# UC Berkeley UC Berkeley Electronic Theses and Dissertations

# Title

Structure-Function Relationships in Semiconducting Polymers for Organic Photovoltaics

Permalink https://escholarship.org/uc/item/83w7t7zw

Author Kavulak, David Fredric Joel

Publication Date 2010

Peer reviewed|Thesis/dissertation

Structure-Function Relationships in Semiconducting Polymers for Organic Photovoltaics

By

David Fredric Joel Kavulak

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate Division of the University of California, Berkeley

> Committee in Charge: Professor Jean M. J. Fréchet, Chair Professor Peidong Yang Professor Vivek Subramanian

> > Spring 2010

# Structure-Function Relationships in Semiconducting Polymers for Organic Photovoltaics

© 2010

by

David Fredric Joel Kavulak

#### Abstract

# Structure-Function Relationships in Semiconducting Polymers for Organic Photovoltaics

By

David Fredric Joel Kavulak

Doctor of Philosophy in Chemistry

University of California, Berkeley

Professor Jean M. J. Fréchet, Chair

The major body of this work investigates how the chemical structure of conjugated polymers relates to the fundamental operating mechanism of organic photovoltaic devices. New conjugated polymers were characterized and their optical and electronic properties tested and correlated with their power conversion efficiencies as the active layer in polymer solar cells. From these experiments general structure/function relationships are drawn with an eye toward developing universal guidelines for conjugated polymer design and synthesis.

Starting with light absorption, three major steps in the photovoltaic mechanism are examined. First, photogeneration of excited states and the migration of these states through the active layer are correlated to the polymeric backbone chemistry and the resulting device performance. Next, separation of these excited states at an interface between electron donors and electron acceptors is examined as a function of donor-acceptor distance and active layer dielectric constant. These two variables were tuned by chemical modification of polythiophene side groups. Third, charge carrier conduction is related to both polymer electronic states and to solid-state packing morphology. Design principles for effective conduction of both holes and electrons are outlined and the ambipolar nature of conjugated organic materials is discussed.

In the final chapters, the solid-state polymer morphology in a solution processed thin film is examined. The impact that this morphology has on all steps in the photovoltaic mechanism is highlighted. How chemical modification of the polymer can influence this packing structure is examined as well as how new fabrication procedures can be used to pre-form nanostructured materials in solution before thin film deposition. To my Parents, Mal Kavulak and Linda Friedman

For everything they have done.

# **Table of Contents**

CHAPTER 1: FUNDAMENTAL OPERATION AND MATERIAL DESIGN OF ORGANIC POLYMER PHOTOVOLTAICS	1
1.1 Introduction	2
1.2 Operation of an Organic Photovoltaic Cell	3
1.2.1 Photovoltaic Process and Measurement	3
1.2.2 Operation of Organic Photovoltaics	6
1.3 Chemistry of Conjugated Polymers	11
1.3.1 Band Structure of Conjugated Materials	11
1.3.2 Resonance	13
1.3.3 Electronegativity	14
1.3.4 Sterics	16
1.4 Device Fabrication and Testing	17
1.4.1 OPV Device Architectures	18
1.4.2 Space Charge Limited Conduction	20
1.5 Dissertation Overview	22
References	23
CHAPTER 2: CONTROL OF ELECTRON-HOLE EXCITED STATES IN CYCLOMETALATED PLATINUE POLYMERS	M 26
Abstract	26
2.1 Introduction	
2.2 Controlling the Exciton of Cyclometalated Platinum Polymers	
2.1.1 Materials	
2.1.2 Optical and Electronic Properties	30
2.1.3 Photoluminescence and Singlet Oxygen Generation	32
2.1.4 Photovoltaic Performance	36
2.3 Conclusion	38
2.4 Experimental	38
References	39
CHAPTER 3: CONTROL OF CHARGE SEPARATION THROUGH CHEMICAL MEANS	42
Abstract	42
3.1 Introduction	43
3.2 Controlling Donor-Acceptor Distance	43

	3.2.1 Material	44
	3.2.2 Optical and Electronic Properties	44
	3.2.3 Photovoltaic Performance	45
	3.3 Exciton Separation Efficiency	46
	3.3.2 Modeling	47
	3.3.3 X-ray Diffraction	49
	3.3.4 Photothermal Deflection Spectroscopy	50
	3.4 Altering Active Layer Dielectric	51
	3.4.1 Material	52
	3.4.2 Optical and Electronic Properties	52
	3.4.3 Photovoltaic Performance	54
	3.5 Exciton Separation	55
	3.5.1 Dielectric Constant	55
	3.6 Conclusion	56
	3.7 Experimental	57
	References	60
CF	IAPTER 4: ENERGY LEVEL CONTROL OF SUBSTITUTED POLYTHIOPHENES	62
	Abstract	62
	4.1 Introduction	63
	4.2 Controlling the HOMO and LUMO of Polythiophene Copolymers	63
	4.2.1 Materials	64
	4.2.2 Optical and Electronic Properties	65
	4.3 P-type Mobility	70
	4.3.1 OFET Performance	70
	4.3.2 Oxygen Stability	71
	4.3.5 Photovoltaic Performance as a Donor	74
	4.4 N-type Mobility	76
	4.4.1 Photovoltaic Performance	77
	4.5 Conclusion	79
	4.6 Experimental	79
	References	81
Сн н¤	APTER 5: POLYTHIOPHENE MODIFICATION FOR CHEMICAL CONTROL OVER BULK	84
111	Abstract	0-

5.1 Introduction	
5.2 Controlling Morphology Through Disorder	
5.2.1 Materials	
5.2.2 Optical and Electronic Properties	
5.3 Morphology	
5.3.1 <i>TEM/AFM</i>	
5.3.2 Photovoltaic Performance	
5.4 Controlling P3HT and CNT Thin Film Morphology	
5.4.1 Materials	
5.4.2 Optical and Electronic Properties	
5.5 Morphology	
5.7 Conclusion	
5.8 Experimental	
References	
CHAPTER 6: DESIGN OF SEMICONDUCTING POLYMER NANOPARTICLES FOR ELE DEVICES	ECTRONIC THIN FILM
Abstract	
6.1 Introduction	
6.2 Probing Conjugated Polymer Nanoparticles	
6.2.1 Materials	
6.2.2 PNP Size Control	
6.2.3 Characterization of P3HT PNPs	
6.2.4 Field Effect Transistor Performance of P3HT PNPs	
6.4 Molecule Encapsulation in Semiconducting PNPs	
6.4.1 P3HT:PCBM Nanoparticles	
6.5 Conclusion	111
6.6 Experimental	

### ACKNOWLEDGEMENTS

Upon contemplation of my graduate studies, I find many, many names deserving of thanks and appreciation. Progression through a PhD program cannot be done without countless interactions and exploring the unknown edges of human science requires many collaborators. During my time here, I have found that from every individual I meet, there is something I can learn. And it is learning, about all aspects of the world, and tying this knowledge together inside, which is how one truly progresses.

From The Professor, one of the most important things I have learned was not scientific. It is instead, that results, no matter how useful or not, must be communicated effectively to be of importance. Therefore writing, speaking and presenting scientific concepts, as well as discussing and arguing about them, is just as important as learning them or doing them. Both with peers, with superiors, with other members of the research communicate your work to another person you have neither progressed your scientific field nor truly completed the task that you were undertaking.

Special mention must be made for those researchers who helped me start towards my goal. Dr. Kevin Sivula, Prof. Christine Luscombe and Prof. Barry Thompson were more than just mentors and collaborators. They were also friends and extremely patient human beings when dealing with me. From my collaborators and colleagues, who there are too many to list here, I am deeply in debt. All of those who worked with conjugated polymers at one point or another and especially to those who never did, I learned more than I was ever anticipating. Also a specific mention is needed for all of those collaborators outside of the Fréchet labs.

On a personal note; I want to recognize Claire Woo, who somehow managed to put up with me. Cezar Ramiro and Chona DeMesa. They do so much for all of us in the Fréchet group and can never get enough thanks. Tabitha Clem, who has been my partner in crime for five years, and who hopefully will be for many more down the road. To my best friends and soon to be PhDs; Pradeep Nair and James Johns. We started out together and somehow wound up finishing together. I don't know where things will take us from here, but I know you two will always be there when I need you. Special thanks to Dr. Jill Millstone for her energy and support. Without her I would not be who I am. And to Kirsten Clemmensen who has always helped point my way and without whom these last years would not have been possible.

# CHAPTER 1: FUNDAMENTAL OPERATION AND MATERIAL DESIGN OF ORGANIC POLYMER PHOTOVOLTAICS

#### **1.1 INTRODUCTION**

Polyaromatic materials have been an area of growing interest since the discovery of their semiconducting properties over 60 years ago.<sup>1</sup> Although they were initially investigated for use as an alternative to metal wiring in thin film devices, their utility and the basic research surrounding them has evolved greatly in the last few decades. No longer is the conductivity of the polymers studied in their doped form, but instead the intrinsic semiconducting nature of the materials has moved to the forefront. Both before as conducting polymers and more recently as semiconducting polymers, the low cost advantages afforded by using plastic materials remain a primary driving force for their investigation.<sup>2</sup> And perhaps of equal interest to the scientific community, is the fundamental physics behind how conjugated organic molecules the optical and electronic behaviors long-associated with inorganic materials.

As semiconductors with material properties such as high absorption coefficients, efficient charge conduction, and solution processibility, polyaromatics are particularly suited to the development of new solar energy systems. Indeed, the last decade has seen a rapid increase in the attention placed on inexpensive solar energy as a solution for the global problems of energy consumption and carbon dioxide emission. While current inorganic solar technologies are starting to become a competitive component in the energy industry, organic photovoltaic (OPV) materials offer the promise of cheap and disposable devices, which will become an attractive complement for traditional inorganic devices. For example, soluble conjugated polymers can be inexpensively incorporated as the electroactive layer in lightweight and flexible solar modules using current roll-to-roll fabrication techniques.<sup>3,4</sup> Even though current organic photovoltaic efficiencies are not high enough for large scale commercial applications, active research on conjugated polymers also offers insight into the juxtaposition between modern solid state physics and organic materials chemistry. Fundamental investigations of how synthetic molecular manipulation alters the electronic properties of these materials will allow OPV cells to achieve the necessary efficiencies to be a viable alternative in the energy generation landscape.



Figure 1.1 Flexible organic photovoltaic device (OPV) under simulated sunlight.

Today, small area laboratory cells have reached efficiencies up to 7.4% and commercial solar modules have shown full light power conversion efficiencies of ~4%.<sup>5</sup> Recent increases in device performance have been achieved largely by a combinatorial approach of testing well-known conjugated polymer derivatives in existing OPV architectures. However, to enhance the selection of synthetic targets, it is extraordinarily beneficial to understand how the changes in the chemical designs of the conjugated molecules alter their fundamental optoelectronic and physical properties, and ultimately lead to an increase in performance.

The correlation of structure with function requires a recursive process as depicted in Figure 1.2. The first step is in understanding the physical photo-electronic mechanism by which organic solar cells operate, and then to isolate inefficient processes within a specific system. After targeting a particular photophysical process, the design, synthesis and characterization of new organic materials with different optical or electronic properties begins. These new materials can then be processed into OPVs where the efficiency and overall performance of the cell is tested. These results simultaneously produce new technological understanding while also feeding back into the knowledge of how the chemical structure of conjugated materials influences the fundamental mechanisms of the solar cell.



Figure 1.2 Recursive process by which fundamental understanding of the OPV mechanism and conjugated polymer design can lead to improved solar cell performance.

# **1.2 OPERATION OF AN ORGANIC PHOTOVOLTAIC CELL**

### **1.2.1 Photovoltaic Process and Measurement**

Regardless of the materials, all photovoltaic cells operate on the basic principle that an asymmetric junction in the semiconductor provides an electrochemical potential, which directs a photoexcited state in the semiconducting material to separate into a free electron and a free hole, and which are then transported out of the device and into an external circuit. When a potential

load is applied across the electrodes of a solar cell an external current is generated. The asymmetrical junction in the active layer that is necessary for the photocurrent production only allows the external current to flow if it is in the reverse direction to the photocurrent. This reverse current can flow through the device in one direction irrespective of whether the device is in the light or the dark and therefore is often called the dark current although these terms are not always interchangeable.<sup>6</sup>

In simple electronic terms, the total current density (current per unit area, mA/cm<sup>2</sup>) in the device will be the sum of the photocurrent density ( $J_{ph}$ ) plus the current flowing in the opposite direction ( $J=J_{ph}+J_D$ ,  $J_D$  being the current in opposition to  $J_{ph}$ ). In classical electronics this system is represented by a perfect current source in parallel with a non-ideal leaky diode which is diagramed in Figure 1.3. Arbitrarily,  $J_{ph}$  will be taken to be a negative current and thus the equivalent circuit for a solar cell can be modeled by Equation 1.1. Where,  $J_0$  is the reverse saturation current density, V the applied potential, A is the area of the device, n is the diode ideality factor, kT the Boltzmann temperature, and  $R_S$  and  $R_{SH}$  are the series and parallel (shunt) resistances respectively.



Figure 1.3 Equivalent circuit diagram of a solar cell. Jph is chosen to be traveling in the negative current (-J) direction.

The testing of a solar cell is straightforward. Place the device under simulated sunlight and apply a variable load that starts at 0 V, in order to obtain the photocurrent, and then linearly increase the load until the reverse current exactly balances the photocurrent. This will give you the maximum load that can be attached to the solar cell. The maximum load is termed the open circuit voltage ( $V_{oc}$ ) and the photocurrent density at zero bias is termed the short circuit current density ( $J_{sc}$ ) and these points are highlighted in Figure 1.4. Along the measured JV curve lies the maximum power per unit area (power/A = V\*J) and is usually measured in mW/cm<sup>2</sup>.



Figure 1.4 (Top) General JV curve for a solar cell in the dark and under illumination. (Bottom) AM0 and AM1.5 spectral solar flux as a function of wavelength.

The curving nature of both the dark current and the photocurrent JV traces are a complicated result of the exponentially dependant diode coupled with ratio of  $R_S$  to  $R_{SH}$ . While elucidating the causes for various curve shapes is the goal of many experiments it is clear that the shape of the JV curve alters the maximum power point. In an effort to somewhat quantify the shape of the curve it is often useful to calculate the fill factor (FF) for the device as the ratio of the maximum power point ( $V_{mpp} \times J_{mpp}$ ) to the absolute power point ( $V_{oc} \times J_{sc}$ ). In this way, the FF represents how close the JV curve is to a curve with a step function at the point  $V_{oc} \times J_{sc}$  and is therefore sometimes referred to as the "squareness" of the curve. Using the values for  $V_{oc}$ ,  $J_{sc}$ , and FF the power conversion efficiency (PCE =  $\eta$ ) of the solar cell is calculated for a given power density of light in Equation 1.2.

$$PCE = \eta = \frac{P_{out}}{P_{light}} = \frac{V_{mpp} \times J_{mpp}}{P_{light}} = \frac{V_{oc} \times J_{sc} \times FF}{P_{light}}, \quad FF = \frac{V_{mpp} \times J_{mpp}}{V_{oc} \times J_{sc}}$$
(Equation 1.2)

For photovoltaic cells of all kinds and from all laboratories to be comparable, the light sources used for testing can be referenced to the solar spectrum after interactions with different air masses (AM). The most common testing condition is AM 1.5 global (AM 1.5G), which represents the amount of atmosphere the sun light must travel through at an incident angle of 48.19° from normal and is related to the spectrum and intensity (100 mW/cm<sup>2</sup>) of sunlight found in the continental United States. The spectra for solar radiation before and after passing through AM 1.5 are presented in Figure 1.4. It can be clearly seen that the atmosphere reduces both the overall intensity of solar radiation but also introduces characteristic absorption bands. These bands stem from common atmospheric molecules; primarily water, oxygen, and ozone. The referencing of different light sources to the AM 1.5G spectrum and making sure that an exact power density of 100 mW/cm<sup>2</sup> is achieved during photovoltaic testing is outside the scope of this chapter.<sup>7</sup>

## **1.2.2 OPERATION OF ORGANIC PHOTOVOLTAICS**

The above section is an overview of solar cells in general and as such is applicable to all photovoltaic systems regardless of material or operating mechanism; including traditional inorganic solar cells, dye sensitized solar cells (DSSCs) and organic photovoltaics (OPVs). DSSCs and OPVs along with some inorganic nanoparticle solar cells make up a subclass of photovoltaics designated as excitonic photovoltaics.<sup>8</sup> While there are subtle differences between them, these systems share the trait that the absorption of a photon in the semiconductor leads to an excited state that exists as a mobile Coulomb-bound electron-hole pair (termed an "exciton"). In OPVs, the excitonic nature stems from both the low average dielectric constant of the active layer (typically  $\varepsilon = 3$ -4), which allows for a larger Coulomb potential between electrons and holes and from the non-covalent interactions between neighboring molecules, resulting in a smaller and more confined set of electronic states. The result is that the excited state is usually localized to the molecular orbitals of the chromophore.

$$U_{\rm E} = \frac{e^2}{4\pi\epsilon_0\epsilon R}$$
 (Equation 1.3)

The potential well for the Coulomb binding of the exciton can be approximated as the potential energy between two point charges (U<sub>E</sub>) in a dielectric medium (Equation 1.3). Where e is the elementary charge,  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon$  is the dielectric constant of the medium and R is the distance between the charges. If  $\varepsilon = 4$  and R = 4 Å then the potential energy of the exciton is approximately 900 meV which is an order of magnitude higher than the excess thermal energy at room temperature (kT @ 300K = 25.9 meV). Therefore, in order for organic semiconductors to operate as photovoltaic materials a system based on a donor-acceptor heterojunction was developed by Tang in 1986.<sup>9</sup> This system is often described using a similar vocabulary to that of a traditional p-n junction silicon solar cell, yet an OPV operates by a very different mechanism (Figure 1.5).<sup>2</sup>



**Figure 1.5** The physical mechanism of an organic solar cell. (1) Absorption of light, (2) Diffusion of the exciton to an interface, (3) Separation of the exciton across the donor/acceptor interface, (4) Conduction of free charges to the electrodes. Upper figures Physical cartoon of a donor/acceptor heterojunction (upper) and energy diagram of donor/acceptor heterojunction (lower).

In the first step a photon of light is absorbed by the organic semiconductor and forms an exciton between the excited electron and the hole left behind in the ground state. A chemical perspective explains that the electron is excited from the highest occupied molecular orbital (HOMO) into the lowest unoccupied molecular orbital (LUMO). It is possible to excite an electron into a higher energy state above the LUMO of the molecule but this usually requires a photon with energy in the ultraviolet and so this process will be ignored here.

When existing in a single material an exciton is unlikely to become separated and the electron and hole will recombine either radiatively or non-radiatively, usually within a few nanoseconds. During its lifetime an exciton can only travel by hopping between localized states on neighboring molecules (Step 2 of Figure 1.5). In order for the exciton to be separated it must reach a molecular heterojunction between two materials with different energy states. The tight binding and close molecular distance between the electron and hole cause it to act as a neutral species that is unaffected by electric fields and therefore it only moves by a diffusion process.<sup>8</sup> Typical diffusion lengths (L<sub>D</sub>) for short lived excitons in most organic materials are between 5 and 50 nm. Therefore, for efficient charge collection, the distance between the molecular phases must be on the order of the exciton diffusion length for that given semiconductor,  $L_D = (\tau D)^{1/2}$ , where D is the diffusion coefficient and  $\tau$  is the exciton lifetime.<sup>10,11</sup>

At an interface between two materials with different electron affinities  $(E_A)$  a thermodynamic driving force exists for the separation of the exciton, which could result in the electron jumping to the more electron deficient (electron acceptor) molecule, which has the lower LUMO level

(greater  $E_A$ ).<sup>12</sup> Similarly, an exciton can be split if there is a driving force for the hole to separate to a more electron rich (electron donor) material which has a higher HOMO level (smaller ionization potential,  $I_P$ ). These two scenarios are energetically and physically symmetric and it is convention to only talk about the process from the point of view of the exciton on the donor (Step 3 of Figure 1.5) unless a large amount of photocurrent is being generated on the acceptor material.

Unfortunately, the physical separation of the electron onto the acceptor and the hole on the donor does not necessarily lead directly to free charges. The low dielectric constant of the active layer still allows the electron and hole to be trapped in a Coulomb well across the donor/accepter interface. This state is usually referred to as a charge-transfer (CT) state.<sup>12,13</sup> The CT state may either recombine back to the initial ground state or undergo further separation into free charges. The final energy for the charge separated (CS) state is equal to the I<sub>P</sub> of the donor plus the E<sub>A</sub> of the acceptor ( $E_{CS} = I_P(D) + E_A(A)$ ). It is important to note here that the energy of the charge separated state ( $E_{CS}$ ) is also the maximum potential difference that the electron and hole can reach as they travel towards the electrodes and thus is also the maximum for the V<sub>oc</sub> of a given system.



Figure 1.6 Energy level diagram of donor (blue)/acceptor (red) interface. Difference between  $I_P(D)$  and  $E_A(A)$  is also the maximum possible  $V_{oc}$  attainable for the OPV.

Two possible scenarios for charge separation are possible at these D/A interfaces depending on the relative rates of the CS process and the electron relaxation process to the lowest charge transfer state (CT<sub>1</sub>) state. When the electron first hops across from the donor to the acceptor molecule it most likely lands in a vibrationally excited state, which is "hot" compared to the CT<sub>1</sub> state. Vibrationally excited states in organic molecules tend to relax rapidly to the lowest vibrational state shedding the excess energy as heat, which then must be dissipated by phonons. The rate of this thermal relaxation and dissipation ( $k_{VR}$ ) can be competitive with the rate of charge separation ( $k_{CS}$ ), since both processes are on the order of 100 fs – 10 ps.

Depending on the system if  $k_{CS} > k_{VR}$  the electron can couple to the phonon modes (extra vibrational energy of the state) to overcome the Coulomb potential between the charges and

continue to move away from the interface into the acceptor material, thereby reaching a CS state (Figure 1.7). If  $k_{VR} > k_{CS}$  then the electron will relax to the CT<sub>1</sub> state and the excess thermal energy will be dissipated. At this point the electron can still try to hop out of the potential well or undergo other processes such as intersystem crossing or recombination. The relative energies of the initial and final states as well as the Coulomb potential and the excess vibrational thermal energy must also be considered from a thermodynamic perspective in order for efficient charge separation to occur.



**Figure 1.7** Energy diagram of donor/acceptor interface with electronic CT states shown in relation with the donor excited state (S<sub>1</sub>) and the charge separated state (CS). The rate difference between k<sub>VR</sub> and k<sub>CS</sub> will determine the kinetics of the charge separation behavior for each photovoltaic system.

Complete charge separation of the exciton results in the electrons and holes being spatially separated across the donor/acceptor interface and outside the range of the Coulomb attraction. The holes must now travel through the donor material and the electrons through the acceptor to their respective electrodes (Step 4 of Figure 1.5). The driving force for charge transport in an OPV is an electrochemical gradient ( $\nabla E_n(x)$ ) which is comprised of two parts; an electric field gradient ( $\nabla U_n(x)$ ) generated by the equilibrium of the Fermi level throughout the cell and a chemical energy potential gradient ( $\nabla \zeta_n(x)$ ) which forms from the high concentration of localized electrons and holes that are separated across the D/A interface.<sup>8</sup> The current density of electrons or holes ( $J_n(x)$ ) within the cell is expressed by Equation 1.4, where  $n_n(x)$  is the concentration of electrons or holes and  $\mu_n$  is the electron or hole mobility.

 $J_n(x)=n_n(x)\mu_n\nabla E_n(x), \quad \nabla E_n=[\nabla U_n(x)+\nabla \zeta_n(x)]$  (Equation 1.4) The chemical potential gradient is often overlooked in OPVs because the electrical potential dominates the charge conduction in inorganic p-n junction cells. However, in OPVs, all charge carriers are generated at the D/A interface with electrons on the acceptor and holes on the donor. This provides a highly localized but separated chemical potential between the two materials and thus provides a significant driving force for charge conduction away from the interface. This high  $(\nabla \zeta_n(x))$  allows OPVs to have a high photovoltaic effect, even when no net electrical potential is present in the cell. This helps to explain how organic cells fabricated from identical electrodes can still produce a significant photovoltaic effect.

The conduction of charges in organic materials can proceed by either a hopping mechanism from localized state to localized state or through band like conduction in the case of highly crystalline conjugated materials with good intermolecular  $\pi$ - $\pi$  overlap.<sup>14</sup> The electron mobility ( $\mu_e$ ) or hole mobility ( $\mu_h$ ) represents the speed at which a carrier will travel through the material under a given applied potential and therefore typically has the units of cm<sup>2</sup>/Vs. Described in this way the carrier mobility along a single conjugated polymer chain can be quite high ~100 cm<sup>2</sup>/Vs, but as the typical conjugated length for a polymer is only between 5-20 nm this conduction path cannot be solely responsible for charge transport in the bulk. Thus, in a thin film the carrier mobility is dominated by 3D intermolecular interactions between conjugated segments and is highly dependent on the solid state packing morphology.

The final step of the OPV mechanism is the extraction of the free carriers by the electrodes, and is not depicted in Figure 1.5. The electrons travel through the acceptor phase and are extracted at the cathode while the holes are conducted through the donor and are extracted at the anode. At first, this may seem counter to the usual nomenclature used with electrochemical cells and batteries, in so far that the acceptor is being oxidized at the cathode and the donor is being reduced at the anode. But as described in Section 1.2.1 a solar cell is an ideal current source and when a load is applied to it a current is produced in opposition to  $J_{ph}$ . This applied current is used to reduce the acceptor material at the cathode and oxidize the donor at the anode and keeps the nomenclature for solar cells in line with traditional electrochemical reactions.

The metal/organic interface is an often overlooked interaction in the study of OPVs and yet can have a profound effect on the efficiency of charge extraction and PCE. For a zero order approximation, the work function of the metal contact should have roughly the same energy as the HOMO of the donor or the LUMO of the acceptor in order to produce the least energetic barrier to charge hopping from organic to metal. Surface traps, interface dipoles and metal-organic reactions can all play a role in altering the energy barrier for charge extraction and may ultimately behave differently for each material system.<sup>15</sup>

The efficiencies of all of the processes in the OPV mechanism combined together are what determine the overall efficiency of the cell as outlined by Equation 1.5. Each fundamental step can be controlled and varied by choices in active layer material, solar cell architecture and fabrication processing. The goal is to understand which step(s) is limiting the overall performance of the system and then to synthesize materials with new properties designed to address the deficiencies. Since alterations intended to improve one step may impact others, the reiterative scheme shown in Figure 1.2 is crucial for the optimization and improvement of any OPV.

 $PCE = \eta_{Absorption} \eta_{Diffusion} \eta_{Separation} \eta_{Conduction} \eta_{Extraction} \quad (Equation 1.5)$ 

### **1.3 CHEMISTRY OF CONJUGATED POLYMERS**

The chemical modification of conjugated polymers alters both their photoelectronic properties (e.g. absorption, ionization potential, charge carrier mobility) and their mechanical properties (e.g. crystallinity, mixing, viscosity, solubility), resulting in both performance changes and changes in the fabrication process. It is crucial to understand how the synthetic alterations made to conjugated polymers impacts all of these parameters in order to effectively design new systems that can address inefficiencies in the photovoltaic process.

The structure/function relationships in conjugated polymers, can be intuitively understood by correlating three basic organic principles; steric interactions, electron negativity and resonance structures, with the overall optical and electronic properties of the material. These three effects coupled with basic principles from molecular orbital theory are all that is really needed to grasp the fundamental behavior behind how chemical modification of a polymer can affect its semiconducting properties.

# **1.3.1 BAND STRUCTURE OF CONJUGATED MATERIALS**

The inherent semiconducting nature of most conjugated polymers can be understood best by looking at simple molecular orbital theory. While there are two special classes of conducting polymers typified by polyacetylene and polyaniline, the majority of conjugated polymers follow the band structure depicted in Figure 1.8, which is based on polyaromatics.<sup>16</sup> As aromatic units are coupled together the hybridization of their HOMO and LUMO levels leads to a decrease in the energy between the two states, which can also be termed a reduction in the band gap (Eg).<sup>17</sup> Since the HOMO and LUMO of aromatic rings are the  $\pi$  and  $\pi^*$  orbitals respectively this coupling allows the  $\pi$  electrons on each ring to sample all attached rings through the fully conjugated system. The energy spacing between the occupied orbitals and the unoccupied orbitals decreases significantly with each additional ring and this coupled with the full delocalization of the  $\pi$  electrons allows these systems to be approximated as continuous energy bands similar to the band structure that describes intrinsic inorganic semiconductors.



