Bulk Heterojunction Blend. *Semicond. Sci. Technol.* **2015**, *30*, 064006.
- (102) Clarke, T. M.; Peet, J.; Nattestad, A.; Drolet, N.; Dennler, G.; Lungenschmied, C.; Leclerc, M.; Mozer, A. J. Charge Carrier Mobility, Bimolecular Recombination and Trapping in Polycarbazole Copolymer:fullerene (PCDTBT:PCBM) Bulk Heterojunction Solar Cells. Org. Electron. 2012, 13, 2639–2646.
- (103) Branker, K.; Pathak, M. J. M.; Pearce, J. M. A Review of Solar Photovoltaic Levelized Cost of Electricity. *Renew. Sustain. Energy Rev.* 2011, *15*, 4470–4482.
- (104) Snaith, H. J. Perovskites: The Emergence of a New Era for Low-Cost, High-Efficiency Solar Cells. J. Phys. Chem. Lett. **2013**, *4*, 3623–3630.
- (105) Park, N. Organometal Perovskite Light Absorbers Toward a 20% Efficiency Low-Cost Solid-State Mesoscopic Solar Cell. J. Phys. Chem. Lett. 2013, 4, 2423–2429.
- (106) Service R. F. Perovskite Solar Cells Keep On Surging. *Science (80-.).* **2014**, *344*, 2014.
- (107) Xing, G.; Mathews, N.; Sun, S.; Lim, S. S.; Lam, Y. M.; Grätzel, M.; Mhaisalkar, S.; Sum, T. C. Long-Range Balanced Electron- and Hole-Transport Lengths in Organic-Inorganic CH3NH3PbI3. *Science (80-.)*. 2013, *342*, 344–347.
- (108) Chen, Q.; Zhou, H.; Fang, Y.; Stieg, A. Z.; Song, T.-B.; Wang, H.-H.; Xu, X.; Liu, Y.; Lu, S.; You, J.; et al. The Optoelectronic Role of Chlorine in CH3NH3PbI3(Cl)-Based Perovskite Solar Cells. *Nat. Commun.* 2015, *6*, 1–9.

- (109) Edri, E.; Kirmayer, S.; Kulbak, M.; Hodes, G.; Cahen, D. Chloride Inclusion and Hole Transport Material Doping to Improve Methyl Ammonium Lead Bromide Perovskite-Based High Open-Circuit Voltage Solar Cells. *J. Phys. Chem. Lett.* 2014, *5*, 429–433.
- (110) Yin, W.-J.; Shi, T.; Yan, Y. Unique Properties of Halide Perovskites as Possible Origins of the Superior Solar Cell Performance. *Adv. Mater.* **2014**, *26*, 4653–4658.
- (111) Edri, E.; Kirmayer, S.; Henning, A.; Mukhopadhyay, S.; Gartsman, K.; Rosenwaks, Y.; Hodes, G.; Cahen, D. Why Lead Methylammonium Tri-Iodide Perovskite-Based Solar Cells Require a Mesoporous Electron Transporting Scaffold (but Not Necessarily a Hole Conductor). *Nano Lett.* **2014**, *14*, 1000–1004.
- (112) Wen, X.; Sheng, R.; Ho-Baillie, A. W. Y.; Benda, A.; Woo, S.; Ma, Q.; Huang, S.; Green, M. A. Morphology and Carrier Extraction Study of Organic–Inorganic Metal Halide Perovskite by One- and Two-Photon Fluorescence Microscopy. J. Phys. Chem. Lett. 2014, 5, 3849–3853.
- (113) Docampo, P.; Hanusch, F. C.; Giesbrecht, N.; Angloher, P.; Ivanova, A.; Bein, T. Influence of the Orientation of Methylammonium Lead Iodide Perovskite Crystals on Solar Cell Performance. *APL Mater.* 2014, 2, 081508.
- (114) Huang, W.; Huang, F.; Gann, E.; Cheng, Y.; McNeill, C. R. Probing Molecular and Crystalline Orientation in Solution-Processed Perovskite Solar Cells. *Adv. Funct. Mater.* **2015**, *25*, 5529–5536.
- (115) Yin, J.; Cortecchia, D.; Krishna, A.; Chen, S.; Mathews, N.; Grimsdale, A. C.; Soci, C. Interfacial Charge Transfer Anisotropy in Polycrystalline Lead Iodide Perovskite Films. J. Phys. Chem. Lett. 2015, 6, 1396–1402.
- (116) Song, T.; Chen, Q.; Zhou, H.-P.; Jiang, C.; Wang, H.-H.; Yang, Y.; Liu, Y.; You, J. Perovskite Solar Cells: Film Formation and Properties. *J. Mater. Chem. A* 2015, *3*, 9032–9050.
- (117) Stranks, S. D.; Eperon, G. E.; Grancini, G.; Menelaou, C.; Alcocer, M. J. P.; Leijtens, T.; Herz, L. M.; Petrozza, A.; Snaith, H. J. Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in an Organometal Trihalide Perovskite

Absorber. Science (80-.). 2013, 342, 341–344.