Figure 1.8 Band structure diagram of polyaromatics. Eg decreases as more conjugated rings are added. Leading to a narrowing of the HOMO-LUMO gap up to a saturation point determined by the bond alteration lengths between single and double bonds in the two resonance states.

The point at which this delocalization can be approximated by continuous bands is not necessarily straightforward nor is it the same for all conjugated polymers. Likewise the alterations to the electronic structure of a polymer begin to saturate with each additional ring unit, and the point at which this change becomes practically indeterminate is also different for the various polymers. This effective conjugation length is ultimately related to the difference in energy between the  $\pi$  and  $\pi^*$  states, which for most polymers is the difference between the aromatic and quinoid configurations.<sup>18</sup> This implies that the energy gap is also related to the difference in bond alternation length between single and double bonds in the two states. The conjugation length, therefore, is different for each polymer system, but most polyaromatics have a conjugation length between 5 - 20 repeat units. This is the point at which the electronic properties of the material saturate, even though the physical conjugation along a single chain can be greater than 100 repeat units in some polymers.<sup>19</sup> While this chemical picture is often used to describe the band structure in one dimension along a single polymer chain, interchain  $\pi$ - $\pi$  interactions can lead to a further electron delocalization causing a lowering of the E<sub>g</sub> in two or three dimensions.

The size of the band gap in conjugated polymers controls the onset of the optical absorption spectrum. Since no electronic states exist in the band gap the lowest energy photon able to promote an electron from the HOMO to the LUMO must be greater than or equal to the energy of  $E_g$ . The band gap also controls the total amount of useful energy in the system because electrons promoted to higher excited states thermalize to the lowest excited state within a short time scale (fs – ps) by the release of heat into the system.<sup>20</sup>

#### **1.3.2 RESONANCE**

Aromatic ring polymers have at least two resonance structures, one based on the aromatic state and one on the quinoid state. As stated in the previous section the similarity in energy between these two states is oftentimes responsible for the magnitude of the band gap energy. In pure polyaromatics this resonance is largely controlled by the aromatic stabilization energy of the material. Polyparaphenylene (PPP) and poly(p-phynelene vinylene) (PPV) based polymers have larger band gaps (2.2-3 eV) than polythiophene (PT) materials (1.9 eV) in part because of the stronger aromatic stabilization energy of benzene compared to thiophene (Figure 1.9).<sup>18</sup>



Figure 1.9 Band gap control of conjugated polymers due to differences in aromatic stabilization energy. Stronger stabilization energy by benzene prevents delocalization of  $\pi$  system along backbone leading to larger band gap.

The more the aromatic structure dominates the electronic orbitals of the polymer the more time the electrons spend localized to individual monomer units. This has two effects. The first is to localize the electronic states, which can raise the band gap energy as stated previously as well as prevent delocalization along the polymer chains. This shortens the effective conjugation length of the polymer as well as prevents exciton migration through the material. Alternatively, the strong aromatic stabilization lessens the double bond character of the interring bonds, which keeps the dihedral twist energy between monomer units low. This provides even slightly substituted PPPs and PTs with remarkable solubility in common organic solvents considering the strong intermolecular forces in polyaromatics that generally lead to extensive aggregation.

Resonance structures of polymers synthesized from fused ring systems (Figure 1.10) complicate the situation. Competing forces now exist between conjugation along the backbone of the polymer with conjugation into the fused rings perpendicular to the polymer chain. The aromatic driving force of the fused ring forces the polymer to adopt an electronic structure with a more quinoidal component in the ground state. Similarly, the excited state of the polymer now has more aromatic character. Since the quinoid state is higher in energy than the aromatic state, the effect of these two alterations raises the energy of the polymer ground state (S<sub>0</sub>) and lowers the energy of the polymer first excited state (S<sub>1</sub>) thereby reducing E<sub>g</sub>. This effect was first studied in poly(isothianaphthene) (PITN) which has a low band gap of 1.1 eV, where the ground state energy is a relatively even mix between  $\Psi_{\text{Aromatic}}$  and  $\Psi_{\text{Quinoid}}$ .<sup>21</sup> This compared to polythiophene, which has a ground state mostly comprised of aromatic character and a band gap

of 1.9 eV. Replacing the benzene ring with a thiophene ring in the structure poly(thieno[3,4-b]thiophene) (PT34bT) has a similar effect on the magnitude of the band gap (Figure 1.10), but the greater electron density of the thiophene compared to the benzene increases the HOMO and LUMO levels. A family of copolymers employing the T34bT unit has recently seen success in OPVs with PCE between 5-7.4%.<sup>5,22,23</sup>



**Figure 1.10** Resonance structures between a) aromatic and quinoid ground states for polymers such as PITN or PT34bT reduce the band gap by destabilizing the ground state compared to a completely aromatic conjugated polymer such as PT. b) The greater electron density of the thiophene ring in PT34bT compared to PITN raises both the HOMO and LUMO but the resonance effects keep the band gap about the same.

#### **1.3.3 ELECTRONEGATIVITY**

The band structure of conjugated aromatic polymers is generally controlled by the relative energetic differences between the ground and excited states and these sates correspond to the HOMO and LUMO levels of the resulting material. The absolute values of these electronic states are more closely related to the ionization potential and electron affinity of the polymer and thus are controlled by the electronegativity of the atoms. An example can be seen using PT and PPP. Having six delocalized  $\pi$  electrons per five atom thiophene ring, along with the large atomic size and low ionization potential of the sulfur heteroatom generates a fairly "electron rich" unit when compared to benzene. This electron density lowers the ionization potential and the electron affinity of the polymer and thus shifts the HOMO and LUMO values of PT to a higher value relative to PPP.

Substitution along the polymer backbone can also influence the energy levels of the conjugated polymer. Electron withdrawing substituents such as carboxylates, nitriles, and electronegative atoms (F, Cl, etc.) decrease the electron density of the aromatic ring causing an increase in the  $I_P$  and  $E_A$ .<sup>24</sup> Electron donating groups such as alkyl, alkoxy, and electron rich atoms (S, Se, P, etc) decrease the  $I_P$  and  $E_A$ . These two effects can be combined in donor-acceptor copolymers where an electron rich and electron poor aromatic unit are coupled together to form a conjugated polymer.

Donor-acceptor copolymers exhibit optical band gaps and electronic properties that can be tuned by varying either or both donor or acceptor unit, giving access to a broad range of materials properties. While  $\pi$ -conjugated homopolymers exhibit a lower band gap relative to small molecule counterparts primarily as the result of extended delocalization along the polymer backbone, the mechanism by which lower band gaps are achieved in donor-acceptor polymers is primarily based on preferential localization of the HOMO of the polymer to the donor unit, and the LUMO of the polymer to the acceptor unit.<sup>25</sup> This is shown schematically in Figure 1.11. It is important to note that while low band gaps can be achieved in this way, these "push-pull" methods can localize the HOMO to the donor and LUMO to the acceptor almost entirely and result in poor orbital overlap between the ground and excited states. This can result in lowered absorption coefficients, on the order of  $10^3$ - $10^4$  cm<sup>-1</sup> when compared to coefficients of >10<sup>5</sup> for many polymers with strong electronic state overlap. This problem is somewhat, although not exactly analogous to the lower absorption strength of indirect band gap inorganic semiconductors such as silicon.<sup>6</sup> Thus, not every donor-acceptor pairing is reasonable for photovoltaic applications and often the inclusion of other monomer units to help control the orbital overlap is necessary.



Figure 1.11 Donor-acceptor copolymers (push-pull polymers) have tunable band gaps depending on the coupling between the electron rich and electron poor monomers. The resulting polymer has a LUMO similar to the LUMO of the acceptor unit and a HOMO similar to the HOMO of the donor unit.

The electronegativity of aromatic heteroatoms and inductive effects from chemical substituents also impact the ability of conjugated polymers to be oxidized or reduced. Free charge carriers generated during the photovoltaic process can be thought of as cationic or anionic species without a supporting counter ion present. The ease by which polyaromatics can form these ionic species as well as how stable they are will greatly impact the carrier conduction of free charges through the organic layer.<sup>26</sup> Polymers with a low I<sub>P</sub> and large heteroatoms capable of supporting positive charges tend to operate best as hole transporting materials. Similarly, a polymer with a high E<sub>A</sub> and incorporating electronegative heteroatoms like N is often a promising candidate for

an electron transporting material. Care must be taken to balance these properties in any conjugated polymer to avoid large electronegativity differences that may result in charge trap states within a thin film. In addition, all organic semiconductors are technically ambipolar materials and can conduct either electrons or holes under a given set of conditions. This does not imply that both carrier mobilities will be equal, but that there is no intrinsic n or p type organic molecule.

The electronic energy states of conjugated polymers are controlled by their electronegativities and dictate their operation as either electron donor or electron acceptor in a given OPV system. The energy levels also relate to the type of electronic junction formed with different metal electrodes as well as determine the polymers stability to repeated oxidation or reduction during the photovoltaic process. The HOMO and LUMO levels are also directly related to the maximum theoretical voltage produced in an OPV heterojunction system.

# 1.3.4 STERICS

As previously stated, one main contributor to the band gap of conjugated polymers is the effective conjugation length of the molecule. Conjugation based on resonance of  $\pi$  orbitals is highly dependent on the interannular twist angle between neighboring aromatic rings and is approximately proportional to the cosine of the twist angle. Thus, it is important to keep in mind mechanisms by which the polymer chain can become kinked and twisted. Synthetic defects, solvent molecules, heat, and steric hindrance can all prevent the polymer backbone from aligning in a planar fashion.<sup>27</sup> These are typically unwanted processes, since the reduction in conjugation leads to lower electronic performance by preventing strong packing structures. Occasionally this decrease in packing can be utilized to allow for more intimate mixing of two conjugated molecules that would otherwise separate in the solid state as the result of the strong packing. Careful synthetic control of these defect sites can be used to stabilize the mixing without fully compromising the optical and electronic properties.<sup>28</sup>

Both intermolecular and intramolecular steric effects must be considered when analyzing the chemical structure of conjugated polymers. One classic example of intramolecular sterics is para coupled phenyl monomers leading to a competition between resonance stabilization of the planar conformation and steric twisting due to impeding hydrogen atoms (Figure 1.12a).<sup>18</sup> In the case of  $\beta$ -substituted polythiophenes, head-to-tail coupling of the monomer repeat units is often necessary to avoid steric interactions of the solubilizing groups leading to chain torsion, which can limit the conjugation length (Figure 1.12b).<sup>29</sup>



**Figure 1.12** a) Intrachain steric interaction from H on neighboring rings leads to a twisting of the polymer backbone. The lowest energy for the annular rotation is at 30 degrees. b) Solubilizing groups in P3HT can cause steric twisting of the backbone when monomers are not coupled in a 100% head-to-tail fashion. These sterics can disrupt both intra and intermolecular packing.

Sterics are often the most important consideration in the intermolecular interactions between conjugated polymers in the solid state. Planar conjugated polymers have a strong intermolecular driving force for face-to-face aggregation, which is usually referred to as  $\pi$ - $\pi$  stacking. While not as strong or as close as covalent bonds  $\pi$  orbital overlap does allow  $\pi$  electrons to sample a more delocalized orbital system. The increase in delocalization lowers the overall energy of the system, causing a reduction in the band gap and facilitates intermolecular charge conduction.<sup>30</sup> This aggregation is the primary reason for insoluble or intractable material. Non-planar side chains can be used to help reduce the amount of intermolecular aggregation allowing polyaromatics to remain solution processable. Twisted phenyl rings and branched alkyl chains are typical examples of such side groups. Straight chain alkyls and alkoxy groups tend to facilitate  $\pi$ -stacking and can only be utilized with conjugated polymers that have none or few fused aromatic units. Too much intermolecular separation from overly bulky side groups becomes detrimental to the electronic properties of the material in the solid state; by increasing the intermolecular distance far enough to inhibit charge conduction.

# **1.4 DEVICE FABRICATION AND TESTING**

The third step in the iterative optimization of new materials for OPVs is the processing, fabrication and testing of the photovoltaic devices. The fundamental mechanism of an OPV was shown in Figure 1.5 and gives a description of the general operating conditions necessary for photogenerated charge extraction. A primary requirement for the operation of the OPV mechanism is the interaction between an electron donating organic semiconductor and an electron accepting organic semiconductor. Individual conjugated materials can be tuned for

optimized light absorption, carrier transport or HOMO-LUMO levels, but it is ultimately the solid state interactions between the donor and acceptor that determine the overall effectiveness of an OPV system.

### **1.4.1 OPV DEVICE ARCHITECTURES**

In OPV devices there are two main architectures controlling the interactions between the donor and acceptor materials. The simplest system is a bilayer heterojunction architecture and is shown in Figure 1.13a. The electron donor and acceptor are deposited sequentially and sandwiched between to electrodes usually with the form indium tin oxide anode (ITO)/poly(3,4ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS)/Donor/Acceptor/Cathode. Indium tin oxide is a transparent conductor and when used as the anode is often coated with a thin layer (20-60 nm) of a conductive polymer, which is typically PEDOT doped with PSS. The PEDOT:PSS layer results in a better interface between the active layer and the electrode and different formulations can be used to modify the electrode work function to better match the donor material being used. The cathode is generally a thermally evaporated low work function metal such as aluminum, magnesium or calcium. For potentially low cost OPVs, the conjugated polymers are cast from solution directly onto the substrate. Typical laboratory procedure usually requires spin coating concentrated solutions (1-5 wt% polymer in solvent) of the conjugated material with a total resulting thickness for both layers usually between 60 - 100 nm. Dip coating and drop casting are two other laboratory techniques. In future commercial applications, ink-jet printing and aerosol spraying are two potentially attractive methods that work well in rollto-roll processing.

The bilayer architecture is simple in design and operation and is therefore useful in studying certain fundamental properties of conjugated polymers, since each layer can be optimized for solid state packing and thickness independently. This structure also eliminates variability in performance as a result of poor or unstable miscibility between the donor and acceptor. The PCE of bilayer heterojunctions are typically limited however since charge generation can only occur at the single interface between the donor and acceptor.<sup>31</sup> In conjugated polymers with low diffusion lengths, only photons absorbed within a narrow width from the D/A interface have a chance at generating free charges. This usually limits the overall thickness of absorbing material that can effectively contribute to photocurrent to 10-20 nm and therefore limits the overall PCE of bilayer devices. This raises the question of why the active layer usually requires a thickness of almost 100 nm to generate the best working device, since only about 20% has the potential of generating photocurrent. No completely satisfactory explanation has been developed to date, but the most probable mechanism involves interference of the exciton separation process at the D/A heterojunction by either metal electrodes. In effect, the thicker polymer layer provides a buffer zone for the photoactive material from the electrodes resulting in better performance. The construction of a true bilayer device also requires an orthogonal processing technique for the two layers and this condition often makes this architecture difficult to realize in solution processed OPVs.<sup>32</sup>



Figure 1.13 Schematic diagram of a typical OPV device. The active layer is designed either as a) a bilayer structure or b) a bulk heterojunction depending on the desired properties of the solar cell.

The other general class of OPV device is depicted in Figure 1.13b and is usually referred to as a bulk heterojunction (BHJ) device.<sup>33</sup> Here, the donor and acceptor material are codeposited usually from a mixed solution of the two materials. The device architecture for this OPV class is generally ITO/PEDOT:PSS/Donor:Acceptor/Cathode with the donor and acceptor being deposited in a specific ratio. The active layer thickness for these devices is generally between 50 – 300 nm. If the two materials have a reasonable affinity for each other, the resulting blend morphology can have a nanometer size phase separation, which eliminates the problem of the short exciton diffusion length by providing a D/A interface close enough to any exciton generated. This allows the thickness of the resulting film to be increased leading to higher incident light absorption.

Charge transport in a BHJ device can be more difficult to analyze. In order for effective conduction of free charges, each free charge separated at a D/A interface must have a continuous pathway from its point of origin to the relevant electrode; anode for holes and cathode for electrons. The high D/A surface area along the conductive pathways allows for high probability of bimolecular recombination (free electron-free hole recombination) and therefore requires both materials to have sufficiently high carrier mobilities to minimize recombination events.

Effective BHJ devices require a nanoscale phase separated morphology with a bicontinuous but interpenetrating network of donor and acceptor. Control over the formation and stabilization of this delicate blend morphology often requires optimization of both the polymer structure and device fabrication conditions such as donor-acceptor ratio, solvent choice, small molecule additives, deposition technique and post-fabrication annealing.<sup>34</sup> Figure 1.14 shows an in focus transmission electron microscopy image of a polymer:fullerene BHJ layer. The greater electron scattering ability of the fullerene cage makes it appear as the darker regions in the film. The

blend morphology has been controlled to keep individual phases on the order of 10-100 nm which allows for a good bicontinuous interpenetrating network with high surface area between the donor and acceptor.



Figure 1.14 An in focus TEM of a polyer:fullerene showing the proper BHJ morphology on the nanoscale.

# **1.4.2 Space Charge Limited Conduction**

An organic photovoltaic can often be approximated as a metal-semiconductor-metal diode, where a thin film (~100 nm) is sandwiched top and bottom with electrodes. This device architecture requires that the charge conduction within the semiconductor flow perpendicular to the plane of the substrate. Thus the vertical charge carrier mobility of the organic material in a thin film morphology is of particular importance. This can be especially true for semicrystalline conjugated polymers, which can often have highly anisotropic packing structures.

P3HT is a well studied example of anisotropic crystal polymers and prefers to pack in long nanofibrils. These crystalline polymer fibers can be 10 - 500 nm in width and can be 20 - 10000 nm in length.<sup>35,36</sup> The fibers form with the intermolecular  $\pi$ - $\pi$  stacking along the long axis of the fiber, as shown in Figure 1.15. P3HT also crystallizes in the z direction due to van der Waals interactions between the alkyl solubilizing groups and the polymer chains are generally orientated as shown in Figure 1.15 due to interactions between the polymer and the substrate surface chemistry.<sup>37-39</sup> This type of packing structure has a large effect on the hole mobility of P3HT. When the positive charges are generally kept within the fiber and traveling parallel to the substrate, P3HT has been shown to have hole mobilities greater than 0.1 cm<sup>2</sup>/Vs.<sup>19</sup> When holes travel perpendicular to the substrate, as in OPVs, their conduction is hampered by the aromatic backbone-backbone separation distance due to the alkyl chain spacing. The charges must therefore travel vertically in less crystalline portions of the film or travel in short crystals that are potentially oriented with a different directionality. These factors reduce the hole mobility of P3HT to approximately  $10^{-4}$ - $10^{-3}$  cm<sup>2</sup>/Vs in the vertical direction.<sup>40</sup>



**Figure 1.15** The packing structure of P3HT into nanofibrils. The approximate unit cell shown is orthorhombic with lattice spacings 16.1Å (100), 7.6 Å (010), and 7.6 Å (001).

Relevant mobilities for OPV materials are therefore best taken using the same device architecture utilized in the OPV itself and where charges flow in the same direction as they do in solar cell operation. This can be accomplished by fabricating a metal-semiconductor-metal diode in the same way as an OPV is made. The only difference is that both metals should have similar work functions matched to only one semiconducting energy level instead of the dissimilar work functions generally employed in an OPV. This allows for preferential injection of only holes or only electrons into the diode.<sup>41</sup>

When the diode is biased in the forward direction the injection of either holes or electrons occurs preferentially based on the electrodes chosen. As charges enter the device they are transported across the film in accordance with Equation 1.6, which relates the current density of charges to a given electric field. Conduction in this manner is referred to as Ohmic conduction, where  $N_0$  is the charge density, q is the fundamental charge,  $\mu_n$  is the charge mobility,  $V_R$  is the voltage drop due to the resistances of the electrodes only and L is the thickness of the device. This equation cannot be used to determine the carrier mobility directly because it is difficult to correctly obtain the value for the concentration of free charges in the device under these conditions.

$$J = N_0 q \mu_n \frac{V - V_R}{L}$$
 (Equation 1.6)

As higher potentials are applied to the diode, the current begins to reach a point at which it cannot move across the device at a rate directly proportional to the rate of new charges being injected into the film. This inability to move charges away from the metal/semiconductor interface begins the buildup of space charge (Figure 1.16a).



**Figure 1.16** Space charge builds up at the charge injecting electrode. a) Positively charged holes accumulate at the positive terminal creating space charges, which slowly move across the device. b) The transition between an Ohmic current and a space charge limited current plotted against V for P3HT.

The buildup of charges alters the electric field within the device according to Poisson's equation. The carriers escaping away from the space charge region now travel at a rate that is not related to the carrier density and thus current flow is only controlled by the intrinsic mobility of the material. Charges traveling in this way are said to be space charge limited. The altered drift equation modified by the space charge buildup is shown in Equation 1.7. As can be seen, the mobility of the device can now be calculated from a J-V curve of a device with a known thickness that is operating in the space charge limited regime. Here,  $\varepsilon$  is the dielectric constant of the material and  $\varepsilon_0$  is the permittivity of free space.

$$J_{SCLC} = \frac{9}{8} \epsilon \epsilon_0 \mu_n \frac{V - V_R}{L^3}$$
 (Equation 1.7)

A typical space charge limited conduction (SCLC) curve for P3HT is shown in figure 1.16b. At the junction point between the Ohmic region and the SCLC region Equation 1.6 and 1.7 are equivalent and the charge carrier density ( $N_0$ ) at this point can be calculated. This carrier density can be compared to the carrier density of charges in an illuminated OPV and can therefore help determine whether the OPV will be operating in an Ohmic region or SCLC region for a given intensity of light.

#### **1.5 DISSERTATION OVERVIEW**

Conjugated polymer photovoltaic modules are promising candidates for diverse renewable energy applications. They are solution processable at room temperature allowing them to be cheap, lightweight, flexible and potentially disposable. To realize the future potential of these new devices, fundamental research into how the polymer chemical structure affects the solar cell performance must be continued. Chapter 1 gives a general overview into the process by which the chemistry of conjugated polymers can be altered to alter the optical and electrical semiconductor properties and improve the solar cell PCE. This requires a reiterative process whereby first, the OPV mechanism is understood and inefficient mechanistic steps are identified. This is followed by the synthesis of conjugated polymers which have been chemically tailored for improvement in optical, electronic or morphological properties. The fabrication and testing of solar cells and related devices such as thin film diodes and transistors probe the performance of the modified materials. This collected data allows for the reevaluation of the OPV mechanism to explain the resulting solar cell performance and to focus back on inefficient processes that need to be addressed.

The generation and movement of the excited exciton are the first two steps in the OPV mechanism. Utilizing new conjugated polymers with planar metal complexes based on incorporating platinum are explored in chapter 2. The chemical structure of these new materials is related to their photophysical properties and long exciton lifetimes. BHJ solar cells with fullerene acceptors are presented.

Chapter 3 explores the effects of chemical structure on the exciton separation efficiency at the donor/acceptor interface in all-polymer OPVs. The charge separation step can be influenced by distance and dielectric constant. Polymer structure impacts these two parameters and directly affects the performance of all-polymer solar cells.

The energy levels of conjugated polymers can be controlled through the use of electronic side chain substituents. Chapter 4 focuses on the energetic and structural differences of carboxylate substituted polythiophenes and how these changes relate to charge mobility, donor and acceptor efficiency and environmental stability.

Chapter 5 relates how the chemical modification of polythiophene side chains can control the BHJ blend morphology of the polymer with either PCBM or carbon nanotubes. Control of the solubilizing group distribution can impact the crystallinity of the conjugated polymer and alter its miscibility with other materials. Functional groups with affinities for highly aromatic molecules can also be appended to the polymer backbone to allow for direct interaction with other materials.

The morphology of the active layer can be performed in solution by the development of conjugated polymer nanoparticles. Chapter 6 outlines the polymer properties that influence polymer nanoparticle formation during a new nanoprecipitation method. The nanoparticle properties are examined by UV-Vis and XRD and are related to their performance in organic field effect transistors.

# REFERENCES

- (1) Ullmann's Encyclopedia of Industrial Chemistry; Wiley-VCH Verlag GmbH & Co. KGaA, Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000.
- (2) Thompson, B. C.; Fréchet, J. Angewandte Chemie International Edition 2008, 47, 58-77.
- (3) Hoth, C. N.; Choulis, S.; Schilinsky, P.; Brabec, C. Advanced Materials **2007**, *19*, 3973-3978.

- (4) Brabec, C. J. Solar Energy Materials and Solar Cells 2004, 83, 273-292.
- (5) Liang, Y.; Xu, Z.; Xia, J.; Tsai, S.; Wu, Y.; Li, G.; Ray, C.; Yu, L. *Adv. Mater.* **2010**, NA-NA.
- (6) Nelson, J. *The physics of solar cells*; Imperial College Press, 2003.
- (7) Li, G.; Shrotriya, V.; Yao, Y.; Huang, J.; Yang, Y. J. Mater. Chem. 2007, 17, 3126-3140.
- (8) Gregg, B. A. .
- (9) Tang, C. W. Appl. Phys. Lett. 1986, 48, 183.
- (10) Markov, D. E.; Amsterdam, E.; Blom, P. W. M.; Sieval, A. B.; Hummelen, J. C. *The Journal of Physical Chemistry A* **2005**, *109*, 5266-5274.
- (11) Clem, T. A.; Kavulak, D. F. J.; Westling, E. J.; Fréchet, J. M. J. Chemistry of Materials 0.
- (12) Brédas, J.; Norton, J. E.; Cornil, J.; Coropceanu, V. Accounts of Chemical Research 2009, 42, 1691-1699.
- (13) Zhu, X.; Yang, Q.; Muntwiler, M. Accounts of Chemical Research 2009, 42, 1779-1787.
- (14) Coropceanu, V.; Cornil, J.; da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Brédas, J. Chemical Reviews 2007, 107, 926-952.
- (15) Koch, N.; Kahn, A.; Ghijsen, J.; Pireaux, J.; Schwartz, J.; Johnson, R. L.; Elschner, A. *Appl. Phys. Lett.* **2003**, *82*, 70.
- (16) Nalwa, H. S. Handbook of Organic Conductive Molecules and Polymers: Conductive polymers : synthesis and electrical properties; Wiley, 1997.
- (17) Gettinger, C. L.; Heeger, A. J.; Drake, J. M.; Pine, D. J. J. Chem. Phys. 1994, 101, 1673.
- (18) Roncali, J. Chem. Rev 1997, 97, 173–206.
- (19) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. Nature 1999, 401, 685-688.
- (20) Turro, N. J. Modern molecular photochemistry; University Science Books, 1991.
- (21) Bredas, J. L.; Heeger, A. J.; Wudl, F. J. Chem. Phys. 1986, 85, 4673-4678.
- (22) Liang, Y.; Xiao, S.; Feng, D.; Yu, L. *The Journal of Physical Chemistry C* 2008, *112*, 7866-7871.
- (23) Liang, Y.; Wu, Y.; Feng, D.; Tsai, S.; Son, H.; Li, G.; Yu, L. Journal of the American Chemical Society 2009, 131, 56-57.
- (24) Murphy, A. R.; Liu, J.; Luscombe, C.; Kavulak, D.; Frechet, J. M. J.; Kline, R. J.; McGehee, M. D. *Chemistry of Materials* **2005**, *17*, 4892-4899.
- (25) Peet, J.; Heeger, A. J.; Bazan, G. C. Accounts of Chemical Research 2009, 42, 1700-1708.
- (26) Horowitz, G. Advanced Materials 1998, 10, 365-377.
- (27) Inganäs, O.; Salaneck, W.; Österholm, J.; Laakso, J. Synthetic Metals 1988, 22, 395-406.
- (28) Woo, C. H.; Thompson, B. C.; Kim, B. J.; Toney, M. F.; Fréchet, J. M. J. Journal of the American Chemical Society 2008, 130, 16324-16329.
- (29) Zhokhavets, U.; Erb, T.; Gobsch, G.; Al-Ibrahim, M.; Ambacher, O. *Chemical Physics Letters* **2006**, *418*, 347-350.
- (30) Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Liu, J.; Frechet, J. M. J.; Toney, M. F. *Macromolecules* 2005, *38*, 3312-3319.
- (31) Heremans, P.; Cheyns, D.; Rand, B. P. Accounts of Chemical Research 2009, 42, 1740-1747.
- (32) Kim, B. J.; Miyamoto, Y.; Ma, B.; Fréchet, J. M. J. Advanced Functional Materials **2009**, 19, 2273-2281.
- (33) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. Science 1995, 270, 1789-1791.

- (34) Sivula, K.; Luscombe, C. K.; Thompson, B. C.; Fréchet, J. M. J. *Journal of the American Chemical Society* **2006**, *128*, 13988-13989.
- (35) Kim, D. H.; Han, J.; Park, Y.; Jang, Y.; Cho, J.; Hwang, M.; Cho, K. *Advanced Materials* **2006**, *18*, 719-723.
- (36) Berson, S.; De Bettignies, R.; Bailly, S.; Guillerez, S. Advanced Functional Materials **2007**, *17*, 1377-1384.
- (37) Liu, S.; Wang, W. M.; Briseno, A. L.; Mannsfeld, S. C. B.; Bao, Z. Advanced Materials **2009**, *21*, 1217-1232.
- (38) Joseph Kline, R.; McGehee, M. D.; Toney, M. F. Nat Mater 2006, 5, 222-228.
- (39) Ihn, K. J.; Moulton, J.; Smith, P. *Journal of Polymer Science Part B: Polymer Physics* **1993**, *31*, 735-742.
- (40) Blom, P. W. M.; Mihailetchi, V.; Koster, L.; Markov, D. Advanced Materials 2007, 19, 1551-1566.
- (41) Koster, L. J. A.; Mihailetchi, V. D.; Blom, P. W. M. Appl. Phys. Lett. 2006, 88, 052104.

# CHAPTER 2: CONTROL OF ELECTRON-HOLE EXCITED STATES IN CYCLOMETALATED PLATINUM POLYMERS

#### ABSTRACT

The chemistry of conjugated polymers can alter the photogenerated exciton lifetime and diffusion length. This chapter presents the characterization of new platinum-containing conjugated polymers in which the platinum atom is attached to the conjugated backbone via a  $C^N$  ligand. The polymers exhibit optical bandgaps between 2.1 and 1.65 eV depending on the choice of comonomer. Triplet exciton formation is detected indirectly by measuring photosensitized emission of singlet oxygen in both solution and in film. The ability of the materials to sensitize formation of singlet oxygen varies both with excitation wavelength and with the change from solution to solid state. This study provides design principles for developing conjugated polymers with significant triplet yields in the solid state. The photovoltaic performance of these polymers was also evaluated in preliminary experiments with power conversion efficiencies as high as 1.46% obtained for a bulk heterojunction cell with PC<sub>70</sub>BM.

Portions of this chapter were published previously: Chem. Mater., 2010, 22, 1977.

#### **2.1 INTRODUCTION**

The first three processes in an organic photovoltaic device, (1) light absorption followed by (2) the diffusion of the exciton to a donor/acceptor interface and (3) the subsequent separation of that exciton into free charges are all based on an excitonic solar cell model.<sup>1</sup> To increase OPV performance it is necessary to maximize the efficiency of each of these processes. Fundamental examinations of how the chemical structure of conjugated polymers influences the exciton states is therefore a vital route in the improvement of organic solar cells.

The photophysics of conjugated polymers in a thin film can often be viewed from the basis of a localized chromophore interacting in close proximity to other chromophores. This simply requires dealing with tradiational organic photophysics, but on larger chromophore units, which may exist in a range of sizes and energies based on the structural disparity often found in polydisperse materials. The intrachain and interchain polymer morphology must also be taken in to consideration when designing materials for excitonic devices.



Figure 2.1 Magnetic spin vectors for singlet and triplet electron pairs.

Direct excitation of an organic chromophore often leads to a localized singlet exciton unless there is a method for preserving the total angular momentum of the system. After excitation though, the exciton can undergo intersystem crossing from a singlet state to a triplet state (Figure 2.1) through a number of possible pathways such as spin-orbit coupling or spin-spin coupling. Materials with large triplet yields may well provide access to increased current in organic photovoltaic devices.<sup>2</sup> Triplet excited state lifetimes are typically in the microsecond regime, which is three orders of magnitude longer than the nanosecond decays typically observed for singlet excited states in conjugated polymers. Given that exciton diffusion length ( $L_D$ ) is determined by exciton lifetime ( $\tau$ ) and exciton diffusivity (*D*) according to Equation 2.1 a significant increase in lifetime should lead to a longer exciton diffusion length, which would be advantageous for bilayer photovoltaic devices.

$$L_D = \sqrt{\tau D}$$
, (Equation 2.1)
Triplet-forming polymers have also been reported to inhibit geminate pair recombination<sup>3</sup> and to increase the exciton diffusion length<sup>4</sup> in bulk heterojunction devices. Since charge separation in a well-mixed bulk heterojunction occurs on the femtosecond time scale<sup>13</sup> while intersystem crossing occurs in the nanosecond regime,<sup>5</sup> in a bulk heterojunction system which has a closely mixed morphology, charge separation will most likely occur before triplet excitons can form. Thus, any improvement in photovoltaic performance for triplet-forming materials in a bulk heterojunction is expected to be primarily the result of decreased geminate recombination or another factor.

## 2.2 CONTROLLING THE EXCITON OF CYCLOMETALATED PLATINUM POLYMERS

Recently, there has been significant interest in conjugated organometallic polymers as donor polymers for use in bulk heterojunction (BHJ) solar cells in combination with fullerene acceptors.<sup>3,6-12</sup> In particular, polyplatinynes have drawn some attention as a result of their absorption profiles extending as far as the near infrared,<sup>12</sup> and their promising charge transport properties with reported hole mobilities as high as  $1.0 \times 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in field-effect transistors (FETs).<sup>11</sup> In addition, polyplatinynes have demonstrated triplet exciton formation utilizing the "heavy atom effect" to increase the intersystem crossing rate.<sup>3,9</sup>

However, the conjugated organometallic polymers that have actually been experimentally shown to form triplets in the solid state are also large bandgap systems<sup>4</sup> (>2.5 eV), and therefore power conversion efficiencies are limited by the poor overlap of their absorption spectrum with the solar irradiance. While lower band gap systems have demonstrated formation of triplet excitons in solution, this result does not necessarily translate to the solid state. Furthermore, performance of these lower band gap polymers is limited by their charge mobility.<sup>9</sup>

In polyplatinynes the poor size and energetic overlap between the 5d Pt and 2p C orbitals leads to a significantly smaller effective conjugation length when compared to structurally analogous poly(phenylene ethynylenes).<sup>13</sup> Given that exciton diffusion length is a function of both lifetime and diffusivity, this exciton localization, or decreased effective conjugation length, may ultimately limit the photovoltaic performance and/or the exciton diffusion lengths observed for these polymers even if long-lived triplets are realized. Organometallic conjugated polymer architectures other than polyplatinynes are therefore worthy of investigation as donor materials to better understand the role of heavy atoms on triplet formation in conjugated polymers for possible application in photovoltaics.

### 2.1.1 MATERIALS

A new class of platinum-containing conjugated polymers<sup>14</sup> with optoelectronic properties that are suitable for photovoltaic applications is shown in Figure 2.2. These polymers contain a 2-(2'-thienyl)thiazole  $C^N$  ligand with an  $O^O$  diketonate ligand that creates a structure analogous to a fused bithiophene system but in which platinum is adjacent to the conjugated backbone and connects the aryl groups into a coplanar conformation. Fused bithiophenes have recently received attention as a building block in low bandgap conjugated polymers, where the optical

and electronic properties of the polymer vary with the choice of connecting atom.<sup>15-18</sup> In contrast to the platinum acetylides, the platinum atom is peripheral to the conjugated polymer backbone, leading to a greater involvement from the orbitals of Pt in both the ground and the excited states of the material.<sup>19</sup> This design attempts to minimize any potential decrease in effective conjugation length from the poor overlap of Pt and C orbitals, and creates a platform for the study of the influence of a heavy atom on more diffuse excitons. This design also provides flexibility in tuning the absorption profile and energy levels of the materials simply by varying the Pt ligand and comonomer.



Figure 2.2 General structure of cyclometalated Pt polymers.

A 2-(2'-thienyl)thiazole C^N ligand was chosen in order to take advantage of the high photovoltaic efficiencies,<sup>20-22</sup> high charge carrier mobilities<sup>23</sup> and strong light absorption<sup>24</sup> associated with polythiophenes. The thiazole unit should also contribute favorably to charge mobility,<sup>25,26</sup> while providing a nitrogen atom for Pt coordination and minimizing donor-acceptor interactions in the polymer. The diphenyl ketonate ligand provides solubility via the peripheral dialkoxy groups. Since platinum complexes containing the 2-(2'-thienyl)thiazole ligand have not been reported previously, model complex PtTZ (Figure 2.3) was synthesized to enable a comparison of optical and electronic properties of the repeat unit to those of the corresponding polymers.<sup>14</sup> Stille and Suzuki polymerizations led to the formation of Pt-T1 and F8TZPt (Figure 2.3), using Pd( $P^tBu_3$ )<sub>2</sub> and reaction conditions based on those developed by the Fu group.<sup>27,28</sup> This palladium system was used in place of the Pd(PPh<sub>3</sub>)<sub>4</sub> analog, because the metal complex was found to degrade under polymerization conditions using the more classical catalyst. The exact nature of this degradation is unknown, but Pt(acac)<sub>2</sub> complexes have been shown to react with triaryl phosphine ligands by displacing one of the O atoms of the diketonate ligand<sup>29</sup> or by forming a pentacoordinate complex.<sup>30</sup> The tri(*tert*-butyl)phosphine ligand is significantly more bulky than triphenylphosphine, as evidenced by its ability to form a stable divalent Pd(0)complex at room temperature,<sup>28</sup> and by its larger cone angle of 182° versus the 145° determined for triphenylphosphine.<sup>31</sup> This bulkiness likely hinders coordination of the ligand on the Pt center, allowing the polymerization to proceed without disturbance to the metal complex. In addition, the high activity of the Pd(P<sup>t</sup>Bu<sub>3</sub>)<sub>2</sub> catalyst system makes it possible to achieve high molecular weight polymers via both Stille and Suzuki coupling routes at 40 °C, a lower reaction temperature than the 80 - 100 °C frequently used for analogous Pd-catalyzed polymerizations. The reduced reaction temperature should also contribute to the improved stability of the platinum complex during polymerization.



Figure 2.3 Chemical structures of PtTZ, Pt-T1 and F8TZPt

The crude polymers were isolated by precipitation into methanol, followed by Soxhlet extraction with methanol and hexanes to remove low molecular weight impurities, and finally chloroform or chlorobenzene to collect the desired polymer fraction. The chlorobenzene fraction of **Pt-T1** and the chloroform fraction of **F8TZPt** were isolated and reprecipitated into methanol and their physical properties are listed in Table 2.1.

Polymer	Mn	Mw	PDI
Pt-T1 <sup>a</sup>	45 kDa	84 kDa	1.9
F8TZPt <sup>b</sup>	24 kDa	47 kDa	1.9

**Table 2.1** Molecular weights of polymers studied. <sup>a</sup> SEC in Dichlorobenzene, <sup>b</sup> SEC in THF (both calibration done with polystyrene standards)

### 2.1.2 Optical and Electronic Properties

The optical and electronic properties of **PtTZ**, **F8TZPt** and **Pt-T1** were studied in order to determine the suitability of these materials for photovoltaic applications, and to further understand the effects of extending conjugation through a cyclometalated platinum complex. Figure 2.4a shows the UV-Vis absorbance spectra for **PtTZ**, **Pt-T1**, and **F8TZPt** in dilute chloroform solution and Figure 2.4b shows the UV-Vis absorbance spectra for **PtTZ**, **Pt-T1** and **F8TZPt** in thin films. Both polymers exhibit a strong transition at approximately 350 nm, which, given the similarity between this peak and the absorption profile of the small molecule **PtTZ**, is attributed to the direct excitation of the metal complex. Both polymers also show strong transitions at longer wavelengths, with peaks at 665 nm and 520 nm for solutions of **Pt-T1** and **F8TZPt**, respectively. These peaks are attributed to excitations delocalized along the conjugated polymer chain. The absorption for **F8TZPt** is significantly redshifted when compared to those of the previously reported platinated polyfluorenes **P-1** and **P-2** shown in Figure 2.4.<sup>32</sup>



Figure 2.4 Overlaid absorption spectra of polymers and small molecule in chloroform solution (a) and thin film (b): PtTZ (black), Pt-T1 (blue), and F8TZPt (red).



Figure 2.5 Previously reported platinum-containing polyfluorenes.<sup>32</sup>

Changing the *C*^*N* ligand in the fluorene copolymers from 2-phenylpyridine in **P1** or **P2** to 2-(2'-thienyl)thiazole in **F8TZPt** causes the lower energy absorption maximum to shift from 450 nm to 520 nm. The small molecule complexes containing 2-phenylpyridine<sup>19</sup> and 2-(2'thienyl)thiazole have similar absorption spectra, so this larger bathochromic shift suggests that **F8TZPt** may have significant donor-acceptor character. Further, these results show that the optical properties of these platinum-containing polymers can be tuned by modifying either or both the platinum complex and the comonomer. The UV-Vis spectrum of **F8TZPt** also exhibits a redshift from 520 nm to 555 nm when changing from solution to film. This shift in absorption to longer wavelengths together with the enhanced vibronic structure is indicative of increased  $\pi$ - $\pi$  stacking in the solid state. In contrast, no significant spectral change is observed for **Pt-T1**, suggesting little increase in organization of the polymer when proceeding from solution to film. Based on the onset of absorption in the solid state, the optical bandgap of **F8TZPt** is 2.1 eV. The optical bandgap of **Pt-T1** is 1.65 eV, close to the theoretically ideal bandgap of 1.5 eV for a donor material in a polymer:PCBM solar cell.<sup>17</sup>

In addition to the absorption properties, the HOMO and LUMO of the donor material are key parameters that influence the overall performance of a photovoltaic device by affecting the efficiency of charge separation and the maximum attainable open-circuit voltage (V<sub>OC</sub>). Cyclic voltammograms (CV) of **Pt-T1**, **F8TZPt**, and **PtTZ** were used to determine their oxidation and

reduction potentials. The HOMO level was determined by the onset of oxidation, the LUMO was determined by the onset of reduction when it was observed and determined by the difference between the HOMO and the optical bandgap. The oxidations and reductions observed were all irreversible, which is consistent with previously reported Pt(II) complexes.<sup>33</sup> For PtTZ no reduction peak was observed, but an irreversible oxidation was observed at 0.3 V corresponding to a HOMO of -5.4 eV. This HOMO level is comparable to that of the C^N ligand, which has a HOMO of -5.3 eV, suggesting that the HOMO of the platinum complex is primarily based on the C^N ligand. The polymer Pt-T1 undergoes an irreversible oxidation at -5.4 eV, and an irreversible reduction at -3.5 eV, for an electrochemical bandgap of 1.9 eV. The optical bandgap for Pt-T1 is slightly smaller (1.65 eV). However for F8TZPt the HOMO is lower at -5.6 eV. The HOMO of poly(9,9-dioctyfluorene) (PFO) is -5.7 eV,<sup>23</sup> suggesting that the HOMO of **F8TZPt** is at least partly influenced by the fluorene moiety. An electrochemical reduction was not observed for F8TZPt, but based on the difference between the optical bandgap and the HOMO, the LUMO is estimated to be -3.5 eV. The optical and electronic properties of all the materials are summarized in Table 2.2. Taken together the data indicate that both the optical bandgap and the HOMO levels of the materials may be tuned by varying the comonomer, while the LUMO is primarily determined by the platinum complex.

Sample	λ <sub>max</sub> , CHCl <sub>3</sub> solution	λ <sub>onset</sub> , film	E <sub>g</sub> optical (eV)	HOMO (eV)	LUMO <sup>a</sup> (eV)	LUMO <sup>b</sup> (eV)
PtTZ	330 nm	475 nm	2.6	-5.4	N/A	-2.8
Pt-T1	335 nm	750 nm	1.65	-5.4	-3.5	-3.75
	610 nm					
<b>F8TZPt</b>	375 nm	600 nm	2.1	-5.6	N/A	-3.5
	520 nm					

**Table 2.2** Optical and electronic properties of **PtTZ**, **Pt-T1** and **F8TZPt**. <sup>a</sup>Determined by onset of reduction

 <sup>b</sup>Estimated according to LUMO=HOMO-E<sub>g</sub> optical

## 2.1.3 Photoluminescence and Singlet Oxygen Generation

Organometallic conjugated polymers with large intersystem crossing yields have demonstrated increased photocurrent in photovoltaic devices. This increase in performance has been attributed to decreased geminate recombination<sup>3</sup> and increased exciton diffusion length due to the forbidden nature of recombination from the triplet state.<sup>4</sup> However, these previously reported polymers have bandgaps larger than 2.5 eV, resulting in poor overlap with the solar spectrum. The polymers presented here absorb strongly in the visible spectrum; they are also expected to possess more delocalized excitons than the polyplatinynes, providing a new platform to study the effect of a heavy atom on intersystem crossing in conjugated polymers.

To investigate the influence of the Pt center on the **F8TZPt** and **Pt-T1** polymers the emission spectra of all materials (including monomer precursors) were measured at both long and short excitation wavelengths. All experiments were conducted in degassed benzene solution. At room temperature, **PtTZ** exhibits a phosphorescence peak with an onset at 575 nm (2.16 eV) and a maximum at 660 nm when excited at 370 nm. This peak can be assigned to a  $T_1 \rightarrow S_0$  transition as

evidenced by the large Stokes shift and long lifetime (3.8  $\mu$ s). The triplet energy of the small molecule is at a lower energy relative than reported for several other *C*^*N*Pt(*O*^*O*) complexes, which is most likely due to the electron rich nature of the *C*^*N* and *O*^*O* ligands.<sup>19</sup> Further, the triplet energy of the complex is above the triplet energy of poly(3-octylthiophene) (1.65 eV) and below that of PFO (2.3 eV),<sup>34</sup> suggesting that in **Pt-T1** energy transfer from the triplet of the complex to the triplet of the polymer may occur readily. Conversely, energy transfer from the metal complex may be disfavored for the fluorene copolymer **F8TZPt**. The absorbance and photoluminescence of **PtTZ** are shown in Figure 2.6.



Figure 2.6 Absorbance and emission of PtTZ: Absorbance (black) and emission (red).

The observed phosphorescence of the complex at room temperature is in sharp contrast to the reported behavior of other diphenyl ketonate-substituted platinum complexes, which show no emission from the triplet state as a result of the thermal equilibrium between the *C*^*N* ligand-centered (<sup>3</sup>LC) emissive state and the nonemissive Pt/diphenyl ketonate charge transfer (<sup>3</sup>CT) state.<sup>32</sup> The significant phosphorescence from **PtTZ** at room temperature indicates that the triplet state of C^N ligand lies sufficiently below the triplet state of the diphenyl ketonate ligand to inhibit this nonradiative decay pathway. At room temperature, degassed solutions of both polymers **F8TZPt** and **Pt-T1** show weak emission with small Stokes shifts suggesting emission from the singlet state. Although phosphorescence is not observed for **Pt-T1** or **F8TZPt**, they may still undergo intersystem crossing to the triplet state followed by nonradiative decay pathway, possibly via intersystem crossing, may be more favorable.

In order to probe the formation of triplets before nonradiative decay, the ability of both solutions and films of these materials to generate singlet oxygen was explored as a function of excitation wavelength. The efficiency of singlet oxygen photosensitization is strongly correlated to triplet quantum yield in conjugated polymers.<sup>34</sup> Molecular oxygen is able to quench triplet excited states by a variety of energy transfer pathways, leading to luminescence of singlet oxygen that is readily detected at 1270 nm.<sup>36</sup> The results of these experiments are summarized in Table 2.3.

Sample	Excitation $\lambda$	<sup>1</sup> O <sub>2</sub> Generation
PtTZ <sup>a</sup>	370 nm	yes
Pt-T1 <sup>a</sup>	370 nm	no
Pt-T1 <sup>a</sup>	665 nm	no
Pt-T1 <sup>b</sup>	370 nm	yes
Pt-T1 <sup>b</sup>	665 nm	no
F8TZPt <sup>a</sup>	370 nm	yes
F8TZPt <sup>a</sup>	530 nm	yes

Table 2.3 Singlet oxygen generation by PtTZ, Pt-T1 and F8TZPt. <sup>a</sup>C<sub>6</sub>H<sub>6</sub> solution; <sup>b</sup> 2:1 C<sub>6</sub>H<sub>5</sub>Cl:C<sub>6</sub>H<sub>6</sub> solution

At room temperature, an aerated benzene solution of **PtTZ** shows strong singlet oxygen emission when excited at 370 nm. In contrast, a benzene solution of Pt-T1 does not sensitize singlet oxygen formation at either short or long excitation wavelengths. Because the sample of Pt-T1 used in these studies was isolated from chlorobenzene, aggregation of the polymer in a weaker solvent such as benzene was thought to be responsible for quenching. Aggregation of conjugated polymers has been shown to quench excitons via an energy transfer process occurring on a picosecond timescale,<sup>37</sup> faster than the nanosecond time scale typical for intersystem crossing. Indeed, singlet oxygen formation was observed upon excitation at 370 nm when a more strongly solvating 2:1 mixture of chlorobenzene and benzene was used to dissolve Pt-T1. The solvent dependence for singlet oxygen generation using Pt-T1 as a sensitizer indicates that Pt-T1 is most likely aggregated in pure benzene solution. However, when excited at 665 nm, no singlet oxygen generation is observed from Pt-T1 even in the better solvent system. Excitation of Pt-T1 at 370 nm is analogous to excitation of PtTZ, which quickly undergoes intersystem crossing due to the proximity of the heavy Pt atom and the strong orbital overlap with Pt orbitals in the excited state. Therefore triplet formation is facile when exciting at 370 nm. Exciting at 665 nm corresponds to more delocalized excitations that are spread along the polymer backbones. This more delocalized excitation clearly does not exhibit enhanced intersystem crossing. As the exciton becomes more delocalized, the Pt atomic orbitals are expected to make a proportionally smaller contribution to the molecular orbitals associated with the exciton. Since the excited electron is traveling fastest and therefore feels the highest magnetic torque when it is closest to the heavy atom's nucleus, the probability of intersystem crossing will decrease as the electron becomes more delocalized and less involved with the Pt atom. Given that the singlet energy of Pt-T1 is lower in energy than the triplet energy of PtTZ, it is also expected that the singlet of Pt-T1 will not undergo significant energy transfer to the triplet of PtTZ. Further, it has been suggested that nonradiative decay rates increase relative to the intersystem crossing rate as excitons become more delocalized in a conjugated material.<sup>38</sup>

Benzene solutions of **F8TZPt** exhibit singlet oxygen emission at 1270 nm when excited at either 370 nm or at 530 nm. As was the case for **Pt-T1**, excitation at 370 nm is attributed to excitation of the small molecule chromophore, which rapidly undergoes intersystem crossing. In contrast to **Pt-T1**, **F8TZPt** also generates triplet excitons at longer excitation wavelength. For

**F8TZPt**, the initially delocalized exciton may ultimately localize to the platinum moiety because the platinum monomer unit is lower in energy than the polymer energy levels which are similar to those of poly(9,9-dioctylfluorene).<sup>39</sup> The singlet energy of **F8TZPt** is close in energy to the triplet energy of **PtTZ**, suggesting that energy transfer from the singlet of **F8TZPt** to the triplet of **PtTZ** can occur readily. This more localized exciton exhibits strong spin-orbit coupling through the platinum atom, leading to formation of triplet excitons as evidenced by sensitized formation of singlet oxygen. The difference in triplet formation observed between **F8TZPt** and **Pt-T1** at the longer excitation wavelength is illustrated schematically in Figure 2.7. Red dashed lines represent the excitons initially formed at long excitation wavelengths, with energy transfer occurring to the monomer unit of **PtTZ** in the case of **F8TZPt**.



**Figure 2.7** Different means of promotion and inhibition of triplet formation in **F8TZPt** and **Pt-T1** for long wavelength excitations generating extended excitons. Energy level diagrams for S<sub>1</sub> and T<sub>1</sub> states.

**PtTZ** λ<sub>ev</sub> 665 nm PtTZ

Pt-T1

While both polymers are able to sensitize formation of singlet oxygen in solution, neither polymer was observed to sensitize singlet oxygen formation in a thin film. The difference in triplet formation from solution to solid phase, as evidenced by singlet oxygen generation, most likely arises as the result of intermolecular interactions providing a faster decay pathway, analogous to aggregates in solution. For example, regioregular poly(3-alkyl)thiophenes (P3ATs) have a large triplet yield in solution ( $\%_T$ =0.77),<sup>34</sup> but do not readily form triplets in a film.<sup>44</sup>

Formation of triplet states in the solid state is disfavored for P3ATs in part because the formation of more delocalized, lower energy excimers and polarons is more favorable.<sup>40</sup> Formation of triplet excitons in P3AT films is also partly disfavored as a result of decreased twisting between adjacent thiophene units; an increased twist angle between adjacent thiophenes leads to increased spin-orbit coupling.<sup>41</sup> Given that spin-orbit coupling is dominated by the platinum atom in both **F8TZPt** and **Pt-T1**, the change in triplet formation from solution to solid state in **F8TZPt** and **Pt-T1** (as evidenced by singlet oxygen generation) should be primarily the result of lower-energy excimers forming in the polymer films and not a decrease in twisting between adjacent thiophene units. Together, these results suggest that polymers with excitons centered on molecular orbitals with significant contribution from a heavy atom and with lowered aggregation in the solid state would be desirable to generate triplet excitons in a film for photovoltaic devices.

### 2.1.4 Photovoltaic Performance

The polymers **Pt-T1** and **F8TZPt** were studied in bulk heterojunction photovoltaic devices with  $PC_{60}BM$  to better understand the influence of the cyclometalated platinum moiety on performance. The optimal blending ratio for both **F8TZPt** and **Pt-T1** was found to be 1:4 (polymer: $PC_{60}BM$ ). Results optimized for polymer:PCBM ratio, thickness, and annealing give power conversion efficiencies of 0.40% for **F8TZPt**, and 1.29% for **Pt-T1** under AM 1.5 illumination at 100 mW cm<sup>-1</sup>. Figure 2.8 shows the performance of the devices without annealing. Thermal annealing was found to significantly decrease the performance of the devices, presumably as a result of excessive phase segregation between polymer and  $PC_{60}BM$ . For **F8TZPt** the J<sub>sc</sub> is 3.5 mA cm<sup>-2</sup>, the V<sub>oc</sub> is 0.38 V, and the fill factor is 0.30. For **Pt-T1** the J<sub>sc</sub> is 5.3 mA cm<sup>-2</sup>, the V<sub>oc</sub> is 0.65 V, and the fill factor is 0.37. The performance of **Pt-T1** is significantly better than **F8TZPt**, which is partly the result of its superior overlap with the solar spectrum.



**Figure 2.8** Photovoltaic performance of **F8TZPt** (red) and **Pt-T1** (black) blended with PC<sub>60</sub>BM; **Pt-T1** blended with PC<sub>70</sub>BM (blue). All devices measured under AM 1.5 illumination 100 mW cm<sup>-2</sup>.

In light of its superior performance, **Pt-T1** was also studied in a bulk heterojunction solar cell with  $PC_{70}BM$ .  $PC_{70}BM$  absorbs significantly further into the visible spectrum as compared to  $PC_{60}BM$ , meaning that it can potentially contribute to photocurrent generation. For this system the optimal blending ratio is found to be 1:4 **Pt-T1**:PC<sub>70</sub>BM. The best performance is found without annealing, giving a power conversion efficiency of 1.46%. The J<sub>sc</sub> is 5.15 mA cm<sup>-2</sup>, the V<sub>oc</sub> is 0.69 V, and the fill factor is 0.41 (Figure 2.8). Interestingly, although PC<sub>70</sub>BM is expected to improve device performance by contributing to photocurrent, the short circuit current density in the **Pt-T1**:PC<sub>70</sub>BM devices are lower than in the **Pt-T1**:PC<sub>60</sub>BM devices. Instead, the improvement in device performance arises from an increase in the open circuit voltage and fill factor. This result suggests that **Pt-T1** may form a poor blend morphology with soluble fullerenes.

Based on the electrochemistry described previously, it is possible that holes localize at the platinum unit of F8TZPt and this localization inhibits charge transport in a device. The HOMO of **PtTZ** is higher than the HOMO of **F8TZPt**, suggesting that the platinum-containing monomer may act as a local energy minimum for holes in the device. In order to better understand potential limiting factors on photovoltaic performance of polymers containing the cyclometalated platinum complex, the space charge limited current (SCLC) mobilities of **Pt-T1** and **F8TZPt** were measured. Unlike FETs, SCLC mobility determines charge mobility in the vertical direction under no gate bias, making it potentially a more relevant measurement of charge mobility in the context of photovoltaic devices. The zero-field hole mobility of F8TZPt is 2.5 x 10<sup>-9</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. The inefficient charge transport measured for this polymer clearly contributes to its poor photovoltaic performance, and further suggests that the platinum complex may act as a charge and energy trap in this polymer in which the platinum complex is copolymerized with the wider bandgap fluorene unit. In contrast, the zero-field hole mobility of Pt-T1 was measured as  $1 \times 10^{-5}$  cm<sup>-2</sup> V<sup>-1</sup> s<sup>-1</sup>. The SCLC mobilities for the pristine polymers and the bulk heterojunction photovoltaic device parameters are summarized in Table 2.4. The striking difference in SCLC hole mobility between Pt-T1 and F8TZPt demonstrates that comonomer selection may affect both charge transport and photophysics of the resulting polymer. The SCLC hole mobility of Pt-**T1** is lower than that of polythiophenes<sup>42,40</sup> ( $10^{-4}$  to  $10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>), but higher than the reported SCLC hole mobilities of polyplatinynes<sup>9</sup> ( $10^{-8}$  to  $10^{-7}$  cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup>). The improved SCLC hole mobility observed for Pt-T1 relative to the polyplatinynes shows that platinum-containing conjugated polymers with connectivity via a C^N ligand are an attractive alternative route to organometallic polymers for photovoltaics.