- (118) de Quilettes, D. W.; Vorpahl, S. M.; Stranks, S. D.; Nagaoka, H.; Eperon, G. E.; Ziffer, M. E.; Snaith, H. J.; Ginger, D. S. Impact of Microstructure on Local Carrier Lifetime in Perovskite Solar Cells. *Science (80-.).* 2015, *348*, 683–686.
- (119) Deschler, F.; Price, M.; Pathak, S.; Klintberg, L. E.; Jarausch, D. D.; Higler, R.; Hüttner, S.; Leijtens, T.; Stranks, S. D.; Snaith, H. J.; et al. High Photoluminescence Efficiency and Optically Pumped Lasing in Solution-Processed Mixed Halide Perovskite Semiconductors. *J. Phys. Chem. Lett.* 2014, *5*, 1421–1426.
- (120) Chen, Q.; Zhou, H.; Hong, Z.; Luo, S.; Duan, H. S.; Wang, H. H.; Liu, Y.; Li, G.; Yang, Y. Planar Heterojunction Perovskite Solar Cells via Vapor-Assisted Solution Process. J. Am. Chem. Soc. 2014, 136, 622–625.
- (121) Chen, Q.; Zhou, H.; Hong, Z.; Luo, S.; Duan, H.; Wang, H. Planar Heterojunction Perovskite Solar Cells via Vapor Assisted Solution Process Planar Heterojunction Perovskite Solar Cells via Vapor Assisted Solution Process. 2013, 3–6.
- (122) Liu, M.; Johnston, M. B.; Snaith, H. J. Efficient Planar Heterojunction Perovskite Solar Cells by Vapour Deposition. *Nature* 2013, 501, 395–398.
- (123) Eperon, G. E.; Burlakov, V. M.; Docampo, P.; Goriely, A.; Snaith, H. J. Morphological Control for High Performance, Solution-Processed Planar Heterojunction Perovskite Solar Cells. *Adv. Funct. Mater.* 2014, *24*, 151–157.
- (124) Christians, J. A.; Miranda Herrera, P. A.; Kamat, P. V. Transformation of the Excited State and Photovoltaic Efficiency of CH 3 NH 3 PbI 3 Perovskite upon Controlled Exposure to Humidified Air. J. Am. Chem. Soc. 2015, 137, 1530–1538.
- (125) Zhang, T.; Yang, M.; Zhao, Y.; Zhu, K. Controllable Sequential Deposition of Planar CH₃ NH₃ PbI₃ Perovskite Films via Adjustable Volume Expansion. *Nano Lett.* 2015, *15*, 3959–3963.
- (126) Liu, D.; Wu, L.; Li, C.; Ren, S.; Zhang, J.; Li, W.; Feng, L. Controlling CH3NH3PbI3-xClx Film Morphology with Two-Step Annealing Method for

Efficient Hybrid Perovskite Solar Cells. *ACS Appl. Mater. Interfaces* **2015**, 150708153132004.

- (127) Yin, W.-J.; Shi, T.; Yan, Y. Unusual Defect Physics in CH3NH3PbI3 Perovskite Solar Cell Absorber. *Appl. Phys. Lett.* **2014**, *104*, 063903/1–063903/4.
- (128) Adams, D. M.; Kerimo, J.; Liu, C.; Bard, A. J.; Barbara, P. F. Electric Field Modulated Near-Field Photo-Luminescence of Organic Thin Films. J. Phys. Chem. B 2000, 104, 6728–6736.
- (129) Chin, X. Y.; Cortecchia, D.; Yin, J.; Bruno, A.; Soci, C. Lead Iodide Perovskite Light-Emitting Field-Effect Transistor. *Nat. Commun.* **2015**, *6*, 7383.
- (130) Thompson, B. C.; Fréchet, J. M. J. Polymer-Fullerene Composite Solar Cells. *Angew. Chem. Int. Ed. Engl.* **2008**, *47*, 58–77.
- (131) Lee, C.-K.; Wodo, O.; Ganapathysubramanian, B.; Pao, C.-W. Electrode Materials, Thermal Annealing Sequences, and Lateral/Vertical Phase Separation of Polymer Solar Cells from Multiscale Molecular Simulations. ACS Appl. Mater. Interfaces 2014.
- (132) Frost, J. M.; Butler, K. T.; Brivio, F.; Hendon, C. H.; van Schilfgaarde, M.; Walsh, A. Atomistic Origins of High-Performance in Hybrid Halide Perovskite Solar Cells. *Nano Lett.* **2014**, *14*, 2584–2590.
- (133) Hailegnaw, B.; Kirmayer, S.; Edri, E.; Hodes, G.; Cahen, D. Rain on Methyl-Ammonium-Lead-Iodide Based Perovskites: Possible Environmental Effects of Perovskite Solar Cells. J. Phys. Chem. Lett. 2015, 150407164831001.
- (134) Ullal, H. S.; Zwelbel, K.; Roedern, B. Von. Current Status of Polycrystalline Thin-Film PV Technologies. *Conf. Rec. Twenty Sixth IEEE Photovolt. Spec. Conf.* -1997 1997, 0–4.
- (135) Powalla, M.; Dimmler, B. CIGS Solar Cells on the Way to Mass Production: Process Statistics of a 30 Cm × 30 Cm Module Line. *Fuel Energy Abstr.* 2002, 43, 202.