Active Layer	Voc	$\mathbf{J}_{\mathbf{sc}}$	FF	η	$\mu_h$ (SCLC)
F8TZPt:PC <sub>60</sub> BM	0.38 V	$3.5 \text{ mA cm}^{-2}$	0.30	0.40%	$2.5 \text{ x } 10^{-9} \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$
Pt-T1:PC <sub>60</sub> BM	0.65 V	$5.3 \text{ mA cm}^{-2}$	0.37	1.29%	$1.0 \ge 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$
Pt-T1:PC <sub>70</sub> BM	0.69 V	$5.15 \text{ mA cm}^{-2}$	0.41	1.46%	$1.0 \text{ x } 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$

Table 2.4 Photovoltaic performance for **F8TZPt**:PC<sub>60</sub>BM, **Pt-T1**:PC<sub>60</sub>BM and **Pt-T1**:PC<sub>70</sub>BM. Hole mobility values measured in pure films by Space Charge Limited Current method.

### **2.3 CONCLUSION**

This work presents a new approach to low bandgap platinum-containing conjugated polymers based on a platinum monomer with  $C^N$  and  $O^O$  diketonate ligands. In these materials the platinum atom is attached adjacent to the conjugated backbone, and therefore does not inhibit exciton delocalization along the polymer chain, providing a means to study the effect of a heavy atom on diffuse excitons. Photovoltaic devices fabricated from these materials yield efficiencies approaching 1.5%, demonstrating that cyclometalated platinum polymers are an attractive new class of materials for organic photovoltaics. Photophysical studies indicate that for some materials long wavelength excitations experience rapid nonradiative decay leading to no observable triplet exciton. This localization promotes triplet formation but is disadvantageous to charge transport in a photovoltaic device. The results presented here suggest that the development of conjugated materials having both significant triplet yields and overlap with the visible spectrum in the solid state will require new materials designed to minimize nonradiative decay pathways at longer excitation wavelengths.

#### **2.4 EXPERIMENTAL**

Cyclic voltammetry (CV) was performed using a Solartron 1285 potentiostat. For the polymers, CV was performed on thin films dip-coated onto a Pt wire working electrode and submerged in CH<sub>3</sub>CN freshly distilled from CaH<sub>2</sub>. For small molecules, the cyclic voltammograms were measured in dichloromethane solution with a Pt wire working electrode. All measurements were performed using a silver wire pseudo-reference electrode, a platinum auxiliary electrode, and were referenced to the ferrocene/ferrocenium couple, which was taken to be -5.1 eV relative to vacuum.<sup>43</sup> Tetrabutylammonium tetrafluoroborate (NBu<sub>4</sub>BF<sub>4</sub>) was the supporting electrolyte for all measurements.

UV-Visible absorption spectra were obtained using a Cary 50 UV-Visible spectrophotometer. For thin film measurements polymers were spin coated onto untreated glass slides from chlorobenzene solution (10 mg mL<sup>-1</sup>). A model P6700 Spincoater was used to spin coat the films at 1500 rpm for 60 s.

Photoluminescence spectra were obtained using a Horiba Jobin Yvon Nanolog fluorimeter using a xenon lamp for steady state excitation spectra and a 345nm 10 kHz NanoLED for lifetime measurements. In both cases the detectors were either a Hamamatsu R928 PMT or 5509 PMT, for visible and infrared detection respectively. For deoxygenated samples, the solvent was degassed by three freeze-pump-thaw cycles, and then the solutions were freshly prepared inside of a glove box under argon atmosphere. For aerated samples, the solution was purged with air for 5 minutes prior to measurement.

Photovoltaic devices consisted of a standard ITO/PEDOT:PSS/Pt-polymer:PCBM/Al architecture. Indium-doped tin oxide (ITO) coated glass substrates were purchased from Thin Film Devices, Inc. The substrates (150 nm sputtered pattern,  $10 \Omega \Box^{-1}$ ) were cleaned by 20 minutes of sonication in acetone, 2 percent Helmanex soap in water, and finally isopropanol. The substrates were then dried under a stream of air before being coated immediately with a filtered

(0.45 µm GHP) dispersion of PEDOT:PSS in water (Baytron-PH) via spin coating for 30 s at 4000 rpm. The resulting polymer layer was ~30 nm thick after baking at 140 °C for 20 min. All subsequent device fabrication was performed inside a glove box under inert Ar atmosphere with water and oxygen levels below 1 ppm. Each Pt-polymer was dissolved at a concentration of 16 mg mL<sup>-1</sup> in chlorobenzene. PCBM and PC<sub>70</sub>BM (purchased from Nano-C) were dissolved separately at 40 mg mL<sup>-1</sup> in chlorobenzene and all solutions were allowed to stir overnight at 120 °C. The solutions were then combined in various ratios from 1:1 to 1:6 polymer:fullerene along with additional chlorobenzene as needed to a final polymer concentration of 8 mg mL<sup>-1</sup>, before spin casting onto the PEDOT:PSS-treated ITO at 1200 rpm for 30 seconds. 100 nm aluminum electrodes were deposited by thermal resistance evaporation at pressures of approximately  $10^{-6}$ torr to complete the device structure. The shadow mask used during thermal deposition yielded eight independent devices per substrate each with a surface area of 0.03 cm<sup>2</sup>. Completed devices were then tested under Ar(g) using a 300 W Thermo-Oriel Xenon arc-lamp with flux control spectrally corrected to AM 1.5 G with one filter (Thermo-Oriel #81088). The AM 1.5 G light was further attenuated using a 0.5 O.D. neutral density filter, and the intensity of the AM 1.5 G light was calibrated to be 100 mW cm<sup>-2</sup> by a spectrally-matched Hamamatsu S1787-04 photodiode (calibrated by NREL and obtained through Nanosys Inc.). I-V behavior was measured using a computer-controlled Keithley 236 SMU.

Polymer mobility was measured using a diode configuration of ITO/PEDOT:PSS/Polymer/Al in the space charge limited current regime. At sufficient potential the conduction of charges in the device can be described by Equation 1.7, where  $\varepsilon_0$  is the permittivity of space,  $\varepsilon_R$  is the dielectric of the polymer (assumed to be 3),  $\mu$  is the mobility of the majority charge carriers, V is the potential across the device (V = V<sub>applied</sub> – V<sub>bi</sub> - V<sub>r</sub>), and L is the polymer layer thickness. The series and contact resistance of the device (13-21  $\Omega$ ) was measured using a blank (ITO/PEDOT/Al) and the voltage drop due to this resistance (V<sub>r</sub>) was subtracted from the applied voltage. The built-in voltage (V<sub>bi</sub>), which is based on the relative work function difference of the two electrodes, was also subtracted from the applied voltage. The built-in voltage can be estimated from the difference in work function between the cathode and anode and is found to be about 1 V.

#### REFERENCES

- (1) Gregg, B. A. .
- (2) Shao, Y.; Yang, Y. Advanced Materials 2005, 17, 2841-2844.
- (3) Guo, F.; Kim, Y.; Reynolds, J. R.; Schanze, K. S. Chem. Commun. 2006, 1887-1889.
- (4) Schulz, G. L.; Holdcroft, S. Chemistry of Materials 2008, 20, 5351-5355.
- (5) Turro, N. J. *Modern molecular photochemistry*; University Science Books, 1991.
- (6) Wong, W. Macromolecular Chemistry and Physics 2008, 209, 14-24.
- (7) Wong, W.; Wang, X.; He, Z.; Chan, K.; Djurišić, A. B.; Cheung, K.; Yip, C.; Ng, A. M.; Xi, Y. Y.; Mak, C. S. K.; Chan, W. *Journal of the American Chemical Society* **2007**, *129*, 14372-14380.
- (8) Wu, P.; Bull, T.; Kim, F. S.; Luscombe, C. K.; Jenekhe, S. A. Macromolecules 2009, 42,

671-681.

- (9) Mei, J.; Ogawa, K.; Kim, Y.; Heston, N. C.; Arenas, D. J.; Nasrollahi, Z.; McCarley, T. D.; Tanner, D. B.; Reynolds, J. R.; Schanze, K. S. ACS Applied Materials & Interfaces 2009, 1, 150-161.
- (10) Sudha Devi, L.; Al-Suti, M. K.; Zhang, N.; Teat, S. J.; Male, L.; Sparkes, H. A.; Raithby, P. R.; Khan, M. S.; Ko□hler, A. *Macromolecules* 2009, *42*, 1131-1141.
- (11) Baek, N. S.; Hau, S. K.; Yip, H.; Acton, O.; Chen, K.; Jen, A. K. *Chemistry of Materials* **2008**, *20*, 5734-5736.
- (12) Wang, X.; Wong, W.; Cheung, K.; Fung, M.; Djurisic, A. B.; Chan, W. Dalton Trans. 2008, 5484-5494.
- (13) Silverman, E. E.; Cardolaccia, T.; Zhao, X.; Kim, K.; Haskins-Glusac, K.; Schanze, K. S. *Coordination Chemistry Reviews* **2005**, *249*, 1491-1500.
- (14) Clem, T. A.; Kavulak, D. F. J.; Westling, E. J.; Fréchet, J. M. J. Chemistry of Materials 0.
- (15) Liao, L.; Dai, L.; Smith, A.; Durstock, M.; Lu, J.; Ding, J.; Tao, Y. *Macromolecules* **2007**, *40*, 9406-9412.
- (16) Zhou, E.; Nakamura, M.; Nishizawa, T.; Zhang, Y.; Wei, Q.; Tajima, K.; Yang, C.; Hashimoto, K. *Macromolecules* **2008**, *41*, 8302-8305.
- (17) Soci, C.; Hwang, I.; Moses, D.; Zhu, Z.; Waller, D.; Gaudiana, R.; Brabec, C.; Heeger, A. *Advanced Functional Materials* **2007**, *17*, 632-636.
- (18) Moulé, A. J.; Tsami, A.; Bünnagel, T. W.; Forster, M.; Kronenberg, N. M.; Scharber, M.; Koppe, M.; Morana, M.; Brabec, C. J.; Meerholz, K.; Scherf, U. *Chemistry of Materials* 2008, 20, 4045-4050.
- Brooks, J.; Babayan, Y.; Lamansky, S.; Djurovich, P. I.; Tsyba, I.; Bau, R.; Thompson, M. E. *Inorganic Chemistry* 2002, *41*, 3055-3066.
- (20) Kim, Y.; Cook, S.; Tuladhar, S. M.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C.; Giles, M.; McCulloch, I.; Ha, C.; Ree, M. *Nat Mater* 2006, *5*, 197-203.
- (21) Hong, X. M.; Katz, H. E.; Lovinger, A. J.; Wang, B.; Raghavachari, K. Chemistry of Materials 2001, 13, 4686-4691.
- (22) Chua, L.; Zaumseil, J.; Chang, J.; Ou, E. C.; Ho, P. K.; Sirringhaus, H.; Friend, R. H. *Nature* **2005**, *434*, 194-199.
- (23) Li, W.; Katz, H. E.; Lovinger, A. J.; Laquindanum, J. G. *Chemistry of Materials* **1999**, *11*, 458-465.
- (24) Littke, A. F.; Dai, C.; Fu, G. C. *Journal of the American Chemical Society* **2000**, *122*, 4020-4028.
- (25) Littke, A. F.; Schwarz, L.; Fu, G. C. *Journal of the American Chemical Society* **2002**, *124*, 6343-6348.
- (26) Okeya, S.; Miyamoto, T.; Ooi, S.; Nakamura, Y.; Kawaguchi, S. *Inorganica Chimica Acta* **1980**, *45*, L135-L137.
- (27) Ooi, S.; Matsushita, T.; Nishimoto, K.; Okeya, S.; Nakamura, Y.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3297-3301.
- (28) Tolman, C. A. Chemical Reviews 1977, 77, 313-348.
- (29) Thomas, S. W. I.; Yagi, S.; Swager, T. M. J. Mater. Chem. 2005, 15, 2829-2835.
- (30) Kvam, P.; Puzyk, M. V.; Balashev, K. P.; Songstad, J. Acta Chem. Scand. **1995**, 49, 335-343.
- (31) Burrows, H. D.; de Melo, J. S.; Serpa, C.; Arnaut, L. G.; Monkman, A. P.; Hamblett, I.; Navaratnam, S. J. Chem. Phys. 2001, 115, 9601-9606.

- (32) Rachford, A. A.; Goeb, S.; Castellano, F. N. *Journal of the American Chemical Society* **2008**, *130*, 2766-2767.
- (33) Schweitzer, C.; Schmidt, R. Chemical Reviews 2003, 103, 1685-1758.
- (34) Fakis, M.; Anestopoulos, D.; Giannetas, V.; Persephonis, P. *The Journal of Physical Chemistry B* **2006**, *110*, 24897-24902.
- (35) Wilson, J. S.; Chawdhury, N.; Al-Mandhary, M. R. A.; Younus, M.; Khan, M. S.; Raithby, P. R.; Kohler, A.; Friend, R. H. *Journal of the American Chemical Society* 2001, *123*, 9412-9417.
- (36) Liao, L. S.; Fung, M. K.; Lee, C. S.; Lee, S. T.; Inbasekaran, M.; Woo, E. P.; Wu, W. W. *Appl. Phys. Lett.* **2000**, *76*, 3582-3584.
- (37) Jiang, X.; Österbacka, R.; Korovyanko, O.; An, C.; Horovitz, B.; Janssen, R.; Vardeny, Z. *Advanced Functional Materials* **2002**, *12*, 587-597.
- (38) Ohkita, H.; Cook, S.; Astuti, Y.; Duffy, W.; Tierney, S.; Zhang, W.; Heeney, M.; McCulloch, I.; Nelson, J.; Bradley, D. D. C.; Durrant, J. R. *Journal of the American Chemical Society* **2008**, *130*, 3030-3042.
- (39) Beljonne, D.; Shuai, Z.; Pourtois, G.; Bredas, J. L. *The Journal of Physical Chemistry A* **2001**, *105*, 3899-3907.
- (40) Huang, Y.; Wang, Y.; Sang, G.; Zhou, E.; Huo, L.; Liu, Y.; Li, Y. The Journal of Physical Chemistry B 2008, 112, 13476-13482.
- (41) Van, P. C.; Macomber, R. S.; Mark, H. B.; Zimmer, H. *The Journal of Organic Chemistry* **1984**, *49*, 5250-5253.
- (42) Thompson, B. C.; Kim, B. J.; Kavulak, D. F.; Sivula, K.; Mauldin, C.; Fréchet, J. M. J. *Macromolecules* **2007**, 40, 7425-7428.
- (43) Lee, J. K.; Ma, W. L.; Brabec, C. J.; Yuen, J.; Moon, J. S.; Kim, J. Y.; Lee, K.; Bazan, G. C.; Heeger, A. J. *Journal of the American Chemical Society* 2008, *130*, 3619-3623.

# **CHAPTER 3: CONTROL OF CHARGE SEPARATION THROUGH CHEMICAL MEANS**

### ABSTRACT

The charge separation process at the donor acceptor interface is heavily controlled by the Coulomb attraction between electrons and holes in a dielectric medium. Alterations in the local chemistry of the donor/acceptor interface can lead to a reduction in the strength of this attraction thereby allowing for a higher percentage of geminate pairs to separate. GRIM-POPT is found to have favorable electronic, optical, and processing properties for organic photovoltaics (OPVs). Space-charge limited current and field effect transistor measurements for POPT yielded mobilities of 1 x 10<sup>-3</sup> cm<sup>2</sup>/Vs and 0.05 V/cm<sup>2</sup>, respectively. An efficiency of 2.1% is achieved in an all-polymer, bilayer OPV with (CNPPV) as an acceptor. This state-of-the-art all-polymer device is analyzed in context to the analogous P3HT/CNPPV device. Counter to expectations based on more favorable energy level alignment, greater active layer light absorption, and similar hole mobility, P3HT/CNPPV devices perform less well than POPT/CNPPV system is related to the steric separation enforced by the twisted phenyl ring. DFT calculations along with XRD and PDS spectroscopy are utilized to probe the donor/acceptor interface.

Further investigations into charge separation utilize a P3HT derivative to examine the correlation between the dielectric constant of the active layer and charge separation efficiency at the interface between P3HT and CNPPV. 15CI, a poly(alkylthiophene) with a terminal camphoric imide moiety appended to the end of 15% of its alkyl chains, increases the dielectric constant of the polymer to 5.6, almost twice that of P3HT. In blends with P3HT the 15CI polymer leads to improved performance over pure P3HT in bilayer all-polymer solar cells with CN-PPV as the acceptor. The higher efficiencies in the P3HT:15CI blend devices are attributed to the higher active layer dielectric constant which facilitates increased charge separation. An optimized device utilizing a 1:1 blend of P3HT:15CI shows a 42% increase in power conversion efficiency compared to a P3HT control device.

Portions of this chapter were published previously: J. Am. Chem. Soc., 2009, 131, 14160.

## **3.1 INTRODUCTION**

In order to achieve high efficiencies with thin film organic solar cells the semiconducting layer must absorb strongly in a large portion of the solar spectrum. Due to the necessity of having a significant amount of both p-type and n-type material present in the active layer in order to achieve good charge generation and conduction, both semiconducting materials should be strong light absorbers, ideally with complimentary absorption spectra in order to harvest the maximum solar flux. The perfect symmetry of  $C_{60}$  prevents it from having a strong optical absorption in the visible or infrared region of the spectrum.<sup>1</sup> Thus, current research has moved to utilizing soluble  $C_{70}$  derivatives which have an enhanced absorption cross section in the visible. An alternative approach for this strategy would be to utilize two semiconducting polymers as the two components for the active layer.

All-polymer solar cells combine typical p-type polymers with more electron deficient conjugated polymers, which act as the n-type component. These photovoltaic active layers generally benefit from both an enhanced light absorption but also from a higher open circuit voltage.<sup>2</sup> The increased  $V_{oc}$  is primarily a result of the higher lying LUMO level of the n-type polymer when compared to PCBM. Unfortunately, the higher LUMO level reduces the energy gained during the electron transfer from the LUMO of the donor to the acceptor. This coupled with general slower electron mobility, when compared to fullerenes, prevents efficient charge separation of the geminate pair exciton. It is primarily the inefficient geminate pair separation that limits the overall performance of all-polymer OPVs.<sup>3</sup>

Thus, in order to realize the potential of all-polymer devices, understanding the charge separation process and how the polymer structure may be altered to enhance geminate pair dissociation is critical. Equation 3.1 describes the potential energy between two point charges inside a dielectric medium, where  $q_1$  and  $q_2$  denote the magnitude of the two charges,  $\varepsilon_s$  is the dielectric constant of the medium between the charges, and r is the separation distance. Quick examination shows that the potential energy holding two charges together decreases as either the dielectric constant or the distance between the charges increases. Both of these parameters can be altered at the donor-acceptor interface by controlling the chemical structure of the conjugated polymers.

$$U_{\rm E} = \frac{q_1 q_2}{4\pi\varepsilon_{\rm s} r}$$
 (Equation 3.1)

### **3.2 CONTROLLING DONOR-ACCEPTOR DISTANCE**

Steric interactions between chemical components often lead to an increase in bond spacing or molecular packing. Poly[3-(4-n-octyl)-phenylthiophene] (POPT)<sup>4,5</sup> is an attractive alternative to P3HT for use in all-polymer solar cells. POPT was first investigated for use in OPVs by Granstrom *et al.* in 1998 using a laminate bilayer POPT:poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-(1-cyanovinylene)phenylene] (CNPPV) device, which yielded the highest photocurrent of its time with peak EQE of 28%.<sup>6</sup> However, more thorough studies of POPT and derivatives have yielded only modest OPV performance ( $\eta < 0.5\%$ ).<sup>7-9</sup>

### 3.2.1 MATERIAL

For this study, POPT was polymerized from the 2-bromo-5-iodo-3-(4-n-octyl)thiophene monomer in ~50% final yield with a modified GRIM procedure. Due to the steric and electronic effects of the 3-phenyl ring, elevated metal-halogen exchange and polymerization temperatures were required to achieve suitable polymer yield and molecular weight. POPT with  $M_n$  up to 75 kDa and PDI < 1.2 was obtained after Soxhlet purification. The purified polymer was >99% RR as determined by NMR.<sup>10</sup>



Figure 3.1 From left to right; structures of P3HT, POPT, CNPPV and PCBM.

### **3.2.2 OPTICAL AND ELECTRONIC PROPERTIES**

As spun-cast from high boiling point solvents, thin films of GRIM POPT display UV-Vis vibronic structure unlike oxidatively synthesized POPT, which does not show such structured absorption without additional processing steps.<sup>4</sup> POPT has a band gap of ~1.75 eV, which is red-shifted about 50 nm from that of P3HT (Figure 3.2). This coupled with the complimentary absorption from CNPPV covers most of the visible light in the solar spectrum and clearly has the potential to absorb more light than P3HT:PCBM layers.



Figure 3.2 Normalized absorption spectra of POPT, P3HT, CNPPV and PCBM overlaid with the normalized solar flux.

The mobility values of POPT were investigated for the first time and showed values of  $\mu_h = 1 \text{ x}$  $10^{-4} \text{ cm}^2/\text{Vs}$  and  $\mu_h = 0.05 \text{ cm}^2/\text{Vs}$  using space-charge limited current and field effect transistor measurements, respectively. No change in mobility was observed upon thermal annealing. These mobility values are similar to those obtained for P3HT and suggest that hole extraction in OPV devices is not likely to differ much between these polythiophenes.

### **3.2.3 Photovoltaic Performance**

The relatively high solvent resistance of GRIM POPT resulting from its high Mn and regioregularity enables a better examination of the all-polymer system first explored by Friend.<sup>6</sup> CNPPV can be spin-coated directly on top of a POPT film using solvents such as tetrahydrofuran or ethyl acetate which are too weak to dissolve POPT, leading to bilayer devices as opposed to the previously explored laminate design. A bilayer architecture was used to hopefully simplify the interfacial morphology between POPT and CNPPV in an effort that changes in device performance could more readily be associated with the interaction of geminate pairs between POPT and CNPPV. A peak efficiency of 2.0% was achieved with this system after 2 hrs of thermal annealing at 110°C (average  $\eta = 1.5\%$ ). This constitutes the highest reported efficiency to date for a solution processed all-polymer OPV.<sup>11-13</sup> Significantly, similar all-polymer devices optimized from GRIM P3HT yielded a max efficiency of 0.93% with an average of 0.75%. As seen in Figure 3.3A this lower efficiency is due primarily to a reduction in the short circuit current (Jsc).



Figure 3.3 (A) JV curves for POPT and P3HT devices under AM 1.5 100 mW/cm<sup>2</sup> illumination. (B) Material energy band levels. (C) Absorption spectra of bilayers at optimized thicknesses for devices. (D) EQE plots of optimized devices.

The increased Jsc exhibited by the POPT/CNPPV devices does not derive from increased absorption, as illustrated by the absorption spectra of Figure 3.3C. Under optimized conditions, the POPT/CNPPV bilayer absorbs ~75% as much light as P3HT/CNPPV bilayers, but exhibits about twice the photocurrent. The photocurrent is enhanced across the entire absorption spectrum

of the device (Figure 3.3D). Since a thin film solar cell with a reflective back contact becomes an optical cavity where incident and reflective light can interact, the thickness of each layer in a bilayer device becomes increasingly important. Having only one interface at which charge separation can occur coupled with a short exciton diffusion length results in a device that is more sensitive to the light intensity throughout the device. Therefore, the absorption spectra are not fully adequate to rule out the number of absorbed photons near the interface as the reason for the larger J<sub>sc</sub>. To rule out interference effects as a reason for the higher current density in the POPT devices, bilayers of both POPT/CNPPV and P3HT/CNPPV were fabricated at different thicknesses. The summary of this data in Table 5.1 shows that the POPT based devices outperform the P3HT devices regardless of thickness. Since neither light absorption nor hole mobility can explain this difference in photocurrent, an increase in the charge separation efficiency between POPT and CNPPV is most likely.

POPT conc. in PhCI	CNPPV conc. in THF	V <sub>oc</sub>	J <sub>sc</sub> (mA/ cm²)	FF	<b>η</b> %
2 mg/ml	8 mg/ml	0.40	1.33	0.25	0.13
6 mg/ml	8 mg/ml	0.64	2.79	0.26	0.46
10 mg/ml	8 mg/ml	1.04	2.16	0.29	0.65
12 mg/ml	8 mg/ml	1.08	1.79	0.26	0.50
10 mg/ml	6 mg/ml	1.08	2.21	0.24	0.57
10 mg/ml	9 mg/ml	1.04	1.70	0.26	0.46
РЗНТ	CNPPV				
6 mg/ml	8 mg/ml	0.75	0.41	0.31	0.10
9 mg/ml	8 mg/ml	0.69	0.39	0.28	0.08
10 mg/ml	8 mg/ml	0.88	1.23	0.27	0.29
13 mg/ml	8 mg/ml	0.79	0.74	0.25	0.15

Table 3.1 Performance parameters for POPT/CNPPV and P3HT/CNPPV solar cells at various thicknesses (based on solution concentrations).

## **3.3 EXCITON SEPARATION EFFICIENCY**

Recent literature has attempted to relate  $\Delta G_{CSrel}$  (the relative free energy of charge separation) to the excited state energy (E<sub>s</sub>) and the relative band offsets in the abbreviated Weller equation  $\Delta G_{CSrel} = E_S - (HOMO_{donor} - LUMO_{acceptor})$ .<sup>14</sup> Values for  $\Delta G_{CSrel}$  calculated from this equation correlate well with the observed short circuit currents for several polymer:PCBM devices.<sup>11</sup> However, in this case the equation predicts a larger driving force for charge separation in the P3HT/CNPPV device, as  $\Delta G_{rel}$  is 0 eV for POPT/CNPPV but is 0.3 eV for P3HT/CNPPV (Figure 3.3B). The large difference in Jsc between these polythiophene devices indicates that

charges are either extracted or generated more efficiently from the POPT device, contrary to measured hole mobilities, light absorption and predicted  $\Delta G_{rel}$ . Notably, the abbreviated Weller equation does not include energy contributions from lattice polarization energy or Coulomb attraction between bound electron-hole pairs. We believe these neglected terms (specifically the Coulomb attraction) are important in explaining the increased Jsc in POPT/CNPPV devices.

### 3.3.2 MODELING

Initial investigation using theoretical modeling was used to further probe the characterization of P3HT and POPT at the interface with CNPPV. The B3LYP/6-31G(d,p) optimized geometries of the neutral ground-states of these polymers are shown in Figure 3.4. The two structures for POPT shown represent different possible geometries for the polymer. The first structure allows for the phenyl rings to come into conjugation with the thiophene backbone (Figure 3.4b) and the second structure (Figure 3.4c) forces the phenyl rings to stay perpendicular to the backbone and thereby eliminating conjugation effects from the added aromatic ring.



Figure 3.4 B3LYP/6-31G(d,p) optimized neutral ground-state structures of the hexamers of (a) P3HT, (b) POPT, (c) POPT-*perp* and (d) CNPPV shown from the top-view (top) and side-view (bottom).

The electronic structures of these oligomers were calculated in order to generate Kuhn fits of the vertical transition energies from which the S0  $\rightarrow$  S1 transition energies of the polymers could be extrapolated. These plots for the two POPT structures as well as for P3HT are presented in Figure 3.5. To obtain a good fit with experiment for POPT (Eg<sub>(optical)</sub> = 1.75 eV), it was necessary to force the pendant phenyl rings to be perpendicular to the polymer backbone. This suggests that the majority structure for POPT in the solid state is with the phenyl rings out of plane with the polymer backbone.



Figure 3.5 Vertical S0  $\rightarrow$  S1 transition energies of (a) P3HT and (b) POPT and POPT-perp where the phenyl group is constrained to be perpendicular to the polymer backbone. *N* is the number of double bonds.

Using these optimized geometries the interface between the donor molecules and CNPPV as the acceptor were constructed and time dependent DFT calculations, using the B3LYP/6-31G(d,p) set, were used to probe the geminate pair energies. Energies for the three donor cases, P3HT, POPT and POPT-*perp* were evaluated at different donor-acceptor distances in both the gas state and in a quasi solid state approximation using an intrinsic dielectric field (Figure 3.6).

The difference in energy between these three states represents the relative amount of trapping of the geminate pair at the molecular interface due to the Couloumbic binding energy between the hole and electron. Figure 3.6 help to illustrate how the higher the energy of the geminate pair state leads to a lowering of the potential barrier for separation of the geminate pair into free charges.



Figure 3.6 Schematic energy diagram for the two-step process for charge separation at an excited donor-acceptor interface along with calculated geminate pair energies for P3HT/CNPPV, POPT/CNPPV and POPT-*perp*/CNPPV interfaces in the gas phase (top) and solid state (bottom).

As can be seen from the calculations, the geminate pair located at the interface between CNPPV and POPT-*perp* has the highest energy of the three donor situations for all distances and therefore is predicted to have the highest separation efficiency. This follows the logical assumption that the phenyl ring twisted out of plane in POPT helps to separate the electron from the hole across the donor-acceptor interface. The regular POPT conformation has the lowest energy trap state with P3HT/CNPPV having an intermediate energy state. These calculations support the experimental solar cell data taken, where higher separation efficiency for the POPT/CNPPV bilayer devices is the most probable explanation for the higher power conversion efficiency compared to P3HT/CNPPV.

#### **3.3.3 X-RAY DIFFRACTION**



Figure 3.7 XRD pattern of POPT on Si substrate using a) 2D grazing incidence geometry and b) an x-ray line scan taken parallel to the substrate surface showing peaks at d spacing equal to 28.6, 5.1 and 3.8 Å corresponding to 100 and two different 010 peaks respectively.

X-ray diffraction spectroscopy (XRD) can give structural information on the solid state packing of organic polymers in crystalline regions.<sup>15</sup> Figure 3.7a shows the two dimensional grazing incidence XRD of POPT spun onto a silicon wafer. A grazing incidence of 0.12° was used to prevent the beam from interacting with the substrate. A line scan from this 2D image, taken parallel to the substrate surface, is shown in Figure 3.7b. Three peaks are present corresponding to crystalline d-spacings of 28.6 Å, 5.1 Å and 3.8 Å. The peak at 28.6 Å corresponds well to the predicted value for the 100 intermolecular stacking direction of POPT assuming an orthorhombic crystal lattice similar to P3HT. The peak at 3.8 Å is close to the intermolecular 010 direction for the same lattice and falls within the range of 010 values seen for many polythiophenes (3.4 - 4.0 Å).<sup>16</sup> This close of a  $\pi$ - $\pi$  stacking distance would only be possible if the phenyl ring was in plane with the polymer backbone. The peak at 5.1 Å would be a reasonable distance for the  $\pi$ - $\pi$  interaction between neighboring chains assuming the phenyl ring was twisted out of plane with the backbone and therefore sterically separating the interpolymer distance. The XRD data suggests that both conformations in the solid state are possible and this matches with the two lowest energy states calculated from density functional theory.

#### **3.3.4 Photothermal Deflection Spectroscopy**

Photothermal deflection spectroscopy (PDS) is a highly sensitive technique for studying the change in temperature of a thin film as a function of absorbed light. This technique allows detection of sub-band gap absorptions that arise in OPVs from the low probability absorptions corresponding to charge transfer (CT) excitations. CT excitations are direct absorption events which populate the excited state of an acceptor molecule from the ground state of the donor molecule across the donor-acceptor interface. Figure 3.8c shows possible B3LYP/6-31G(d,p) calculated HOMO (top) and LUMO (bottom) levels for a polythiophene/CNPPV interface. Upon absorption of a photon, an electron can be excited directly from the HOMO of the donor molecule across the interface to the acceptor forming a geminate pair exciton directly (Figure 3.8a to 3.8b). Thus PDS is a spectroscopic technique, which can directly probe the energy of the geminate pair state between a donor and acceptor.<sup>17</sup>



Figure 3.8 Cartoon of (a) direct charge transfer excitation (b) forming a geminate pair at a donor-acceptor interface. B3LYP/6-31G(d,p) calculated (c) HOMO and LUMO levels and (d) schematic energy diagram of CT excitation.

PDS spectra of P3HT:CNPPV blend films and POPT:CNPPV blend films are compared to the pure polymer control spectra in Figure 3.9. Blend films were necessary during the experiment to insure enough interfacial area to obtain a signal. The POPT:CNPPV spectrum shows two subband gap peaks (~1.2 eV and ~1.5 eV) corresponding to two different energy excitations for electrons from the POPT to CNPPV. P3HT:CNPPV films show one sub-band gap excitation at ~1.3 eV, which is between the energies of the two POPT:CNPPV peaks. The data confirms that there is a geminate pair state between POPT and CNPPV that is more energetic than the geminate pair state between P3HT and CNPPV, suggesting that this state is more likely to be separated during photovoltaic operation.

The spectroscopic results showing two different states for POPT:CNPPV with a P3HT:CNPPV state between them matches the DFT calculated states and the XRD spectrum qualitatively.

Together the PDS and XRD data with the theoretical modeling provide strong support for the increase in solar cell performance of POPT over P3HT as being a product of the phenyl ring twist providing an enhancement for the separation efficiency most likely due to an increase in polymer spacing.



Figure 3.9 PDS spectra of P3HT:CNPPV and POPT:CNPPV blended thin films (1:1 ratio) compared to the PDS spectra of pure P3HT, POPT and CNPPV thin films. Arrows denote sub-band gap absorption peaks in the blend films.

### **3.4 ALTERING ACTIVE LAYER DIELECTRIC**

A major difference between inorganic and organic solar cells is the dielectric constant ( $\epsilon$ ) of the semiconductor and this difference leads to dramatically different photovoltaic operating mechanisms.<sup>18</sup> Inorganic semiconductors have a relatively high  $\epsilon$  (typically > 10) and thus generate free charges directly upon photoexcitation.<sup>19</sup> On the other hand, organic semiconductors with their lower  $\epsilon$  (~ 3) form strongly bound excitons.<sup>20</sup>

Due to their excitonic nature, charge generation in an OPV device must occur at a donor/acceptor interface via a two-step mechanism that involves the ultrafast separation of the exciton into an intermolecular bound radical pair, followed by a slower conversion to mobile carriers.<sup>21,22</sup> The driving force for this charge separation, i.e.  $\Delta G_{CS}$ , is typically defined by the Weller equation, which includes critical terms such as the ionization potential of the donor and the electron affinity of the acceptor.<sup>23</sup>  $\Delta G_{CS}$  is also known to be affected by the dielectric constant.<sup>24,25</sup> Theoretical modeling suggests that increasing  $\epsilon$  of the active layer can increase  $|\Delta G|$  of charge dissociation as well as decrease  $|\Delta G|$  of charge recombination, both of which would facilitate the generation of free charge carriers.<sup>26</sup> Experimental studies on photoinduced charger transfer in solution have also concluded that a higher  $\epsilon$  solvent increases the stabilization of the charge separated species, leading to more facile charge separation.<sup>24,27</sup> These reports and others

suggest the importance of  $\varepsilon$  in the active layer and how it might favorably influence OPV performance.<sup>28-30</sup>

Of particular interest are all-polymer OPVs, which suffer performance loss from poor charge separation. The smaller LUMO-LUMO offset between the donor and the acceptor typical of these devices leads to a reduced driving force for charge separation.<sup>31</sup> Mandoc *et al.* have also ascribed the poor charge dissociation efficiency in an all-polymer system to the lower  $\varepsilon$  of the polymer blend in comparison to polymer-fullerene composites, which benefits from the high polarizability of the fullerene.<sup>32</sup> Therefore, increasing the dielectric constant of the active layer may be particularly useful in facilitating charge separation in all-polymer OPVs by lowering  $\Delta G$  of charge separation and/or reducing recombination losses through the stabilization of separated charges.

### 3.4.1 MATERIAL

Camphoric anhydride has been used as a dopant to increase  $\varepsilon$  of a polystyrene film.<sup>33</sup> A camphor imide (CI) modified P3HT (15CI) was prepared by copolymerizing 2,5-dibromo-3-hexylthiophene and the CI-appended thiophene monomer at a controlled ratio via a Grignard metathesis (GRIM) polymerization. The concentration of CI-modified unit in the final polymer after purification was determined to be ca. 15 mol% based on <sup>1</sup>H NMR analysis.



Figure 3.10 Chemical structure of camphor imide modified polythiophene 15CI.

A regioregular P3HT of similar Mn and PDI was polymerized via the same method as a control polymer. Because the CI moiety is not conjugated to the backbone and does not absorb light, it should have minimal impact on the electronic structure of the polymer. Therefore this material choice and design strategy aims to more easily attribute changes in device performance to the influence of  $\varepsilon$ .

### 3.4.2 Optical and Electronic Properties

Although the conjugated backbone of P3HT is preserved in 15CI, adding the CI group leads to changes in the solid state optical properties. As shown in Figure 3.11a, the thin film absorption of 15CI is reduced in intensity and blue-shifted from that of P3HT. Moreover, vibronic structures seen at ~530 nm and ~560 nm and the low energy shoulder at 620 nm, which are indicative of

crystalline packing,<sup>34,35</sup> are clearly visible in the P3HT spectrum and absent in the 15CI spectrum. The change in absorption is most likely a consequence of appending the bulky CI unit, which leads to the disruption of the long range solid-state packing of the thiophene backbone, although local ordering may still exist throughout the thin film. A film consisting of a 1:1 ratio by weight of P3HT and 15CI has an absorption in which the vibronic structures are again visible, suggesting that the crystallinity of P3HT is largely retained upon blending the two polymers.



Figure 3.11 (a) Absorption spectra of P3HT, 15CI, and a 1:1 P3HT:15CI blend. (Inset) The structure of 15CI. GIXS patterns from thin films of (b) P3HT, (c) 15CI, and (d) 1:1 P3HT:15CI.

A comparison of the two dimensional grazing incidence X-ray scattering (GIXS) patterns of Figures 3.11b and 3.11c shows that 15CI has much weaker diffraction peaks than P3HT. Differential scanning calorimetry (DSC) data supports the lower crystallinity finding for 15CI as evidenced by a reduced crystallization peak (Figure 3.12). In contrast, the diffraction peaks of the 1:1 P3HT:15CI blend are more comparable in intensity to those for P3HT (Figure 3.11b & 3.11d). This is again confirmed by DSC data of the blend sample, which shows thermal properties similar to P3HT. The DSC of the blend is also notable because it shows only a single peak corresponding to the melting and one peak corresponding to the crystallization of the polymer. This confirms that the blended polymers completely mix essentially forming a single polymeric material with unique structural properties.

Further characterization of the solid state morphology was accomplished by space charge limited current (SCLC) mobility measurements. P3HT shows a hole mobility of approximately  $10^{-3}$  cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup>, which is an order of magnitude higher than the mobility for the thin film of 15CI, which is a result of the lower crystallinity. The blend film of P3HT with 15CI has a hole mobility about double of the pure 15CI confirming that the blended material posses a higher crystalline packing.



Figure 3.12 DSC graphs and SCLC carrier mobilities of P3HT, 15CI and a P3HT:15CI (1:1) blend.

Cyclic voltammetry was performed on Pt wire coated with polymer from a chloroform solution and measured in dry acetonitrile using ferrocene as a reference (Figure 3.13). Both polymers have the same oxidation onset at ~0.1 V above ferrocene, confirming that the appended CI does not impact the electronics of the polymer  $\pi$  system.



Figure 3.13 CV of P3HT and 15CI referenced to the Fc/Fc<sup>+</sup> oxidation potential using a three electrode geometery in dry acetronitrile.

## 3.4.3 Photovoltaic Performance

Solution processed all-polymer bilayer solar cells were fabricated using either P3HT, 15CI or a blend of the two as the donor layer and a separate layer of poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-(1-cyanovinylene)phenylene] (CN-PPV) as the acceptor. The device architecture consisted of

ITO/ PEDOT:PSS/ P3HT:15CI (40 nm)/ CN-PPV (40 nm)/ LiF/ Al. As shown in Figure 3.13, the performance of pure 15CI/CN-PPV bilayer devices (average PCE = 0.32%) is slightly lower than that of P3HT/CN-PPV devices (average PCE = 0.38%). The main difference is the photocurrent, where the 15CI/ CN-PPV devices have a lower average short circuit current ( $J_{sc}$ ) of 1.03 mA cm<sup>-2</sup> compared to the P3HT/ CN-PPV devices with an average  $J_{sc}$  of 1.24 mA cm<sup>-2</sup>. This decrease is likely due to the losses in absorption and crystallinity shown for 15CI.



Figure 3.14 *J-V* curves of the best bilayer devices fabricated from P3HT, 15CI, and a 1:1 blend as the donor layer with CN-PPV as the acceptor in architecture ITO/PEDOT:PSS/P3HT:15CI/CNPPV/LiF/A1.

Devices made from blend films of P3HT and 15CI showed improved performance with higher  $J_{sc}$ , FF and overall PCE compared to either homo-polymer (Table 3.2). In Figure 3.14, the *J-V* curves of the best devices fabricated from P3HT, 15CI and a 1:1 blend illustrate that devices from the 1:1 blend show both enhanced photocurrent ( $J_{sc} = 1.51 \text{ mA cm}^{-2}$ ) and an improved PCE of 0.54%.

	<b>P3HT:15CI</b>	Voc	$\mathbf{J}_{\mathbf{sc}}$	FF	PCE	
	100:0	0.98	1.24	0.32	$0.38\% \pm 0.02$	
	80:20	0.97	1.31	0.36	$0.45\% \pm 0.02$	
	50:50	0.95	1.55	0.37	$0.54\% \pm 0.05$	
	20:80	1.00	1.36	0.36	$0.49\% \pm 0.04$	
	0:100	0.97	1.03	0.32	$0.32\% \pm 0.02$	
-	11 00 1			( DO		11

Table 3.2 Average device parameters of P3HT:15CI/CN-PPV bilayer cells.

## **3.5 EXCITON SEPARATION**

#### 3.5.1 DIELECTRIC CONSTANT

The dielectric constant of P3HT, was determined from impedance spectroscopy of a metal/polymer/metal capacitor, to be  $2.9 \pm 0.3$  at 1000Hz, consistent with literature values.<sup>36</sup> The complex impedance of the ITO/PEDOT:PSS/polymer/Al devices were measured using a Solartron SI 1260 impedance analyzer by applying an oscillating voltage of 100 mV. All measurements were performed in the dark at ambient conditions and at a range of frequencies from 10 MHz to 10 Hz. An equivalent circuit (inset Figure 3.15) for a leaky capacitor was used, with a capacitance C, a parallel resistance R<sub>p</sub> and a series resistance R<sub>s</sub>. The series resistance R<sub>s</sub>

is the lump sum resistance of the both electrodes and the measurement probes. The capacitance (C) was used to calculate the dielectric constant of the polymer film by using Equation 3.2, where d is the thickness of the film (60-70 nm),  $\varepsilon_0$  is the permittivity of free space, and A is the area of the electrode (1 cm<sup>2</sup>).

$$\varepsilon = \frac{Cd}{\varepsilon_0 A}$$
 (Equation 3.2)

The higher capacitance of the 15CI, due to the polar champor imide, results in a larger  $\varepsilon$  value (5.6 ± 0.4 at 1000Hz) nearly twice that of P3HT as illustrated in Figure 3.15. The dielectric constants of blend films made from three different ratios of P3HT and 15CI (4:1, 1:1, 1:4) were also measured and show a trend of increasing  $\varepsilon$  with increasing percent 15CI in the film.



Figure 3.15 Real part of the impedance spectra showing dielectric constant for P3HT:15CI blend films (1:0, 4:1, 1:1, 1:4, 0:1) and the equivalent circuit diagram for a leaky capacitor used to fit the data.

Because the absorption and solid state packing of the blend films are not superior to pure P3HT, the improvement in device efficiency is attributed to the larger  $\varepsilon$  resulting from incorporation of the 15CI polymer. The increased J<sub>sc</sub> and FF strongly suggest that charge separation is more efficient at the D/A interface in these films. The improved charge separation efficiency is likely due to the higher  $\varepsilon$  of the active layer, which lowers the Coulomb binding energy of geminate pair excitons and allows for a more efficient charge generation process. The improvement could potentially be due to the stabilization of charge separated species by the surrounding dipoles, which can reduce recombination losses. Further studies will examine the exact relationship between the dielectric constant and charge separation dynamics using PDS.

### **3.6 CONCLUSION**

This chapter highlights the importance of examining the two-step process for charge separation at all-polymer donor/acceptor interfaces. Coulombically bound geminate pairs are a fundamental loss mechanism in all-polymer devices but are can be affected by increasing either the donoracceptor distance or the dielectric constant surrounding the interface. The AM 1.5 efficiency of 2% achieved with POPT/CNPPV is, to date, the highest reported allpolymer photovoltaic. POPT outperforms P3HT in these all-polymer devices due to a doubling of the Jsc, even though this increased performance is counter to expectations based on absorption, charge mobility and energy level comparisons. This emphasizes the importance of understanding charge separation processes in OPV devices, particularly the effects of Coulombic attraction and lattice polarization energy.

DFT calculations and PDS experiments confirm that the increase in POPT/CNPPV efficiencies over those of P3HT/CNPPV come from a reduction in the stability of the geminate pair state, which results in less of an energetic barrier for complete charge separation. The less stable excimer is most likely due to a larger separation between the donor and acceptor at the molecular interface. This separation is controlled by the steric twisting of the phenyl ring out of plane with the polythiophene backbone, which is the spontaneous geometry of POPT in the solid state.

The bulk dielectric constant of a polymer film has been controlled through the designe and synthesis of a CI-modified polythiophene. Although adding the CI moiety leads to reductions in absorption and chain packing in 15CI, these losses can be recovered in P3HT:15CI blend films while maintaining a higher dielectric. In all-polymer bilayer solar cells using CN-PPV as the acceptor, a blend of 15CI and P3HT as the donor layer leads to clear improvements in device performance. This enhancement is attributed to the higher active layer dielectric constant and subsequent destabilization of bound geminate pairs at the donor/acceptor interface.

#### **3.7 EXPERIMENTAL**

Cyclic voltammograms were collected using a Solartron 1285 potentiostat under the control of CorrWare II software. A standard three electrode cell based on a Pt button working electrode, a silver wire pseudo reference electrode (calibrated vs. Fc/Fc+), and a Pt wire counter electrode was purged with nitrogen and maintained under a nitrogen atmosphere during all measurements. Acetonitrile was distilled over CaH<sub>2</sub> prior to use and tetrabutyl ammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. Polymer films were drop cast onto a Pt button working electrode from a 1% (w/w) chloroform solution and dried under nitrogen prior to measurement.

UV-Visible absorption spectra were obtained using a Carey 50 Conc UV-Visible spectrophotometer. For thin film measurements polymers were spin coated onto untreated glass slides from chlorobenzene solution (10 mg/ml). A model P6700 Spincoater was used to spin coat the films at 1200 RPM for 60 s.

TEM images were obtained using a FEI TECNAI G2 with a 200 kW accelerating voltage. Samples were prepared by spin-casting films from chlorobenzene as used for device measurement on to freshly cleaved NaCl single crystal substrates at 1500RPM for 60s. The films were floated onto water and placed onto a 600 mesh copper TEM grid (Electron Microscopy Science, Inc.). Atomic force microscopy was performed using a Veeco (Digital Instruments) Multimode microscope with a Nanoscope V controller. Imaging was performed in semi-contact (tapping) mode using Veeco RTESP tips.

Thin-film transistors were fabricated on 300 nm SiO<sub>2</sub> dielectric substrates on heavily doped silicon. Bottom contact source-drain electrodes (Cr = 5 nm, Au = 100 nm) were fabricated by conventional photolithography using a transparency photomask. Channel lengths of 10 and 20  $\mu$ m and channel widths of 100 and 200  $\mu$ m were used for discrete transistors. The active semiconducting layer was applied by spin-casting 5-10 mg/mL solutions in anhydrous chlorobenzene at 2000 rpm. The films were then vacuum-dried overnight and measurements were carried out in ambient conditions using an Agilent 4156C Precision Semiconductor Parameter Analyzer.

Polymer mobility was measured using a diode configuration of ITO/ PEDOT:PSS/ Polymer/Al in the space charge limited current (SCLC) regime. At sufficient potential the conduction of charges in the device can be described by Equation 1.7 where  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon$  is the dielectric constant of the polymer,  $\mu$  is the mobility of the majority charge carriers, V is the potential across the device (V = V<sub>applied</sub> – V<sub>bi</sub> - V<sub>r</sub>), and L is the polymer layer thickness. The series and contact resistance of the device (~15  $\Omega$ ) was measured using a blank device (ITO/PEDOT/Al) and the voltage drop due to this resistance (V<sub>r</sub>) was subtracted from the applied voltage. Polymer film thickness was measured by a Veeco Dektak profilometer.

Modeling was done in collaboration with the Bredas group using the B3LYP/6-31G(d,p) bases set in a Gaussian package. Photothermal deflection spectroscopy was done in collaboration with the Salleo group.

All solar devices have a layered structure with the photoactive layer consisting of separate donor and acceptor layers sandwiched between the two electrodes, ITO and LiF/Al. Glass substrates coated with a 150 nm sputtered ITO pattern of  $20 \Omega \Box^{-1}$  resistivity were obtained from Thin Film Device, Inc. The ITO-coated glass substrates were ultrasonicated for 20 min each in acetone, and then 2 % Helmanex soap water, followed by extensive rinsing and ultrasonication in deionized water, and then isopropyl alcohol. The substrates were then dried under a stream of air.

For the study on interface separation; a dispersion of PEDOT:PSS (Baytron-PH500) in water was filtered (0.45 $\mu$ m glass) and spin coated at 3400 RPM for 60s, affording a ~20-30 nm layer. The substrate was dried for 15 min at 140 $_{\circ}$ C in air and then transferred into an Argon glove box for subsequent procedures. P3HT and POPT solutions were prepared in chlorobenzene at a concentration of 2-13mg/ml and were heated to 120 $_{\circ}$ C for complete dissolution. CNPPV solution was prepared in ethyl acetate or THF at concentrations of 6-9 mg/ml. The solutions were stirred for 24 hrs and passed through 0.2  $\int$ m PTFE syringe filter before they were spin coated. The donor layer, consisting of P3HT or POPT, was spin coated first onto the substrate at 1200 RPM for 60s on top of the PEDOT:PSS layer. Subsequently, the CN-PPV layer was spin coated on top of the donor layer at 2000 RPM for 60s. The substrates were then placed in an evaporation chamber and pumped down in vacuum (~10<sup>-7</sup> torr) before evaporating a 1 nm Li/F layer and subsequently a 100 nm Al layer through a shadow mask on top of the photoactive layer. The

configuration of the shadow mask afforded eight independent devices on each substrate, and each device has an active layer of ~0.03cm<sub>2</sub>. The mechanical removal of part of the organic layer allowed contact with the ITO, and adding conductive Ag paste to the removed area to ensure electrical contact completed the device. We note that the RMS roughness (measured by AFM over a 10<sup>2</sup> micron area) of both the P3HT and POPT layers was between 2 and 4 nm as prepared, and these layers stayed between 2 and 4 nm after spincasting pure THF or ethyl acetate on top of these layers to simulate CNPPV deposition. Layer thickness was the first parameter explored to optimize efficiency after determining the necessity of Li/F as a top electrode.

For the study on dielectric constant modification; a dispersion of PEDOT:PSS (Baytron PH500) in water was filtered (0.45 µm glass) and spin coated at 3400 RPM for 60 s, affording a ~20-30 nm layer. The substrates were dried for 15 min at 140°C in air and then transferred into an Argon glove box for subsequent procedures. P3HT and 15CI solutions were prepared in chlorobenzene at a concentration of 10 mg/ml and were heated to 120°C for complete dissolution. CN-PPV solution was prepared in ethyl acetate at a concentration of 8 mg/ml. Ethyl acetate was chosen as the solvent because it is a bad solvent for P3HT and this orthogonality afforded true bilayer devices. The solutions were stirred overnight and passed through a 0.2 µm PTFE syringe filer before they were spin coated. For blend solutions, different ratios of P3HT and 15CI solutions were mixed and stirred overnight at 120°C before spin coating. The donor layer, consisting of P3HT or 15CI or a blend of the two, was spin coated first onto the substrate at 1200 RPM for 60 s on top of the PEDOT:PSS layer. Subsequently, the CN-PPV layer was spin coated on top of the donor layer at 2000 RPM for 60 s. The substrates was then placed in an evaporation chamber and pumped down in vacuum ( $\sim 10^{-7}$  torr) before evaporating a 1 nm LiF layer and subsequently a 100 nm Al layer through a shadow mask on top of the photoactive layer. The configuration of the shadow mask afforded eight independent devices on each substrate, and each device has an active area of  $\sim 0.03$  cm<sup>2</sup>. The mechanical removal of part of the organic layer allowed contact with the ITO, and adding conductive Ag paste to the removed area to ensure electrical contact completed the device.

Testing of the devices was performed under an argon atmosphere with an Oriel Xenon arc lamp with an AM 1.5G solar filter. Current–voltage behavior was measured with a Keithley 236 SMU. Eight devices were averaged for each condition.

The dielectric constant of a polymer film was determined by impedance spectroscopy. Diodelike devices were fabricated with the structure ITO/ PEDOT:PSS/ polymer/ Al. The complex impedance of the device was measured using a Solartron SI 1260 impedance analyzer by applying an oscillating voltage of 100 mV. The measurement was performed in the dark at ambient conditions at a range of frequencies from 10 MHz to 10 Hz. The equivalent circuit in Figure 3.15 was used, with a capacitance C, a parallel resistance  $R_p$ , a series resistance  $R_s$  to model the data. The capacitance (C) was used to calculate the dielectric constant of the polymer film by Equation 3.2. Thicknesses of polymer films were ~ 60-70 nm, and the electrode area was  $1 \text{ cm}^2$ . Differential Scanning Calorimetry (DSC) measurements were performed on a TA instrument DSC Q200. The samples (~5 mg) were heated from  $40^{\circ}$ C to  $260^{\circ}$ C at a heating rate of  $10^{\circ}$ C min<sup>-1</sup> under N<sub>2</sub> atmosphere. Samples were prepared by drop casting a 30mg/ml CB solution onto the DSC pan and letting the solvent slowly evaporate under Argon atmosphere before DSC measurements.

Grazing-Incidence X-ray Scattering (GIXS) experiments were conducted at the Stanford Synchrotron Radiation Laboratory on beamline 11-3. The sample was irradiated at a fixed incident angle on the order of  $0.1^{\circ}$  and the GIXS patterns were recorded with a 2-D image detector (MAR345 image plate detector). GIXS patterns were recorded with an X-ray energy of 12.72 keV ( $\lambda = 0.975$  Å). To maximize the intensity from polymer sample, the incident angle (~0.1°-0.12°) was carefully chosen so that the X-ray beam penetrates the polymer sample completely but not the silicon substrate. Typical exposure times were 90-180 s. To produce identical surface condition as samples for device fabrication, a thin layer (20-30 nm) of PEDOT:PSS was spun onto silicon substrates with a native oxide. Then the GIXS samples were prepared by spin-coating the same polymer solutions used for making devices onto silicon substrates at 1200 RPM for 60 s. The substrates were placed directly on top of hot plates under Argon for 3 hours of thermal annealing at 150°C before data acquisition.

#### REFERENCES

- (1) Schlaich, H.; Muccini, M.; Feldmann, J.; Bässler, H.; Göbel, E. O.; Zamboni, R.; Taliani, C.; Erxmeyer, J.; Weidinger, A. *Chemical Physics Letters* **1995**, *236*, 135-140.
- (2) Zhan, X.; Tan, Z.; Domercq, B.; An, Z.; Zhang, X.; Barlow, S.; Li, Y.; Zhu, D.; Kippelen, B.; Marder, S. R. *Journal of the American Chemical Society* **2007**, *129*, 7246-7247.
- (3) Mandoc, M.; Veurman, W.; Koster, L.; de Boer, B.; Blom, P. Adv. Funct. Mater. 2007, *17*, 2167-2173.
- (4) Andersson, M. R.; Selse, D.; Berggren, M.; Jaervinen, H.; Hjertberg, T.; Inganaes, O.; Wennerstroem, O.; Oesterholm, J. *Macromolecules* **1994**, *27*, 6503-6506.
- (5) Pei, Q.; Jarvinen, H.; Osterholm, J. E.; Inganaes, O.; Laakso, J. *Macromolecules* **1992**, *25*, 4297-4301.
- (6) Granstrom, M.; Petritsch, K.; Arias, A. C.; Lux, A.; Andersson, M. R.; Friend, R. H. *Nature* **1998**, *395*, 257-260.
- (7) Chen, L. C.; Godovsky, D.; Inganäs, O.; Hummelen, J. C.; Janssens, R. A. J.; Svensson, M.; Andersson, M. R. Advanced Materials 2000, 12, 1367-1370.
- (8) Brabec, C. J.; Winder, C.; Scharber, M. C.; Sariciftci, N. S.; Hummelen, J. C.; Svensson, M.; Andersson, M. R. J. Chem. Phys. 2001, 115, 7235-7244.
- (9) Roman, L. S.; Arias, A. C.; Theander, M.; Andersson, M. R.; Inganäs, O. Braz. J. Phys. 2003, 33.
- (10) Holcombe, T. W.; Woo, C. H.; Kavulak, D. F.; Thompson, B. C.; Fréchet, J. M. J. *Journal* of the American Chemical Society **2009**, *131*, 14160-14161.
- (11) Kietzke, T.; Horhold, H.; Neher, D. Chemistry of Materials 2005, 17, 6532-6537.
- (12) Alam, M. M.; Jenekhe, S. A. Chemistry of Materials 2004, 16, 4647-4656.
- (13) Jenekhe, S. A.; Yi, S. Appl. Phys. Lett. 2000, 77, 2635-2637.
- (14) Ohkita, H.; Cook, S.; Astuti, Y.; Duffy, W.; Tierney, S.; Zhang, W.; Heeney, M.;

McCulloch, I.; Nelson, J.; Bradley, D. D. C.; Durrant, J. R. *Journal of the American Chemical Society* **2008**, *130*, 3030-3042.