- (136) Jasenek, a.; Rau, U. Defect Generation in Cu(In,Ga)Se[sub 2] Heterojunction Solar Cells by High-Energy Electron and Proton Irradiation. J. Appl. Phys. 2001, 90, 650.
- (137) Boden, A.; Braunig, D.; Klaer, J.; Karg, F. H.; Hosselbarth, B.; La Roche, G. Proton-Irradiation of Cu(In,Ga)Se/sub 2/ and CuInS/sub 2/ Thin-Film Solar Cells. In Conference Record of the Twenty-Eighth IEEE Photovoltaic Specialists Conference - 2000 (Cat. No.00CH37036); IEEE, 2000; pp. 1038–1041.
- (138) Powalla, M.; Dimmler, B. Scaling up Issues of CIGS Solar Cells. *Thin Solid Films* **2000**, *361*, 540–546.
- (139) Panthani, M. G.; Akhavan, V.; Goodfellow, B.; Schmidtke, J. P.; Dunn, L.; Dodabalapur, A.; Barbara, P. F.; Korgel, B. A. Synthesis of CulnS2, CulnSe2, and Cu(InxGa(1-x))Se2 (CIGS) Nanocrystal "Inks" for Printable Photovoltaics. *J. Am. Chem. Soc.* 2008, *130*, 16770–16777.
- (140) Guo, Q.; Kim, S. J.; Kar, M.; Shafarman, W. N.; Birkmire, R. W.; Stach, E. a.; Agrawal, R.; Hillhouse, H. W. Development of CuInSe 2 Nanocrystal and Nanoring Inks for Low-Cost Solar Cells. *Nano Lett.* **2008**, *8*, 2982–2987.
- (141) Waldauf, C.; Morana, M.; Denk, P.; Schilinsky, P.; Coakley, K.; Choulis, S. A.; Brabec, C. J. Highly Efficient Inverted Organic Photovoltaics Using Solution Based Titanium Oxide as Electron Selective Contact. *Appl. Phys. Lett.* **2006**, *89*, 233517.
- (142) Olson, J. M.; Kurtz, S. R.; Kibbler, A. E.; Faine, P. A 27.3% Efficient Ga0.5In0.5P/GaAs Tandem Solar Cell. Appl. Phys. Lett. 1990, 56, 623.
- (143) You, J.; Dou, L.; Yoshimura, K.; Kato, T.; Ohya, K.; Moriarty, T.; Emery, K.; Chen, C.-C.; Gao, J.; Li, G.; et al. A Polymer Tandem Solar Cell with 10.6% Power Conversion Efficiency. *Nat. Commun.* **2013**, *4*, 1446.
- (144) Dürr, M.; Bamedi, A.; Yasuda, A.; Nelles, G. Tandem Dye-Sensitized Solar Cell for Improved Power Conversion Efficiencies. *Appl. Phys. Lett.* **2004**, *84*, 3397.
- (145) Müller, J.; Rech, B.; Springer, J.; Vanecek, M. TCO and Light Trapping in Silicon

Thin Film Solar Cells. Sol. Energy 2004, 77, 917–930.

- (146) Panthani, M. G.; Stolle, C. J.; Reid, D. K.; Rhee, D. J.; Harvey, T. B.; Akhavan, V. a.; Yu, Y.; Korgel, B. a. CuInSe 2 Quantum Dot Solar Cells with High Open-Circuit Voltage. J. Phys. Chem. Lett. 2013, 4, 2030–2034.
- (147) Akhavan, V. A.; Panthani, M. G.; Goodfellow, B. W.; Reid, D. K.; Korgel, B. A. Thickness-Limited Performance of CuInSe2 Nanocrystal Photovoltaic Devices. *Opt. Express* 2010, 18, A411–A420.
- (148) Hamilton, C. E.; Flood, D. J.; Barron, A. R. Thin Film CdSe/CuSe Photovoltaic on a Flexible Single Walled Carbon Nanotube Substrate. *Phys. Chem. Chem. Phys.* 2013, 15, 3930.
- (149) Reese, M. O.; White, M. S.; Rumbles, G.; Ginley, D. S.; Shaheen, S. E. Optimal Negative Electrodes for poly(3-Hexylthiophene): [6,6]-Phenyl C61-Butyric Acid Methyl Ester Bulk Heterojunction Photovoltaic Devices. *Appl. Phys. Lett.* 2008, 92, 053307.