- (15) Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Liu, J.; Frechet, J. M. J.; Toney, M. F. *Macromolecules* **2005**, *38*, 3312-3319.
- (16) Kline, R. J.; McGehee, M. D. Polymer Reviews 2006, 46, 27.
- (17) Goris, L.; Poruba, A.; Hod'ákova, L.; Vane □c □ek, M.; Haenen, K.; Nesládek, M.; Wagner, P.; Vanderzande, D.; De Schepper, L.; Manca, J. V. Appl. Phys. Lett. 2006, 88, 052113.
- (18) Gregg, B. A.; Hanna, M. C. J. Appl. Phys. 2003, 93, 3605.
- (19) Kittel, C. Introduction to Solid State Physics; Wiley & Sons, 2005.
- (20) Offermans, T.; Meskers, S. C. J.; Janssen, R. A. J. J. Chem. Phys. 2003, 119, 10924-10929.
- (21) Ohkita, H.; Cook, S.; Astuti, Y.; Duffy, W.; Tierney, S.; Zhang, W.; Heeney, M.; McCulloch, I.; Nelson, J.; Bradley, D. D. C.; Durrant, J. R. *Journal of the American Chemical Society* **2008**, *130*, 3030-3042.
- (22) Clarke, T. M.; Ballantyne, A. M.; Nelson, J.; Bradley, D. D. C.; Durrant, J. R. Advanced Functional Materials **2008**, *18*, 4029-4035.
- (23) Weller, A. Z. Phys. Chem. Neue Folge 1982, 133, 93.
- (24) van Hal, P. A.; Janssen, R. A. J.; Lanzani, G.; Cerullo, G.; Zavelani-Rossi, M.; De Silvestri, S. *Phys. Rev. B* **2001**, *64*, 075206.
- (25) Arkhipov, V. I.; Heremans, P.; Bassler, H. Appl. Phys. Lett. 2003, 82, 4605-4607.
- (26) Lemaur, V.; Steel, M.; Beljonne, D.; Bredas, J.; Cornil, J. Journal of the American Chemical Society 2005, 127, 6077-6086.
- (27) Neuteboom, E. E.; Meskers, S. C. J.; Beckers, E. H. A.; Chopin, S.; Janssen, R. A. J. *The Journal of Physical Chemistry A* **2006**, *110*, 12363-12371.
- (28) Severen, I. V.; Breselge, M.; Fourier, S.; Adriaensens, P.; Manca, J.; Lutsen, L.; Cleij, T. J.; Vanderzande, D. *Macromolecular Chemistry and Physics* **2007**, *208*, 196-206.
- (29) Sentein, C.; Rocha, L.; Apostoluk, A.; Raimond, P.; Duyssens, I.; Van Severen, I.; Cleij, T.; Lutsen, L.; Vanderzande, D.; Kazukauskas, V.; Pranaitis, M.; Cyras, V. Solar Energy Materials and Solar Cells 2007, 91, 1816-1824.
- (30) Mandoc, M. M.; Veurman, W.; Sweelssen, J.; Koetse, M. M.; Blom, P. W. M. Appl. Phys. Lett. 2007, 91, 073518-3.
- (31) Westenhoff, S.; Howard, I. A.; Hodgkiss, J. M.; Kirov, K. R.; Bronstein, H. A.; Williams, C. K.; Greenham, N. C.; Friend, R. H. *Journal of the American Chemical Society* 2008, 130, 13653-13658.
- (32) Mandoc, M. M.; Veurman, W.; Koster, L.; de Boer, B.; Blom, P. Advanced Functional *Materials* **2007**, *17*, 2167-2173.
- (33) Madigan, C. F.; Bulović, V. Phys. Rev. Lett. 2003, 91, 247403.
- (34) Yamamoto, T.; Komarudin, D.; Arai, M.; Lee, B.; Suganuma, H.; Asakawa, N.; Inoue, Y.; Kubota, K.; Sasaki, S.; Fukuda, T.; Matsuda, H. *Journal of the American Chemical Society* 1998, *120*, 2047-2058.
- (35) Brown, P.; Thomas, D.; Köhler, A.; Wilson, J.; Kim, J.; Ramsdale, C.; Sirringhaus, H.; Friend, R. *Phys. Rev. B* 2003, 67.
- (36) Knipper, M.; Parisi, J.; Coakley, K.; Waldauf, C.; Brabec, C. J.; Dyakonov, V. Z. *Naturforsch.* **2007**, *62*, 490-494.

# **CHAPTER 4: ENERGY LEVEL CONTROL OF SUBSTITUTED POLYTHIOPHENES**

### ABSTRACT

Random and regioregular polythiophenes containing electron-withdrawing carboxylate substituents have been developed to alter the HOMO and LUMO levels of the parent polymer. Although these polymers have extended conjugation lengths, they provide better oxidative doping stability than conventional polythiophenes due to the lowering of the HOMO energy levels by approximately 0.5 eV. Polymers with unsubstituted thiophene units are highly crystalline and exhibit very small  $\pi$ - $\pi$  stacking distances in the solid state. High charge mobilities are observed as a result of the close ordering of the polymer chains, and top-contact organic field-effect transistors (OFETs) fabricated entirely in air had measured mobilities averaging 0.06 cm<sup>2</sup>/V·s with on/off ratios >10<sup>5</sup>. Off currents in these devices remained low over a period of months demonstrating the low propensity of these materials towards p-doping by molecular oxygen.

Fully substituted polythiophenes also exhibit lowered energy levels compared to P3HT, but show reduced intermolecular stacking. These materials show promising as ambipolar materials, which can act as either electrons donors or as electron acceptors depending on the system. Promising solar cells with efficiencies of 1.9% are fabricated in a bulk heterojunction architecture at an unusually large polymer:fullerene ratio compared to typical OPVs. N-type performance is also demonstrated in solar cells with P3HT and M3EH-PPV acting as donor materials.

Portions of this chapter were published previously: Chem. Mater., 2005, 17, 4892.

### **4.1 INTRODUCTION**

Semiconducting organic polymers have been the subject of intense study in recent years because they have shown potential as alternatives to inorganic semiconductors for low-cost optoelectronic devices, such as organic thin-film transistors<sup>1-4</sup> and photovoltaic cells.<sup>5-9</sup> Among these polymers, polythiophenes have been the most commonly studied due to their strong light absorption and high charge carrier mobility.

The conjugated  $\pi$  and  $\pi^*$  orbitals in aromatic polymers like polythiophenes can be treated as an extended highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) respectively. The energy necessary to remove an electron fully from the HOMO level of the polythiophene corresponds to its ionization potential and likewise the energy gained by placing a free electron into the LUMO level is related to the electron affinity of the polymer.<sup>10</sup>

The absolute energy levels are related to the ambient stability of the polymer to environmental species such as oxygen or water as well as chemical dopants such as iodine. The relative energy of the HOMO and LUMO levels in organic devices impact many of the electrical processes such as charge separation and electron extraction at metal electrodes as well as the built in electric field formed from donor-acceptor pairs.<sup>11</sup> Unlike in inorganic semiconductors, where electron conduction (n-type) and hole conduction (p-type) are determined by the impurity doping levels, in OPVs it is the relative energies between two polymers which determine which material will be the n-type material and which will be the p-type material. Under the right conditions this means that many organic semiconductors can exhibit ambipolar characteristics, conducting either electrons or holes depending on the circumstances. Thus precise control over the HOMO and LUMO levels of conjugated polymers through chemical modification can open the door for better stability, higher electrical performance and improved device architectures.

## 4.2 CONTROLLING THE HOMO AND LUMO OF POLYTHIOPHENE COPOLYMERS

There are several methods for altering the HOMO and LUMO levels of conjugated polymers, such as reducing the effective conjugation length to inhibit delocalization. Copolymers of thiophene with fluorene<sup>12</sup> have been shown to have a lower HOMO level because of the more stable benzene rings. Similarly, the incorporation of a thieno[2,3-b]thiophene<sup>13</sup> or a naphthalene unit<sup>14</sup> into the polymer backbone has been shown to afford greater environmental stability as well. Other research groups have taken the approach of increasing the rotational freedom of the backbone to reduce the  $\pi$ -overlap, which has also been an effective method for increasing stability.<sup>15,16</sup>

Another attractive method that has yet to be fully explored is to reduce the HOMO energy level of a semiconducting polymer through the incorporation of electron-withdrawing substituents. Most of the currently known polythiophene analogs contain either alkyl side chains or electron-donating substituents. Reports of polythiophenes with electron-withdrawing substituents are very few, presumably due to their difficult synthesis.<sup>17,18</sup> Polythiophenes with electron-withdrawing ester groups attached at the 3-position, namely poly(alkyl thiophene-3-carboxylates), have been
synthesized by the Pomerantz group using the Ullmann coupling<sup>19,20</sup> or Kumada coupling reactions.<sup>21</sup> These polymers have shown high oxidation potentials due to the electron-withdrawing side chains; however, they suffered from poor charge transport properties.

# 4.2.1 MATERIALS

New polythiophenes containing electron-withdrawing alkyl carboxylate substituents were synthesized in order to generate a system that exhibits high hole mobility in FETs while maintaining a good level of ambient stability. It was determined that the regularity of the alkyl carboxylate substitution in our polythiophene can induce and facilitate molecular self-assembly in a fashion similar to that exhibited by regioregular P3HT<sup>22</sup> and poly(3,3"'-

dialkylquaterthiophene)s (PQTs).<sup>15</sup> Due to the electron-withdrawing properties of the carboxylate substituents, the polymers also exhibit a lower HOMO energy level, and therefore provide better oxidative doping stability than conventional solution-processible polythiophenes such as P3HT.



Figure 4.1 Structures of synthesized carboxylate polymers.

The design of polymer **PQT-E12** was based on several considerations: (1) The electronwithdrawing carboxylate side chains should increase the ionization potential of the polythiophene, (2) long alkyl (i.e. dodecyl) carboxylates are expected to enhance the solubility of the polymer, and (3) the side chains of the copolymer oriented symmetrically in the same direction in the extended polymer conformation are regularly spaced fairly far apart, similar to that of regioregular PQTs. This structural regularity coupled with the distance between adjacent alkyl chains should enable **PQT-E12** to self-assemble and achieve intermolecular side-chain interdigitation in the condensed phase, therefore giving rise to three-dimensional lamellar  $\pi$ stacking and high charge mobility. For the purpose of comparison, a regiorandom alternating copolymer of thiophene and dodecyl thiophene-3-carboxylate **PE12T-co-T** was also synthesized using an analogous synthetic approach described previously.<sup>23</sup> Polymer **PE12T-co-T** also has poor solubility in common organic solvents at room temperature, but it is very soluble in warm solvents such as chloroform, toluene, and dichlorobenzene.



Figure 4.2 Chemical structures of 2<sup>nd</sup> generation carboxylate polymers.

Long aliphatic chains are usually seen as beneficial in the packing and structuring of polymeric materials for FET applications, but have not proven effective solubilizing groups for solution processed bulk heterojunction solar cells.<sup>24</sup> Incorporation of carboxylate side chaings with shorter alkyl chains, such as n-hexyl, will provide less solubilizing power though and therefore unsubstituted thiophene units cannot be utilized. Using these design considerations a carboxylate homopolymer and a regio-regular copolymer (**P3ET** and **P3HT-co-3ET**) with random incorporation of carboxylate and straight hexyl chains were synthesized in a similar fashion to traditional substituted polythiophenes, such as P3HT, for use in organic photovoltaics.<sup>25</sup> The depressed HOMO level should not only impart ambient stability to the materials but should also increase the open circuit voltage of the photovoltaic devices when these materials are used as donors with classic acceptors such as PCBM. Similarly, lowered LUMO levels should allow these same carboxylate polymers to act as acceptors and conduct free electrons when paired with classical donor molecules such as P3HT.

# 4.2.2 Optical and Electronic Properties

Absorption spectra of polymer **PQT-E12** in *o*-DCB at various temperatures are displayed in Figure 4.3. At temperatures exceeding 50 °C, polymer **PQT-E12** shows a single absorption band at 2.56 eV ( $\lambda_{max} \sim 489$  nm). Below 50 °C the low-energy vibronic bands, especially the lowest energy band (617 nm) representative of  $\pi$ - $\pi$  stacking in polythiophenes, become more pronounced. This thermochromic transition at relatively high temperatures (~45 °C), suggests that the polymer has a very strong propensity for  $\pi$ -stacking.



Figure 4.3 Solution UV-vis spectra of polymer PQT-E12 in *o*-DCB at various temperatures.

These low-energy states are also apparent in spun-cast films of polymer **PQT-E12**, as shown in Figure 4.4a. This vibronic splitting, similar to that seen in other regioregular polythiophenes,<sup>15,22</sup> indicates the formation of highly ordered structures of lamellar  $\pi$ -stacked aggregates in the solid state. We found that the film processing conditions can significantly affect the solid-state absorption of polymer **PQT-E12**. When cast from chloroform, the lowestenergy transition is about 2.07 eV (~600 nm). However, switching the casting solvent to *o*-DCB shifts this transition to 2.0 eV (617 nm). Further annealing of this film at 100 °C increases the absorbance of the film and gives rise to an even more prominent lowest energy band in the spectrum. This significant bathochromic shift can be explained by the relative volatility of the casting solvents. Dichlorobenzene has a much lower volatility than chloroform, which provides a longer equilibration time for the self-assembly of the polymer chains and thus promotes better ordering within the film via  $\pi$ -stacking. The absorption bands for polymer **PQT-E12** have a very large bathochromic shift when compared to those of other types of poly(alkyl thiophene-3carboxylates) reported in the literature, indicating an increased conjugation length.<sup>19,20</sup>



Figure 4.4 UV-vis spectra of films of polymer a) PQT-E12 and b) PE12T-co-T cast from *o*-DCB and CHCl<sub>3</sub>. Spectra from films cast from *o*-DCB then annealed at 100 °C are also given.

Although polymer **PE12T-co-T** shows a regiorandom conformation as indicated by NMR, its absorption spectrum is similar to that of polymer **PQT-E12**, as shown in Figure 4.4b. This observation is very different from the substantial absorption contrast between the regioregular poly(3-alkylthiophenes) and their regiorandom counterparts.<sup>22</sup> Presumably, as an alternating copolymer, polymer **PE12T-co-T** can avoid steric interference from the solubilizing chains even in direct head-to-head coupling which would significantly disrupt the planar backbone conformation as observed in regiorandom poly(3-alkylthiophenes). Solid-state films of polymer **PE12T-co-T** exhibited vibronic splitting similar to that of polymer **PQT-E12**, suggesting that it is also likely to form ordered  $\pi$ -stacked aggregates.



Figure 4.5 UV-Vis of thin film absorption of P3ET (green) compared to thin film of P3HT (blue).

**P3ET** shows a different absorption spectrum when compared to either P3HT (Figure 4.5) or to the two polymers that contain unsubstituted thiophene units. Even though all of the units in **P3ET** are coupled in a regioregular head-to-tail fashion the absorption spectrum in a thin film is blue shifted when compared to P3HT (onset of absorption 565 nm compared to 650 nm), as well as having a much less structured absorption. The slight vibronic shouldering for P3ET shows that there is some intramolecular ordering although not to the same extent as in regioregular P3HT, but the closely spaced carboxylate groups prevents large intermolecular interactions as evidenced by enhanced shouldering around 600 nm.<sup>26</sup> This suggests that the unsubstituted thiophene units in PQT-E12 or PE12T-co-T are necessary for the carboxylate side chains to lie in the plane of the polymer backbone. UV-Vis analysis of P3HT-co-3ET is similar to that of P3HT (Figure 4.6) with a slightly smaller band gap of 680 nm, but without the pronounced vibronic features indicative of ordered packing. The large red shifted onset as well as the slight shouldering around 600 nm does indicate that some portions of the P3HT-co-3ET film are ordered, but the extent of that ordering is limited in scope and may be confined to those areas of the polymer chain that have a large percentage of 3-hexylthiophene units. For both **P3ET** and **P3HT-co-3ET** thermal annealing had no affect on their absorption characteristics.



Figure 4.6 UV-Vis of thin film absorption for P3HT-co-3ET (red) and thin film P3HT (black).

CV results (vs. Ag/AgCl) are shown in Figure 4.7 for films made by dipping the working electrode in a solution of each polymer in *o*-DCB, before and after annealing at 150 °C. Both polymer **PQT-E12** and **PE12T-co-T** show good reversible scans (omitted for clarity) with small fluctuations in peak height stopping after the second cycle. Reversibility is seen for both oxidation and reduction reactions for both polymers, which demonstrates the electrochemical stability of the polymers even in their two ionic states.

The HOMO and LUMO levels of the polymers can be estimated using this CV data.  $E^{HOMO} = -E^{ox} - 4.4 \text{ eV}$  and  $E^{LUMO} = -E^{red} - 4.4 \text{ eV}$ , where  $E^{ox}$  and  $E^{red}$  are the onset potentials of the oxidation and reduction peaks (vs. SCE) respectively and the 4.4 eV relates the SCE reference to vacuum.<sup>27</sup> Onset potentials were calculated as the intersections between two tangent lines extrapolated from the background baseline and the rising peak line and SCE was referenced as 0.27 V with respect to the Ag/AgCl reference used in the electrochemical cell.



Figure 4.7 CV vs. Ag/AgCl of a) polymer PQT-E12 and b) polymer PE12T-co-T before and after annealing at 150 °C.

As seen in Table 4.1, there is only a slight difference in energy levels between polymer **PQT-E12** and polymer **PE12T-co-T** when the films are unannealed. This data supports our hypothesis arising from the UV data that although polymer **PE12T-co-T** is regiorandom, its alternating architecture prevents steric interactions between the alkyl chains and allows the polymer backbone to adopt a planar conformation and therefore have a smiliar electronic structure to the isomeric **PQT-E12**. Upon annealing, polymer **PQT-E12** exhibits a small decrease in the HOMO level by 0.14 eV while the LUMO stays the same, resulting in an increase in the band gap to 2.35 eV. **PE12T-co-T**, however, exhibits a small decrease in both the HOMO and LUMO level upon annealing, leaving the band gap relatively unchanged.

Both polymers show band gaps similar to that of P3HT even though their absolute energy levels relative to vacuum are significantly lower. This data suggests that while electron withdrawing groups added to conjugated polymer backbones do in fact lower HOMO and LUMO levels, both energy levels are affected by approximately the same magnitude. A lower HOMO level suggests that our new polymers should have a better oxidative stability than traditional P3HT.

Figure 4.8 compares the electrochemical oxidation and reduction of thin films of **P3ET** and **P3HT-co-3ET** with that of P3HT using a Ag wire pseudo reference. This reference was compared to the oxidation of ferrocene which was taken to be 5.1 eV below vacuum and the resulting HOMO and LUMO levels are listed in Table 4.1.



Figure 4.8 Comparison of CV curves for P3ET (green) and P3HT-co-3ET (red) compared to P3HT (blue).

As seen from the oxidation of **P3ET** the HOMO level of all the polythiophenes has been lowered the most due to the highest concentration of electron withdrawing ester groups. **P3HTco-3ET** has the highest HOMO level of the four carboxylated polymers and lies approximately between that of P3HT and **P3ET** as would be assumed from their structures. Although a direct linear comparison may not be possible as the size of various copolymer blocks in the random copolymer is unknown and large stretches of a pure block could alter the electrochemical measurements of the bulk material. The electrochemical response of **P3HT-co-3ET** can also be compared to **PE12T-co-T** as they are both random copolymers. When the carboxylate functionalized ring is copolymerized with 3-hexyl substituted thiophenes the resulting HOMO level is higher than when it is copolymerized with unsubstituted thiophene. This results from the electron donating capacity of the hexyl chains and is similar to the increase in energy levels seen when comparing poly(3-alkylthiophene) to pure unsubstituted polythiophene.

	HOMO (eV)	LUMO (eV)	Eg (electrical)	Eg (optical)
P3HT	-5.30	-2.95	2.35	1.9
PQT-E12	-5.68	-3.47	2.21	1.9
annealed	-5.84	-3.49	2.35	1.85
PE12T-co-T	-5.69	-3.47	2.23	1.9
annealed	-5.74	-3.54	2.20	1.9
P3ET	-5.8	-3.4	2.4	2.2
P3HT-co-3ET	-5.5	-3.5	2.0	1.8

Table 4.1 Electrochemical properties and optical band gaps of polymers PQT-E12 and PE12T-co-T before and after annealing at 150 °C as compared to P3ET, P3HT-co-3ET and P3HT. Electrical band gaps are taken as Eg (electrical) = -(HOMO-LUMO). Optical band gap is taken as the onset of absorption in the solid state.

## **4.3 P-TYPE MOBILITY**

## 4.3.1 OFET PERFORMANCE

Table 4.2 lists the average hole mobilities and on/off ratios measured over 5-10 devices for the two polymers **PQT-E12** and **PE12T-co-T**, which were designed for thin film transistor applications. The standard deviations in the mobility values were less than  $\pm 0.001$ , unless noted otherwise.

Maximum mobilities measured for polymer **PE12T-co-T** in bottom contact devices were  $\sim 0.003 \text{ cm}^2/\text{V}\cdot\text{s}$  with on/off ratios ranging from  $10^4$  to  $10^6$ . Top contact devices have slightly higher average mobilities of  $\sim 0.006 \text{ cm}^2/\text{V}\cdot\text{s}$  but with lower on/off ratios ranging from  $10^3$  to  $10^4$ . Varying the processing conditions such as concentration and spin speed has very little effect on the mobility. Annealing the films at a temperature of 150 °C results in an order of magnitude increase in mobility and on/off ratio, but only slight increases are seen when the films are annealed above this temperature.

	Unannealed		150 °C		200 °C	
	$\frac{\mu}{(\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s})}$	on/off ratio	$\frac{\mu}{(cm^2/V \cdot s)}$	on/off	$\frac{\mu}{(cm^2/V\cdot s)}$	on/off ratio
PQT-E12						
<b>Bottom Contact</b>	0.0013	$10^{5}$	0.0077	$10^{6}$	0.0093	$10^{6}$
2 weeks in air	-		-		0.0069	$10^{5}$
4 months in air	-		-		0.0038	$10^{5}$
Top Contact						
<b>Untreated SiO<sub>2</sub></b>	-		-		0.064	$10^{5}$
SiO <sub>2</sub> treated with OTS	0.0081	$10^{3}$	0.030	$10^{4}$	0.053	$10^{5}$
After 2 months in	-		-		0.017	$10^{5}$
air						
PE12T-co-T						
<b>Bottom Contact</b>	0.0004	$10^{4}$	0.0020	$10^{5}$	0.0032	$10^{6}$
4 months in air	-		-		0.0008	$10^{5}$
Top Contact						
Untreated SiO <sub>2</sub>	-		-		0.0040	$10^{3}$
SiO <sub>2</sub> treated with OTS	0.0009	$10^{2}$	0.0059	$10^{3}$	0.0063	$10^{4}$
2 months in air	-		-		0.0013	$10^{2}$
РЗНТ						
Top Contact	0.0064	$10^{3}$				
After 1 week in air	0.0063	10				

Table 4.2 Average hole mobilities and on/off ratios for 5-10 OFET devices made with the polymers indicated.

Varying the processing conditions and device structure resulted in the same trends in charge mobility for the regioregular polymer **PQT-E12**. As seen in Table 4.2, an increase in the average mobility from 0.0013 to 0.0077 cm<sup>2</sup>/V·s can be achieved in bottom contact devices by annealing

the sample at 150 °C prior to testing. Further increases are measured when the annealing temperature is increased to 200 °C, giving an average mobility of  $0.0093\pm0.002 \text{ cm}^2/\text{V}\cdot\text{s}$ . Mobility values can be pushed even higher by constructing top-contact geometry devices and depositing the polymer on untreated SiO<sub>2</sub> or OTS-treated SiO<sub>2</sub> achieves similar results. Mobilities averaging  $0.064\pm0.02 \text{ cm}^2/\text{V}\cdot\text{s}$  and  $0.053\pm0.01 \text{ cm}^2/\text{V}\cdot\text{s}$ , respectively, were measured when films were annealed at 200 °C in this geometry. In all cases, devices routinely exhibited on/off ratios in excess of  $10^5$  demonstrating low propensity for doping by oxygen during the preparation of these devices in air.

Even though both of the polymers tested have similar conjugation lengths and energy levels, in all cases the symmetrical polymer **PQT-E12** was found to have superior mobilities to polymer **PE12T-co-T**. This can be explained by decreased crystallinity as compared to polymer **PQT-E12**, which is apparent from x-ray diffraction (XRD) studies. As shown in Figure 7.7, **PQT-E12** exhibited distinct diffraction peaks at  $2\theta = 4.17$  and  $8.37^{\circ}$  corresponding to an interchain lamellar *d*-spacing of 21.2 Å. A third peak at  $2\theta = 24.6^{\circ}$  corresponds to a  $\pi$ - $\pi$  stacking distance of 3.62 Å. This  $\pi$ - $\pi$  stacking distance falls in the region typically observed in regioregular polythiophenes (3.5-3.8 Å). **PE12T-co-T** exhibited much weaker diffraction peaks at  $2\theta = 3.49$  and 7.15° corresponding to an interchain lamellar *d*-spacing of 25.3 Å. The third broad peak at  $2\theta = 24.8^{\circ}$  corresponds to a  $\pi$ - $\pi$  stacking distance of 3.59 Å. Even though this polymer is regiorandom, the polymer backbone remains very planar in the solid state resulting in a  $\pi$ -stacking distance comparable to that observed in the symmetrical **PQT-E12**, but it shows a much less intense and broader diffraction pattern most likely resulting from smaller crystalline domains.



Figure 4.9 Thick film XRD analysis of PQT-E12 and PE12T-co-T deposited from o-DCB and annealed at 120 °C.

#### 4.3.2 OXYGEN STABILITY

Devices were stored in an ambient atmosphere, where they were not exclusively protected from light but did spend the majority of the time in the dark. As listed in Table 4.2, bottom contact devices exposed to air for up to 4 months showed a drop in mobility of ~60 % for **PQT-E12** and ~75 % for **PE12T-co-T**. In both cases, the on/off ratios lose an order of magnitude in

the first weeks of exposure then stay relatively constant at  $10^5$ , as shown for **PQT-E12** in Figure 4.10a.



Figure 4.10 Transfer characteristics of devices made with PQT-E12 as a function of time in the air. a)  $V_g vs. I_d$  (inset shows  $V_g vs. I_d^{1/2}$ ) for bottom contact devices with  $L = 10 \,\mu\text{m}$  and  $W = 300 \,\mu\text{m}$  at  $V_d = -35 \,\text{V}$ . b)  $V_g vs. I_d$  (inset shows  $V_g vs. I_d^{1/2}$ ) for top contact devices with  $L = 40 \,\mu\text{m}$  and  $W = 400 \,\mu\text{m}$  at  $V_d = -35 \,\text{V}$ .

Top contact devices using OTS-treated SiO<sub>2</sub> faired similarly when exposed to air for up to 2 months. Polymer **PQT-E12** exhibited a measured drop in mobility of ~70% and polymer **PE12T-co-T** decreased by ~80%. In this configuration, the on/off ratio stays constant at  $10^5$  for polymer **PQT-E12** but decreases to  $10^2$  for polymer **PE12T-co-T**. The origin of the drop in on/off ratio in this particular configuration has not been determined.



Figure 4.11 Transfer characteristics in the saturation regime for a device made with PQT-E12 stored in air for 4 months then subjected to operation in nitrogen, air or after a reverse bias scan. Plots of a)  $V_g$  vs.  $I_d$  and b)  $V_g$  vs.  $I_d^{1/2}$  for a bottom contact device with  $L = 10 \,\mu$ m and  $W= 300 \,\mu$ m at  $V_d = -35 \,$  V.

Transfer characteristics of OFETs using polymer **PQT-E12** as the semiconductor were monitored as a function of air exposure. Figure 4.11a and b illustrate that very low off currents are retained in bottom and top contact devices even after months of exposure, confirming the oxidative stability of this polymer. Although the off current stays low in these devices, the saturation current decreases by about 75% in bottom contact devices (after 4 months) and about 40% in top contact devices (after 2 months). Also, large variations and an overall negative increase in threshold voltage (ranging from -10 to -25 V) were seen, particularly in the bottom contact devices, indicating a change in trap density within the films.<sup>28</sup> Changes in threshold voltage due to p-doping by oxygen shifts the threshold to positive voltages, but in this case a negative shift is observed. This type of behavior is difficult to interpret, and has previously been attributed to many effects such as trapping at the dielectric-semiconductor interface,<sup>29,30</sup> the formation of bipolarons within the semiconductor,<sup>31-33</sup> or degradation of the semiconducting material. The transfer characteristics do not change upon repeated testing, indicating that a long-term stress effect is induced in the polymer rather than a transient bias effect. Re-annealing the devices at 200 °C decreases the off current but does not reduce the threshold shift, ruling out moisture effects. Some recovery in the threshold voltage was seen when a positive bias was applied to the transistor (see Figure 4.11) or after operating the device in white light, but the original threshold values could not be restored.

Testing a solution of polymer **PQT-E12** that had been made 4 months prior gave further confirmation of the stability. No precautions were taken to exclude oxygen during storage, and the solution was not fully protected from light. Top-contact device performance, shown in Figure 410b, was similar to those devices made with fresh polymer solutions. Charge mobilities up to  $0.051 \text{ cm}^2/\text{V}$ ·s with on/off ratios of  $10^5$  were obtained.

Finally, devices were constructed using regioregular P3HT for comparison. Top contact devices were fabricated on untreated SiO<sub>2</sub>, and the P3HT was deposited by spin-casting a 10 mg/mL solution in chloroform at 1000 rpm. All processing was done in the air. Initial testing of these devices produced mobility values of  $0.006 \text{ cm}^2/\text{V} \cdot \text{s}$  with on/off ratios ~ $10^3$ . These devices were stored under the same conditions as the other polymers, but after only 1 week severe doping occurred where on/off ratios dropped to less than 10. Transfer characteristics of these devices are shown in Figure 7.12. While our new polythiophene analog does show some long-term environmental effects, these effects are greatly reduced as compared to P3HT.



Figure 4.12 Transfer characteristics of a bottom-contact device of regioregular P3HT. Plots of V<sub>g</sub> vs. I<sub>d</sub> and V<sub>g</sub> vs. I<sub>d</sub> <sup>1/2</sup> for a device with  $L = 20 \ \mu \text{m}$  and  $W = 400 \ \mu \text{m}$  at V<sub>d</sub> = -35 V.

## 4.3.5 Photovoltaic Performance as a Donor

Highly symmetric conjugated structures and long alkyl chains have historically been demonstrated as ideal structural modifications to achieve high carrier mobilities in organic field effect transistors.<sup>34</sup> So far, these same modifications have not been advantageous for use in organic photovoltaics.<sup>24</sup> Molecular structures of this type tend to form highly ordered crystalline structures with large scale domains of well ordered polymer chains. This morphology leads to long defect free pathways, which allows for high carrier conduction. In photovoltaic devices though, large scale domains of a pure material leads to poor morphologies for the processes involved in charge separation. The highly ordered crystal structures exclude the acceptor material and prevent blend morphologies with nanoscale separation. Thus, the highest performing polymers for organic photovoltaics have been those that obtain only a semi-crystalline or amorphous structure. This allows for intimate mixing between the donor and acceptor for good charge separation efficiency.

**P3ET** and **P3HT-co-3ET** were designed to incorporate carboxylate modifying groups while having a less crystalline structure as compared to **PQT-E12** and **PE12T-co-T**. Electron withdrawing moieties are potentially advantageous for use on electron rich donor polymers such as polythiophenes for several reasons. The larger ionization potential of the polymer helps prevent degradation by molecular oxygen and also creates a larger potential between the separated holes and electrons formed during the photovoltaic process. This higher potential difference has been correlated to an increase in the open circuit voltage of the solar cell leading to better efficiencies.<sup>35</sup>

A comparison of initial photovoltaic performance for **P3ET**, **P3HT-co-3ET** and P3HT is provided in Figure 4.13. All polymers were blended with PCBM in a 1:1 ratio and all devices were annealed at 150°C after fabrication. The P3HT:PCBM control device achieved PCE = 4.3% with  $V_{oc} = 0.62$  V,  $J_{sc} = 13$  mA/cm<sup>2</sup>, and FF = 0.53. The **P3ET** based device generated a low performance with PCE of only 0.08%. The FF of 0.25 for this device shows the poor charge generation and carrier conduction in the device. The high recombination rates apparent in this device ruin the diode behavior of the system lowering the  $V_{oc}$  and  $J_{sc}$ . This is most likely caused by the non-planer nature of the polymer due to steric twisting from the closely localized carboxylate groups. While too much crystallinity can lead to poor mixing and device performance, a loss of backbone planarity, confirmed by the blue shifted absorption of **P3ET**, can reduce the hole mobility by to large of a degree, leading to unbalanced charge transport and a buildup of space charge inside the device. The **P3HT-co-3ET** device shows a better performance with PCE = 1.7%. The low FF for this device also points to recombination and transport issues in the system, but the improved PCE compared to **P3ET** is promising enough for further optimization of **P3HT-co-3ET** as a donor material for mixing with PCBM.



Figure 4.13 Initial JV curves and photovoltaic performance for P3HT, P3ET, and P3HT-co-3ET with PCBM in a 1:1 ratio and annealed at 150°C for 30 minutes.

**P3HT-co-3ET**:PCBM devices were optimized for polymer:fullerene ratio, active area thickness and post-fabrication annealing time and temperature. The best processing conditions were found to be an approximately 100 nm thick film of a 2:1 polymer:PCBM ratio annealed at 120°C for 30 minutes. The resulting device yielded PCE = 1.9%, with a  $V_{oc} = 0.65$  V,  $J_{sc} = 6.2$  mA/cm<sup>2</sup> and FF = 0.47, and the JV curve is shown compared to a P3HT:PCBM control device in Figure 4.14. Of note is the ratio of donor to acceptor used for this device. Two to one is the largest polymer to fullerene ratio to be used in a BHJ device with a fullerene acceptor that has achieved over 1% efficiency. One possible reason for the large excess of polymer compared to fullerene is because the copolymer contains approximately 50% 3-hexylthiophene units and this would allow for an approximate 1:1 interaction between 3-hexylthiophene and PCBM. Although without more characterization of the "blockiness" of the copolymer further evidence for this hypothesis is impossible.

While the FF of the optimized device is higher it is still not possible to draw a direct comparison between the solar cell parameters for the **P3HT-co-3ET** device with the control P3HT cell. Therefore the small increase in  $V_{oc}$  when substituting **P3HT-co-3ET** for P3HT cannot be directly attributed to any difference in donor HOMO level. Based on the HOMO levels as measured by CV, **P3HT-co-3ET** has a lower energy than P3HT by approximately 0.2 V, yet the increase in  $V_{oc}$  is 0.03 V. While the relationship between an increase in HOMO level and an increase in  $V_{oc}$  is not unity, it would be hard to rationalize this large of a disparity if there were no other factors involved.



Figure 4.14 JV curves for P3HT-co-3ET:PCBM in a 1:0.5 ratio compared to P3HT:PCBM 1:1.

#### 4.4 N-TYPE MOBILITY

Utilizing conjugated polymers as electron acceptors in all-polymer OPVs has potential benefits over using conventional fullerene acceptors. The absorption coefficients of conjugated polymers tends to be higher than fullerene acceptors in the visible region and thus all-polymer devices should be able to absorb more light in the same thickness films. The energetics of conjugated polymers are also easier to alter as compared to functionalized fullerenes since the electronics of the fullerene are heavily controlled by the  $C_{60}$  cage and cannot be influenced much without destroying the aromatic sphere.<sup>36</sup> Having more control over the energy levels of the acceptor material will ultimately allow for finer control of the photovoltaic performance and applications of donor-acceptor blend systems.



Figure 4.15 HOMO/LUMO diagram of type II heterojunction for possible all-polymer OPV.

The reduction of polythiophene derivatives is usually a stable process but occurs at to high of a potential to generally be accomplished by electrodes other than reactive alkaline earth metals such as Ca or Mg. The large electron withdrawing nature of the carboxylate groups in **P3ET** lowers the LUMO level of polythiophene by almost 0.5 eV. The lower lying energy levels of **P3ET** form a type II heterojunction with traditional organic photovoltaic donors such as P3HT and M3EH-PPV (poly[2,5-dimethoxy-1,4-phenylene-1,2-ethenylene-2-methoxy-5-(2-ethylhexyloxy)–(1,4-phenylene-1,2-ethenylene)]). The incorporation of the ester functionality

should also stabilize the reduced thiophene state through conjugation from the aromatic ring to the more electronegative oxygen atom. The enhanced stability of the reduced state coupled with the larger electron affinity for the polymer should allow **P3ET** to function as both an electron acceptor and electron transporter in OPVs when paired with a strong electron donor material.

#### 4.4.1 Photovoltaic Performance

**P3ET**was incorporated as the electron acceptor into all-polymer OPVs with either P3HT or M3EH-PPV as the electron donating component. Figure 4.16 shows typical JV curves obtained for these devices before and after thermal annealing. P3HT:**P3ET** devices showed poor diode behavior with FF = 0.25 for devices with both sets of donors. Even with poor photovoltaic behavior both sets of devices do provide over 100 µA cm<sup>-2</sup> of photocurrent at zero bias while under 100 mW cm<sup>-2</sup> illumination. This is several orders of magnitude higher than the photocurrent generated by a single conjugated polymer sandwiched between two electrodes.



Figure 4.16 JV curves of P3ET unanealed and annealed (150°C for 30 min) all-polymer solar cells with M3EH-PPV or P3HT as the electron donor.

The higher photocurrent along with the poor FF suggests that **P3ET** does act as an electron acceptor and conductor but that there is still a large amount of recombination events either by geminate pairs or free charges or both. Geminate pair recombination could result from a combination of factors including a morphological component or a low potential difference between LUMOs. The potential driving force for charge separation ( $U_{CS}$ ) can be approximated from Equation 4.1, where  $IP_D$  is the ionization potential of the donor in the solid state,  $Eg_{D \text{ optical}}$  is the optical band gap of the donor and  $EA_A$  is the electron affinity of the acceptor. The driving forces for separation, which is a two step process, for P3HT:**P3ET** and M3EH-PPV:**P3ET** devices are ~0 eV and 0.2 eV respectively.

$$U_{CS} = (IP_D - Eg_{D \ optical}) - EA_A$$

(Equation 4.1)

These values are ~0.8 eV lower than typical values seen for BHJ solar cells with PCBM as the electron acceptor. This reduction in excess energy means that the efficiency for charge separation must be less than the efficiency seen for systems such as P3HT:PCBM, which has an estimated

separation efficiency of around 70%. The advantage of such high energy levels can be seen by examining the  $V_{oc}$  of the devices. Open circuit voltages of 0.75 V and 1.1V are obtained from the P3HT and M3EH-PPV devices respectively. These values are significantly higher than the 0.6 V and 0.7 V values obtained when these polymers are mixed with PCBM.

The electron transport in the **P3ET** could be another limiting factor in these devices. Well ordered **P3ET** should have good electron transporting properties, but the carboxylate groups on every other thiophene most likely prevent good planarization of the polymer backbone in the solid state as evidenced by the blue shifted absorption of **P3ET** compared to typical polythiophenes (Figure 4.5). The twisted backbone resulting from the steric interactions of neighboring carboxylate groups also prevents any long range intermolecular interactions between neighboring chains. While the actual electron mobility has not been measured for **P3ET**, it is most likely much lower than the hole mobility of the more ordered donor materials and therefore a buildup of electron density in the device is likely to occur leading to poor performance.

A poor solid state mixing between donor and acceptor could also be responsible for the decreased charge separation or decreased electron mobility. Imaging the physical blend morphology in all-polymer systems is extremely challenging as the similarities in chemical structure and electronics leads to little contrast when employing typical imaging techniques such as transmission electron microscopy (TEM) or atomic force microscopy (AFM). The best method to elucidate the thin film morphology of the blend system is to compare the external quantum efficiency (EQE) with the absorption spectra of the individual polymers. Figure 4.17 compares the photon to electron conversion efficiency at individual wavelengths of different blend ratios of P3HT:**P3ET** with the solid state absorption spectra for the polymers individually. All the spectra have been normalized as the comparison at each wavelength is the relevant data.



Figure 4.17 Normalized external quantum efficiencies for P3HT:P3ET devices (with ratios 1:1 black squares, 3:7 red circles, 1:4 green triangles). These are compared to the thin film UV-Vis absorption spectra for P3HT (purple) and P3ET (blue).

Normally in a BHJ device, the quantum efficiency for the system matches with the absorption spectra of the individual polymers. Here, there is a large contribution of photocurrent from the

350 nm to 450 nm range where neither homopolymer absorbs. Since conjugated molecules usually experience hypsochromism when they become severally entangled the photocurrent produced from the blue end of the spectrum suggests that some of the polymer chains are intimately mixed causing a reduction in their conjugation length. Post deposition thermal annealing has been used in other OPV systems to regain polymer conjugation length after film formation, but Figure 4.16 shows that thermal annealing even at 150°C has little influence on the device performance. Thus, post-fabrication thermal annealing is ineffective at separating the two polymers from each other and recovering the red-shifted absorption. Overall, while the morphology and charge separation issues must be overcome, these experiments do show that the same conjugated polymers can act as either p-type or n-type depending on the system and that electron withdrawing carboxylate groups are effective handles for tuning the electronics of conjugated polymers.

#### **4.5 CONCLUSION**

A carboxylate side group has been used to generate a new class of soluble polythiophenes. This chemical functionalization along the polymer backbone can be used to tailor the polymer ionization potential and electron affinity The regioregular ester-functionalized polythiophenes were found to have high charge mobilities up to  $0.07 \text{ cm}^2/\text{V} \cdot \text{s}$  with low off currents even when OFET devices were fabricated entirely in air. This showed that the reduction in HOMO level helps to stabilize conjugated materials to oxidation from ambient molecular species. The ability to tune the HOMO and LUMO levels of polythiophenes by introducing electron-withdrawing substituents while still maintaining good charge mobility, will allow for a more practical application of organic devices such as organic photovoltaics and sensors.

Lowering the HOMO and LUMO levels of conjugated polymers also allows these same materials to be utilized as either an electron donor or acceptor in organic devices depending on the other materials. When mixed with an n-type material such as PCBM, ester-thiophene polymers act as a p-type hole transporter and obtain PCE = 1.9% under one sun simulated conditions. The same carboxylate functionalization can be used to stabilize the reduced polythiophene chain and increase the polymer electron affinity. This enables n-type behavior in all-polymer solar cells when the carboxylate polymer is blended with electron rich polymers such as P3HT or M3EH-PPV. These all-polymer devices are attractive due to the much higher open circuit voltage when compared to bulk heterojunction OPVs that use fullerene based acceptors, but care must be taken to redesign the system to avoid loss of efficiency due to inefficient charge separation and poor mixing.

#### **4.6 EXPERIMENTAL**

UV-Vis data were measured with a Varian Cary 50 spectrophotometer. Differential scanning calorimetry was performed using a Seiko Instruments ExSTAR 6000 DSC 6200. Electrochemical measurements were done by cyclic voltammetry (CV) using a Solatron 1285 potentiostat. Measurements were performed using a three electrode airtight cell under nitrogen.

A 2 mm diameter Pt wire was used for both work and counter electrodes with an Ag wire as a pseudo-reference electrode. Polymer thin films were created by dipping the working electrode into the polymer solution with a concentration of 10 mg/mL (solvent was chloroform for P3HT, **P3ET** and **P3HT-co-3ET** and 1,2-dichlorobenzene for polymer **PQT-E12** and **PE12T-co-T**). The electrolyte solution was 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> in dry acetonitrile, which had been distilled over CaH<sub>2</sub>. Current vs. voltage measurements were recorded versus the Ag reference electrode, which had been calibrated by using a standard ferrocene/ferrocenium redox reaction (0.30 V vs. SCE). Four cycles were taken of each polymer at a scan rate of 100 mV/s.

XRD films were drop cast from 100 °C solutions of polymer in *o*-DCB onto silicon substrates in a Petri dish heated to 120 °C. The Petri dish was kept closed to saturate the solvent environment and increase the film formation time. The drop casting procedure was then repeated to increase the film thickness. Resulting films were 5-10 microns thick. XRD measurements were made with a Phillips Expert x-ray diffractometer.

For organic thin film transistors low resistivity n-type silicon wafer substrates were used with the substrate acting as a back-gate. Both top and bottom contact geometry devices were constructed, both using a 1000 or 1250 Å silicon dioxide dielectric thermal oxide, grown at 900 °C from steam. The RMS roughness as measured by a Digital Instruments Nanoscope 3100 Atomic Force Microscope was < 0.20 nm, and the water contact angle as measured by a Karl Seuss Contact Angler Profiler was  $< 20^{\circ}$ . Solvents used for casting were anhydrous and purchased from Aldrich. 3mg/mL solutions of the polymers in *o*-DCB were prepared in a scintillation vial, sonicated for 1 minute then heated to 80 °C on a hot plate to completely dissolve the polymers. Heated solutions were quickly spun onto the wafers at 1000 rpm for 30 seconds. Remaining solvent was removed under high vacuum for 30 minutes, then the films were annealed in a furnace oven at various temperatures for 30 minutes. Spin casting and all heating and annealing was performed in the air. For the devices using P3HT as the active layer, a 10 mg/mL solution of P3HT in chloroform was spun cast at 1000 rpm for 30 seconds. Devices were placed under high vacuum for 30 minutes to remove any remaining solvent.

For top contact devices, shadow masks were used in conjunction with thermal evaporation to pattern electrodes on the top of the active layer. As shadowing effects often lead to device dimensions smaller than those fabricated on the mask itself, both AFM and scanning electron microscopy (SEM) were used to measure the effective dimensions patterned via shadow masking; resulting channel lengths measured from 5  $\mu$ m to 40  $\mu$ m. For gold electrode deposition, a base pressure of  $< 2 \times 10^{-7}$  torr was used, with an evaporation rate of 0.5 nm/s. Overall gold thickness was 50 nm, and bottom contact devices used a 2.5 nm chrome adhesion layer.

To obtain a low surface energy interface, octadecyltrichlorosilane (OTS) was used to form a hydrophobic self-assembled monolayer (SAM) on top of grown thermal oxide. The RMS roughness of the OTS layer was < 0.8 nm, and the contact angle was > 110°. For SAM formation, 10  $\mu$ L of OTS was added to 100 mL of heptane (99%, anhydrous) under atmosphere, and an oxidized wafer was immersed for one hour. After removal, the wafer was further

sonicated in heptane for 30 minutes, and then rinsed in deionized water. Substrates treated in this manner were used for top contact devices only.

The electrical measurements were performed in nitrogen or ambient atmosphere using an Agilent 4156C Precision Semiconductor Parameter Analyzer. As the entire backside of the substrate was used as the gate electrode, the entire thin film was accumulated during device testing. To minimize gate leakage and improve isolation in this type of setup, the active layer was scratched via probe tips around groups of devices. Mobilities were calculated in the saturation regime using Equation 4.21, where gm is the transconductance, W is the channel width, L is the channel length,  $C_{ox}$  is the capacitance of the insulating layer, and  $I_D$  is the saturation current.<sup>44,45</sup>

$$\mu = gm^2 / 2I_D C_{ox}(W/L)$$

(Equation 4.2)

Photovoltaic devices consisted of a standard ITO/PEDOT:PSS/active layer/Al architecture. Indium-doped tin oxide (ITO) coated glass substrates were purchased from Thin Film Devices, Inc. The substrates (150 nm sputtered pattern,  $10 \Omega \Box^{-1}$ ) were cleaned by 20 minutes of sonication in acetone, 2 percent Helmanex soap in water, and finally isopropanol. The substrates were then dried under a stream of air before being coated immediately with a filtered (0.45 µm GHP) dispersion of PEDOT:PSS in water (Baytron-PH) *via* spin coating for 30 s at 4000 rpm. The resulting polymer layer was ~30 nm thick after baking at 140 °C for 20 min. All subsequent device fabrication was performed inside a glove box under inert Ar atmosphere with water and oxygen levels below 1 ppm.

P3HT, **P3ET** and **P3HT-co-3ET** were dissolved at a concentration of 20 mg mL<sup>-1</sup> in chlorobenzene. PCBM (purchased from Nano-C) was dissolved separately at 20 mg mL<sup>-1</sup> in chlorobenzene and all solutions were allowed to stir overnight at 120 °C. The solutions were then combined in various ratios from 1:1 to 1:6 polymer:fullerene before spin casting onto the PEDOT:PSS-treated ITO at 1200 rpm for 30 seconds. For all-polymer devices P3HT or M3EH-PPV were co-dissolved with **P3ET** at 10 mg mL<sup>-1</sup> in chlorobenzene before spin casting at 1200 rpm for 30 seconds. 100 nm aluminum electrodes were deposited by thermal resistance evaporation at pressures of approximately 10<sup>-6</sup> torr to complete the device structure. The shadow mask used during thermal deposition yielded eight independent devices per substrate each with a surface area of 0.03 cm<sup>2</sup>. Completed devices were then tested under Ar(g) using a 300 W Thermo-Oriel Xenon arc-lamp with flux control spectrally corrected to AM 1.5 G with one filter (Thermo-Oriel #81088). The AM 1.5 G light was further attenuated using a 0.5 O.D. neutral density filter, and the intensity of the AM 1.5 G light was calibrated to be 100 mW cm<sup>-2</sup> by a spectrally-matched Hamamatsu S1787-04 photodiode (calibrated by NREL and obtained through Nanosys Inc.). I-V behavior was measured using a computer-controlled Keithley 236 SMU.

#### REFERENCES

- (1) Dimitrakopoulos, C.; Malenfant, P. Advanced Materials 2002, 14, 99-117.
- (2) Horowitz, G. Advanced Materials 1998, 10, 365-377.
- (3) Katz, H. E.; Bao, Z.; Gilat, S. L. Accounts of Chemical Research 2001, 34, 359-369.

- (4) Sirringhaus, H.; Tessler, N.; Friend, R. H. Science 1998, 280, 1741-1744.
- (5) Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Advanced Functional Materials* **2001**, *11*, 15-26.
- (6) Coakley, K. M.; McGehee, M. D. Appl. Phys. Lett. 2003, 83, 3380-3382.
- (7) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. Science 2002, 295, 2425-2427.
- (8) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. Science 1995, 270, 1789-1791.
- (9) Coakley, K. M.; McGehee, M. D. *Chemistry of Materials* **2004**, *16*, 4533-4542.
- (10) Thompson, B. C.; Fréchet, J. Angewandte Chemie International Edition 2008, 47, 58-77.
- (11) Brédas, J.; Norton, J. E.; Cornil, J.; Coropceanu, V. Accounts of Chemical Research 2009, 42, 1691-1699.
- (12) Sirringhaus, H.; Wilson, R. J.; Friend, R. H.; Inbasekaran, M.; Wu, W.; Woo, E. P.; Grell, M.; Bradley, D. D. C. *Appl. Phys. Lett.* 2000, 77, 406-408.
- (13) Heeney, M.; Bailey, C.; Genevicius, K.; Shkunov, M.; Sparrowe, D.; Tierney, S.; McCulloch, I. *Journal of the American Chemical Society* 2005, *127*, 1078-1079.
- (14) McCulloch, I.; Bailey, C.; Giles, M.; Heeney, M.; Love, I.; Shkunov, M.; Sparrowe, D.; Tierney, S. *Chemistry of Materials* **2005**, *17*, 1381-1385.
- (15) Ong, B. S.; Wu, Y.; Liu, P.; Gardner, S. *Journal of the American Chemical Society* **2004**, *126*, 3378-3379.
- (16) Ong, B.; Wu, Y.; Jiang, L.; Liu, P.; Murti, K. Synthetic Metals 2004, 142, 49-52.
- (17) Masuda, H.; Kaeriyama, K. Die Makromolekulare Chemie, Rapid Communications 1992, 13, 461-465.
- (18) Waltman, R. J.; Diaz, A.; Bargon, J. J. Electrochem. Soc. 1984, 131, 1452.
- (19) Pomerantz, M.; Yang, H.; Cheng, Y. Macromolecules 1995, 28, 5706-5708.
- (20) Pomerantz, M.; Cheng, Y.; Kasim, R. K.; Elsenbaumer, R. L. J. Mater. Chem. **1999**, *9*, 2155-2163.
- (21) Amarasekara, A. S.; Pomerantz, M. Synthesis 2003, 2255-2258.
- (22) McCullough, R. D.; Williams, S. P. Journal of the American Chemical Society 1993, 115, 11608-11609.
- (23) Liu, J.; Kadnikova, E. N.; Liu, Y.; McGehee, M. D.; Frechet, J. M. J. Journal of the American Chemical Society **2004**, 126, 9486-9487.
- (24) Thompson, B. C.; Kim, B. J.; Kavulak, D. F.; Sivula, K.; Mauldin, C.; Fréchet, J. M. J. *Macromolecules* **2007**, *40*, 7425-7428.
- (25) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *The Journal of Organic Chemistry* 1993, 58, 904-912.
- (26) Brown, P.; Thomas, D.; Köhler, A.; Wilson, J.; Kim, J.; Ramsdale, C.; Sirringhaus, H.; Friend, R. *Phys. Rev. B* 2003, 67.
- (27) Bredas, J. L.; Silbey, R.; Boudreaux, D. S.; Chance, R. R. *Journal of the American Chemical Society* **1983**, *105*, 6555-6559.
- (28) Brown, A.; Jarrett, C.; de Leeuw, D.; Matters, M. Synthetic Metals 1997, 88, 37-55.
- (29) Lin, Y.; Gundlach, D.; Nelson, S.; Jackson, T. *IEEE Trans. Electron Devices* **1997**, *44*, 1325-1331.
- (30) Torres, I.; Taylor, D. M.; Itoh, E. Appl. Phys. Lett. 2004, 85, 314.
- (31) Salleo, A.; Street, R. A. Phys. Rev. B 2004, 70, 235324.
- (32) Salleo, A.; Street, R. A. J. Appl. Phys. 2003, 94, 471.
- (33) Street, R. A.; Salleo, A.; Chabinyc, M. L. Phys. Rev. B 2003, 68, 085316.
- (34) Ong, B. S.; Wu, Y.; Liu, P.; Gardner, S. Journal of the American Chemical Society 2004,

126, 3378-3379.

- (35) Gadisa, A.; Svensson, M.; Andersson, M. R.; Ingana S, O. Appl. Phys. Lett. 2004, 84, 1609.
- (36) Backer, S. A.; Sivula, K.; Kavulak, D. F.; Fréchet, J. M. J. *Chemistry of Materials* **2007**, *19*, 2927-2929.

# CHAPTER 5: POLYTHIOPHENE MODIFICATION FOR CHEMICAL CONTROL OVER Bulk Heterojunction Morphology

#### ABSTRACT

Obtaining a nanoscale interpenetrating network between donors and acceptors is necessary in order to obtain efficient performance in bulk heterojunction OPVs. Comparison of polythiophene copolymers with equivalent electronic structures, compositions, and molecular weights, indicates that the sequence distribution of alkyl solubilizing groups dramatically influences the efficiency of polymer-fullerene bulk heterojunction solar cells. The amorphous thiophene copolymer with a random distribution of 3-dodecylthiophene and thiophene repeat units (P3DDT-*co*-T), is observed to outperform a perfectly alternating, highly crystalline analogue (PQT-DD), with measured efficiencies more than three times as high. The primary difference is the enhanced ability of the non-crystalline P3DDT-*co*-T to effectively mix with the soluble fullerene PCBM, to generate bicontinuous morphologies.

Strong intermolecular attractive forces can also be generated between the donor polymer and acceptor by functionalizing the polymer side group. A Pyrene substituted poly(3-alkylthiophene) copolymer is reported as a material for use in polymer-nanotube composite solar cells. Morphological characterization reveals that the polymer is capable of forming uniform composites with 10 wt% of multiwalled carbon nanotubes (MWNTs), in contrast to the highly phase segregated composites formed with poly(3-hexylthiophene) as observed by optical microscopy

Portions of this chapter were published previously: Macromolecules., 2007, 40, 7425.

# **5.1 INTRODUCTION**

Recently, power conversion efficiencies approaching 5% have been reported for the poly(3hexylthiophene)/[6,6]-phenyl- $C_{61}$  butyric acid methyl ester (P3HT:PCBM) bulk heterojunction (BHJ) solar cells.<sup>1</sup> The successful combination of P3HT and PCBM is largely based on the ability of the two components to mix homogenously in a pristine cast film and then, under the influence of thermal or solvent annealing,<sup>1,2</sup> undergo a controlled phase segregation yielding a nanometer length-scale bicontinuous network of highly ordered donor and acceptor phases, suitable for charge transport. Much effort has been dedicated to the optimization of these devices, including a focus on developing a deeper understanding of the role that polythiophene structure has on device performance.<sup>3-8</sup> The ability of regionegular (RR) P3HT to form crystalline phases with strong interchain and intrachain  $\pi$ - $\pi$  overlap is credited for the observed hole mobilities as high as  $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  measured in FETs<sup>9</sup> and for the enhanced visible light absorption properties of the polymer.<sup>10</sup> It is this solid state crystallization that begins to exclude the fullerene molecule forming polymer rich and polymer poor regions. This segregation is advantageous for charge conduction and overall device efficiency as long as the two regions stay connected on the nanometer length scale in order to maintain high exciton separation efficiency. It is still unclear exactly how much the crystallinity of the polymer affects the genealogy of the active layer morphology.

Fullerenes and their soluble derivatives are not necessarily the most optimal material for use in bulk heterojunction solar cells based on the relatively high weight percentage of fullerene (generally 45-80%)<sup>11-13</sup> required and the tendancy of fullerenes to phase segregate in polymer blends.<sup>14</sup> A variety of alternatives ranging from inorganic nanoparticles<sup>15,16</sup> and electron transporting polymers<sup>17</sup> to carbon nanotubes<sup>18-20</sup> have been investigated. Semiconducting single walled carbon nanotubes (SWCNTs)<sup>21</sup> are especially attractive as electron accepting materials for solar cell applications<sup>22</sup> based on several potential advantages that they offer relative to fullerenes, such as a longer aspect ratio, which could allow lower acceptor loadings,<sup>23</sup> and enhanced mechanical strength<sup>24</sup> for the realization of robust, flexible devices. Nonetheless, carbon nanotubes also present various challenges, such as insolubility, sample inhomogeneity (due to metallic and semiconducting components), and nanotube bundling. For solubilizing carbon nanotubes both covalent and supramolecular strategies have been employed, although supramolecular interactions offer the advantage that the electronic structure of the carbon nanotube is not compromised.<sup>25</sup>

#### 5.2 CONTROLLING MORPHOLOGY THROUGH DISORDER

Polythiophene analogues that exhibit higher levels of crystallinity and higher hole mobilites than P3HT, such as the regiosymmetric polymers  $poly(3,3 \square \square \square didodecylquaterthiophene)$  (**PQT-DD**)<sup>26,27</sup> and poly(2,5-bis(3-tetradcylthiophen-2-yl)thieno[3,2-*b*]thiophene) (PBTTT),<sup>28</sup> have been studied for use in FETs, displaying mobilities from 0.18 to 0.6 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. Such polymers achieve a greater overall degree of crystallinity than P3HT based on the length and

distribution of alkyl side chains, which favors long range three-dimensional ordering via  $\pi$ - $\pi$  stacking and side chain interdigitation. While such polymers define the state-of-the-art in solution-processed FETs, their photovoltaic performance has not yet been reported, so it is unclear whether the enhanced inherent crystallinity will be beneficial to composite solar cells.

#### 5.2.1 MATERIALS

As a means of investigating such highly ordered polymers and directly assessing the influence of a high degree of crystallinity on solar cell performance, here we examine two thiophenealkylthiophene copolymers with identical molecular weight, composition, and electronic structure, which are composed of equal parts of 3-dodecylthiophene and unsubstituted thiophene. The first polymer is the perfectly alternating copolymer **PQT-DD**, described above, and the other is the random copolymer poly(3-dodecylthiophene-*co*-thiophene) (**P3DDT-***co***-T**).



Figure 5.1 Synthetic scheme for alkyl-thiophene thiophene copolymers.

Figure 5.1 illustrates the synthetic routes used for the synthesis of **PQT-DD** and **P3DDT-***co***-T**. Here, dodecyl substituents were chosen to maintain solubility, while allowing for the incorporation of unsubstituted thiophene rings. The synthesis of **PQT-DD** was achieved via the Stille copolymerization of dibromo monomer **2** and distannyl monomer **3**, rather than the oxidative polymerization reported in the literature.<sup>26</sup> For **P3DDT-***co***-T** a random copolymerization of equimolar amounts of 2-bromo-3-dodecylthiophene and 2-bromothiophene was performed using a modified McCullough route.<sup>29</sup> Based on this synthetic route, **P3DDT-***co***-T** is expected to have a random sequence distribution, but is expected to have predominantly head-to-tail linkages for any sequences of consecutively linked 3-dodecylthiophene repeat units.

Analysis by NMR is uninformative for establishing the precise sequence distribution in such a polymer. The molecular weights of **PQT-DD** and **P3DDT-***co***-T** were estimated via SEC to be 19,800 and 19,400 g/mol respectively, with measured PDI values of 2.11 and 1.99, vs. polystyrene standards. Thus the two polymers are structurally equivalent, except for the sequence distribution of substituted and unsubstituted thiophene rings. Both polymers are less soluble than P3HT of a similar molecular weight, but both are soluble in chloroform, chlorobenzene, and dichlorobenzene.

#### 5.2.2 Optical and Electronic Properties

The electronic and structural properties of the polymers were investigated by UV-Vis spectroscopy, electrochemistry and X-ray diffraction (XRD). Table 5.1 compares the band energies for **PQT-DD** and **P3DDT-***co***-T** with P3HT. The electronic structure of both **PQT-DD** and **P3DDT-***co***-T** are found to be equivalent, with optical band gaps estimated from thin film UV-Vis to be ~2 eV (Figure 5.2) and with similar electrochemical oxidation and reduction levels. Thin film absorption coefficients of 7.6 x  $10^4$  and 5.4 x  $10^4$  cm<sup>-1</sup> are measured for **PQT-DD** and **P3DDT-***co***-T** respectively, which compare favorably to P3HT (8.7 x  $10^4$  cm<sup>-1</sup>).

Polymer	Oxidation vs $Fc/Fc^+(V)^1$	Reduction vs Fc/Fc <sup>+</sup> (V)	HOMO $(eV)^2$	LUMO (eV)	Eg (eV)
PQT-DD	0.25	-1.71	-5.35	-3.39	1.95
P3DDT-co-T	0.35	-1.69	-5.45	-3.41	2.04
P3HT	0.17	-2.02	-5.27	-3.08	2.19

**Table 5.1** Electrochemical energy levels measured by cyclic voltammetry with tetrabutyl ammonium hexafluorophosphate (0.1 M) as the supporting electrolyte. <sup>1</sup> All electrochemical values are reported as onsets. <sup>2</sup> All electrochemical values are converted to vacuum based on the relation that the Fc/Fc<sup>+</sup> redox couple lies 5.1 eV below the vacuum level.



Figure 5.2 Thin film UV-Vis spectra of P3HT, PQT-DD and P3DDT-co-T

Structural ordering within films of the two copolymers was also examined by XRD and transmission electron microscopy (TEM) (Figure 5.3). In both cases, polymer films were dropcast from chloroform and annealed at 100 °C for 30 minutes prior to measurement, followed by slow cooling. It is clear, based on the XRD results and the fibrillar features observed only in **PQT-DD** by TEM, that **PQT-DD** is significantly more crystalline than **P3DDT-***co***-T** under these conditions, as would be expected based on the precise, perfectly alternating nature of the **PQT-DD** primary structure relative to the random structure of **P3DDT-***co***-T**. The XRD pattern in Figure 5.3a represents the reflections from the interchain ordering ( $2\theta$ = 5.2°, 10.5°), side chain ordering ( $2\theta$ = 7.4°, 14.8°, 22.3°) and  $\pi$ - $\pi$  stacking ( $2\theta$ = 21.2°), giving a *d*-spacing of 1.70 nm, 1.19 nm and 0.42 nm, respectively, which shows good agreement with the previous report.<sup>30</sup>



Figure 5.3 XRD for drop cast films of PQT-DD (a) and P3DD-*co*-T (b). Films were annealed at 100 °C for 30 minutes prior to acquisition of data. TEMs of PQT-DD (c) and P3DD-*co*-T (d). Scale bars are 100 nm.

In addition to the band structure of a donor polymer for photovoltaic devices, the other property of great inherent interest is the charge carrier mobility attainable in the polymer. For reference, P3HT is reported to have a hole mobility on the order of  $10^{-3}$ - $10^{-1}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> measured in FETs and **PQT-DD** has been shown to have a mobility as high as 0.18 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> under the most optimal conditions.<sup>27</sup> In diagnostic FET measurements, **PQT-DD** was found give a reproducible mobility on the order of  $10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, which matches with reported average values of 0.07-0.12 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.<sup>26</sup>



Figure 5.4 I-V curves shown for an OFET of P3DD-*co*T with W = 400  $\mu$ m and L = 40  $\mu$ m. Plots of a) I<sub>D</sub> and I<sub>D</sub><sup>1/2</sup> vs. V<sub>G</sub> at VD = -30 V and b) I<sub>D</sub> vs. V<sub>D</sub> at at varying V<sub>G</sub>. In transistors fabricated using the above method, P3DD-*co*T gave an average saturation charge mobility of 0.001 ± 0.0007 cm<sup>2</sup>/V·s and an average on/off ratio of 10<sup>4</sup>.

Measurement of FETs with **P3DDT-***co***-T** (Figure 5.4) showed a mobility of  $10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, reflecting the lower degree of order attainable in **P3DDT-***co***-T**, as evidenced by XRD. Perhaps a more representative measurement of charge carrier mobility, as relevant to solar cells, is the space charge limited current mobility (SCLC),<sup>31</sup> which measures the mobility perpendicular to the electrodes rather than parallel to the substrate and not under the influence of a gate bias, as in FETs. Typical values of SCLC mobility for P3HT are on the order of  $10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. For **PQT-DD** and **P3DDT-***co***-T** the SCLC mobilities were measured to be 2.7 x  $10^{-4}$  and 2.8 x  $10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> respectively. The similarity in SCLC mobilities for these two polymers, which show such disparate abilities to order, is a surprising result, that also suggests a lower relevance to reported FET mobilities, when considering polymers for use in solar cells. The similar SCLC mobilities also suggest that despite the lack of observed long range order in **P3DDT-***co***-T**, locally ordered domains must exist in order to engender such bulk mobility.

## **5.3 MORPHOLOGY**

The alkyl distribution along the polymer backbone clearly changes its physical structure and long range packing in a thin film. Yet the band gap, electron density, and the conduction of charges through the film are more dependent upon the local ordering of the polymer which is present in both materials. Therefore, any difference in the solar cell performance between these two polymers will most likely be due to the active layer morphology.

#### 5.3.1 TEM/AFM

Evidence for how the dodecyl solubilizing groups alter the conjugated polymers mixing with PCBM can be gleaned by examination of the active layer morphology via transmission electron microscopy (TEM). Figure 5.5 represents TEM images for both polymers in blends with PCBM at the optimal composition for device performance. The random polymer forms a bicontinuous donor-acceptor network (Figure 5b), with domain sizes on the order of <50 nm and no such favorable morphology is observed for **PQT-DD** at any composition.



Figure 5.5 TEM images of a 25:75 blend of PQT-DD:PCBM (a) and a 30:70 blend of P3DDT-co-T:PCBM (b).

For **P3DDT***-co-***T** at weight percentages of PCBM above 70%, phase segregation occurs on a much larger length scale (Figure 5.6), leading to diminishing device performance, while at weight percentages of PCBM less than 70%, homogenous blends are observed, which lack the bicontinuous pathways necessary for charge extraction. Unlike the P3HT:PCBM blend system in which thermal annealing can be used to induce a controlled demixing of the two phases with concomitant intraphase ordering, any level of thermal annealing above 50 °C induces macrophase separation and marked decreases in device performance.



Figure 5.6 Additional TEM images showing the progression of morphology with composition. (a) Weight ratio of P3DDT-*co*-T to PCBM = 50 : 50, (b) 30 : 70 and (c) 10 : 90. All scale bars correspond to 250 nm.

Such behavior has been observed previously in dodecyl substituted polythiophenes,<sup>10</sup> and has been explained by the enhanced ability of PCBM molecules to diffuse within the polymer film, engendered by the significantly larger interchain spacing in the bulk polymer caused by the longer alkyl chains. Equivalenlty, the presence of longer alkyl chains may simply decrease the miscibility with the fullerene cage of PCBM. The effect is to render dodecyl substituted poly(alkylthiophenes) unstable to nanoscale phase segregation and renders them less effectively miscible with PCBM in general. However the ability to kinetically trap a favorable morphology with **P3DDT**-co-T but not with **PQT-DD**, suggests that a greater inherent miscibility exists between the random copolymer and PCBM as opposed to the much more highly ordered POT-**DD**, which is attributed to the greater tendency of **POT-DD** to crystallize, favoring the exclusion of fullerene from the polymer phase. Conceptually similar results have been observed concerning the effect of the degree of regioregularity in P3HT.<sup>6</sup> In samples of P3HT with a higher degree of regioregularity, macrophase separation occurs on a much shorter time scale of annealing than for samples with a lower degree of regioregularity, suggesting that polymers capable of attaining a high degree of crystalline order engender macrophase separation. The previous results about the effect of regioregularity, taken with the present results, suggest that a certain degree of disorder in polythiophenes enhances their ability to effectively mix with the small molecule fullerene and favors the formation of bicontinuous networks with a nanometer length scale phase separation.

# 5.3.2 Photovoltaic Performance

The performance of each of the two polymers in PCBM-based composite solar cells was independently optimized according to solvent choice, concentration, and composition. It was found that chlorobenzene gave the most efficient devices with **PQT-DD** and chloroform was most effective for **P3DDT-***co***-T**. Figure 5.7 is a comparison of the compositional dependence of power conversion efficiency for the two polymers in devices cast from their respective preferred solvents.



Figure 5.7 Relationship between power conversion efficiency and composition (plotted as polymer weight fraction) in polymer/PCBM solar cells. Closed squares (■) represent P3DDT-*co*-T blends cast from chloroform and open circles (○) represent PQT-DD blends, cast from chlorobenzene. Error bars indicate the 95% confidence interval of the average value. For optimal performance devices were not annealed.

Several important observations can be made about these results within the context of the most efficient P3HT:PCBM devices. First, for all weight ratios investigated, **P3DDT-***co***-T** outperformed **PQT-DD**. Second, the most efficient P3HT:PCBM devices are realized at approximately a 1:1 weight ratio of the two components due to the excellent miscibility of this pair. Here, neither polymer shows optimal performance in the 1:1 weight ratio range, instead the best efficiencies are recorded for a 30:70 blend (polymer:PCBM) with **P3DDT-***co***-T** ( $\eta$ = 1.84%) and with a 25:75 blend with **PQT-DD** ( $\eta$  = 0.54%). Current-voltage curves for the best performing ratios are shown in Figure 5.8. The random and amorphous polymer clearly outperforms its highly ordered analogue by a factor greater than three. It should also be noted that any thermal annealing above 50 °C, resulted in a significant decrease in device performance for both polymers at all weight ratios, and thus all reported results are for unnanealed films.



Figure 5.8 Current-voltage curves for the best performing devices. PQT-DD,  $\eta = 1.84\%$ ,  $J_{sc} = -5.77 \text{ mA/cm}^2$ ,  $V_{oc} = 0.68 \text{ V}$ , and FF = 0.47. For P3DDT-*co*-T,  $\eta = 0.54\%$ ,  $J_{sc} = -2.78 \text{ mA/cm}^2$ ,  $V_{oc} = 0.59 \text{ V}$ , and FF = 033.

# 5.4 CONTROLLING P3HT AND CNT THIN FILM MORPHOLOGY

Relatively little work has focused on the development of conjugated polymers that have a high affinity for nanotubes through supramolecular interactions that not only solubilize the nanotubes, but lead to solution processable two-component blends. One of the best examples of a conjugated polymer with a high affinity for nanotubes is the polymer poly[(*m*-phenylenevinylene)-*co*-(2,5-dioctoxy-*p*-phenylene-vinylene)] (PmPV) which is known to strongly interact with carbon nanotubes via a suspected wrapping mechanism,<sup>32,33</sup> although the absorption of light by this polymer is limited primarily to the ultraviolet. A more attractive route to a conjugated polymer with a high affinity for carbon nanotubes and electronic properties suitable for solar cells, is to focus on analogues of poly(3-hexylthiophene) (P3HT), which has proven to be one of the most successful polymers in fullerene-based OPVs. Pristine poly(3-octylthiophene) (P3OT) has been found to give operational devices in blends with SWCNTs, although power conversion efficiencies of <0.1% have been reported.<sup>18-20</sup> Since the electronic structure of SWCNTs are compatible with accepting electrons from P3OT, such low efficiencies

are perhaps due to the lack of any specific interaction between P3OT and the nanotubes, leading to a less than ideal composite microstructure. Pendant functionalization of polythiophenes is a way to induce functionality capable of strong interaction with carbon nanotubes, as a tool to generate bicontinuous networks of intimately mixed donor and acceptor while retaining the all thiophene backbone.

# 5.4.1 MATERIALS

A clear choice for such pendant functionalization is the polycyclic aromatic hydrocarbon Pyrene, which is known to give strong  $\pi$ - $\pi$  interactions with carbon nanotubes and has been previously exploited as a pendant group in acrylate and styrenic copolymers for the purpose of solubilizing carbon nanotubes.<sup>34,35</sup> Pyrene is also of interest as it has been used as a small molecule dye in poly(3-octylthiophene)-SWCNT solar cells as a sensitizing agent, resulting in significant improvement of device performance even in the absence of any specific interaction between the polymer and the dye functionalized nanotubes.<sup>18</sup> Figure 5.9 depicts the synthetic scheme of a Pyrene functionalized alkylthiophene copolymer, (poly(3-(2-(pryen-1-yl)vinyl))thiophene-*co*-3-hexylthiophene)) (**P3VpyrT**).



Figure 5.9 The synthesis of the Pyrene-functionalized 3-alkylthiophene copolymer (poly(3-(2-(pryen-1-yl)vinyl)thiophene-*co*-3-hexylthiophene)) (P3VpyrT).

Copolymerization of **4** (0.15 mol%) with 2-bromo-3-hexylthiophene (0.85 mol%) using the McCullough method for regioregular polythiophene synthesis<sup>36</sup> led to the random copolymer **P3VpyrT** which contained ~10 mol% of the Pyrene substituted repeat unit as determined by <sup>1</sup>H NMR. The molecular weight was found to be 10,150 g/mol ( $M_n$ ) by SEC in dichlorobenzene (vs. PS standards) and the polymer was found to be soluble in a variety of common organic solvents including chloroform, THF, and dichlorobenzene.

## 5.4.2 Optical and Electronic Properties

The electronic properties of **P3VpyrT** were investigated by UV-visible absorption spectroscopy in spin-cast films (chlorobenzene) as well as by cyclic voltammetry as drop cast

electrode bound films. Figure 5.10 shows the absorption spectra of the polymer relative to P3HT. It can be seen that the absorption onset for **P3VpyrT** occurs at roughly the same wavelength as that for P3HT, suggesting that the two materials have approximately the same band gap. The major difference in the spectra can be seen at short wavelengths, where a strong shoulder centered at 400 nm in **P3VpyrT** corresponds to the contribution of the Pyrene dye, which is in direct conjugation with the polymer backbone. This type of broadened absorption spectra has been previously observed in 3-vinyl substituted polythiophene copolymers.<sup>37</sup> As further proof of concept that this novel polymer possesses suitable characteristics for use in solar cells, the hole mobility of the polymer was also examined using the space charge limited technique.<sup>38</sup> The mobility of a P3HT sample was found to increase from 2.25 x  $10^{-4}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> to 5.33 x  $10^{-4}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> as a consequence of annealing at 150 °C for 30 minutes, while **P3VpyrT** was found to undergo an increase from 5.48 x  $10^{-5}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> to 1.33 x  $10^{-4}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> under the same conditions, indicating similar hole conduction properties to P3HT after thermal treatment.



Figure 5.10 UV-Visible absorption spectra for spin cast thin films of P3VpyrT (solid line) and P3HT (dashed line).

## 5.5 MORPHOLOGY

As a means to evaluate the physical interaction between **P3VpyrT** and carbon nanotubes, spin coated composites were studied by TEM. Efforts to visualize HiPCO SWCNTs in polymer nanotube blends proved to be essentially uninformative due to difficulties in imaging the SWCNTs within the films of **P3VpyrT** and P3HT. In order to establish the role of the covalently bound Pyrene moiety in **P3VpyrT** for enhancing the compatibility of polymer and nanotube relative to P3HT composites, multi-walled nanotubes were utilized as prepared by the water-assisted chemical vapor deposition method originally described by Ijima.<sup>39</sup> The nanotubes were observed by TEM to contain between 1-5 walls with average diameters of 8-10 nm and lengths on the order of tens of microns. While metallic nanotubes are wholly unsutable for use in the active layer of OPVs, these nanotubes were selected in favor of SWCNTs for imaging purposes based on the ease of visualization. Polymer-MWNT composites containing 10 wt% of nanotube relative to the polymer (10 mg/ml) were prepared by blending **P3VpyrT** and P3HT with multi-walled carbon nanotubes, by first dispersing the nanotubes in dichlorobenzene under ultrasonication conditions, followed by addition of the polymer to the solution. The solutions

were then stirred overnight at room temperature. At a concentration of 10mg/mL in polymer, all solutions were opaque. Upon dilution with dichlorobenzene, the solutions based on P3HT and nanotubes remained opaque and somewhat cloudy, while the solutions based on **P3VpyrT** and nanotbues were more transparent and free of noticeable cloudiness.



Figure 5.11 TEM images of (a) P3HT-MWNT film prepared from a blend solution (dichlorobenzene) of 10 mg/ml in P3HT and 1 mg/ml in MWNTs and (b) P3VpyrT -MWNT film prepared from a blend solution (dichlorobenzene) of 10 mg/ml in P3VpyrT and 1 mg/ml in MWNTs. Scale bars are 500 nm.

The solutions (10 mg/ml in polymer) were used directly to spin coat films onto salt plates for liftoff and analysis by TEM. While TEM did allow direct imaging of MWNTs (Figure 5.11) it did not reveal an obvious difference between the two types of composites. Use of optical microscopy (Figure 5.12) revealed the superior ability of **P3VpyrT** to generate homogenous composite thin films in blends with MWNTs. Figure 5.12 illustrates a comparison between the optical micrographs of P3HT-MWNT (Figure 5.12a) composites with P3VpyrT-MWNT (Figure 5.12c) composites using a control film spin coated from a dichlorobenzene that was 10 mg/ml in P3HT with 10 wt% MWNT and 13 wt% N-(1-pyrenyl)maleimide relative to P3HT. This control is relevant as the 13 wt% of added Pyrene dye closely matches the Pyrene content of P3VpyrT as well as the relative amount of the same dye that was reported for use in P3OT-pyrene dye-SWNT solar cells.<sup>18</sup> From these images, it is clear that P3HT-MWNT and dye doped P3HT-MWNT composites form highly non-uniform films with regions of locally high MWNT concentration dispersed throughout the films. In contrast, films prepared from P3VpyrT-MWNT blend solutions under the same conditions are significantly more uniform than the P3HT based films and suggests that **P3VpyrT** is interacting more strongly as a dispersing agent with the MWNTs even at this high concentration of nanotubes.



Figure 5.12 Optical microscope images recorded at 20X magnification for (a) P3HT-MWNT (10 wt%), (b) P3HTdye (13 wt%)–MWNT 10 wt%, (c) P3VpyrT-MWNT composites cast from dichlorobenzene solution at a concentration of 10 mg/ml in polymer. Scale bars are 50 μm.

# **5.7 CONCLUSION**

The work presented here points to several key concepts about polythiophene based bulk heterojunciton solar cells, which suggest a more general design principle for conjugated polymers intended for use in composite solar cells with varying types of n-type materials. First, the electronic band structure is primarily influenced by the chemical nature of the polymer backbone, rather than the solubilizing groups utilized to make it processable. Changes to the absorption spectra can be realized by the use of conjugated side chains, but it has yet to be determined how efficiently excitons generated on these side chains will contribute to the photocurrent in an OPV.

However, this chapter demonstrates how the choice of solubilizing group and the attachment strategy are critical for determining the ability of the polymer to not only order for effective

charge transport, but to effectively mix with the fullerene acceptor and present the possibility of generating a suitable bicontinuous morphology. Here it is illustrated that for two polythiophenes, which are compositionally and electronically equivalent and differ only in the sequence distribution of the alkyl solubilizing groups, the polymer with the random primary structure is superior to the polymer with the precisely defined primary structure, in the context of solar cell performance. It is suspected that the more than threefold increase in solar cell efficiency for **P3DDT-co-T** relative to **PQT-DD** is based on ability for the formation of bicontinuous structure in the random copolymers, brought about by the decreased tendency for crystallization. As a general conclusion toward the design and optimization of new polymers for photovoltaics, the comparison of P3HT, **P3DDT-co-T**, and **PQT-DD** illustrates an important point. While all three polymers having very similar electronic structures and SCLC mobilities, the difference in peak achieved solar cell efficiencies varies over an entire order of magnitude, influenced by the placement and choice of solubilizing group and how such choices effect polymer crystallinity and miscibility with PCBM.

This chapter also shows how covalent attachment of interactive side groups can lead to improved miscibility with CNTs. Utilizing polymers with functional handles specifically targeted for interaction with n-type materials is a strategy that has shown great promise in organic-inorganic hybrid solar cells. Therefore, these results suggest that **P3VpyrT** is a potentially useful electroactive polymer for the realization of polymer-NT composite solar cells. Furthermore, this chapter underlines how synthetic optimization of new conjugated polymers goes beyond light absorption, energy levels, and mobility, but ultimately must lie in a global structural optimization aimed at balancing electronic performance with material miscibility.

## **5.8 EXPERIMENTAL**

Cyclic voltammograms were collected using a Solartron 1285 potentiostat under the control of CorrWare II software. A standard three electrode cell based on a Pt button working electrode, a silver wire pseudo reference electrode (calibrated vs.  $Fc/Fc^+$ ), and a Pt wire counter electrode was purged with nitrogen and maintained under a nitrogen atmosphere during all measurements. Acetonitrile was distilled over CaH<sub>2</sub> prior to use and tetrabutyl ammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. Polymer films were drop cast onto a Pt button working electrode from a 1% (w/w) chloroform solution and dried under nitrogen prior to measurement.

UV-Visible absorption spectra were obtained using a Carey 50 Conc UV-Visible spectrophotometer. For thin film measurements polymers were spin coated onto untreated glass slides from chlorobenzene solution (10 mg/ml). A model P6700 Spincoater was used to spin coat the films at 1500 rpm for 60 s.

Polymer mobility was measured using a diode configuration of ITO/PEDOT:PSS/Polymer/Al in the space charge limited current regime. At sufficient potential the conduction of charges in the device can be described by Equation 1.7, where  $\varepsilon_0$  is the permittivity of space,  $\varepsilon_R$  is the dielectric of the polymer (assumed to be 3),  $\mu$  is the mobility of the majority charge carriers, *V* is

the potential across the device ( $V = V_{applied} - V_{bi} - V_r$ ), and *L* is the polymer layer thickness. The series and contact resistance of the device (13-21  $\Omega$ ) was measured using a blank (ITO/PEDOT/Al) and the voltage drop due to this resistance ( $V_r$ ) was subtracted from the applied voltage. The built-in voltage ( $V_{bi}$ ), which is based on the relative work function difference of the two electrodes, was also subtracted from the applied voltage.

For photovoltaic devices, indium-doped tin oxide (ITO)-coated glass substrates were obtained from Thin Film Devices, Inc. The 150 nm sputtered ITO pattern had a resistivity of 10  $\Omega/\Box$ . The substrates were subjected to ultrasonication for 20 min in acetone, and then 2% Helmanex soap in water for 20 min, followed by extensive rinsing with deionized water and ultrasonication in deionized water and then 2-propanol. The substrates were then dried under a stream of air. Then a filtered (1 µm glass) dispersion of PEDOT:PSS in water (Baytron-PH500) was applied immediately afterward by spin coating at 4000 RPM for 60 s, affording a 50 nm layer after baking for 10 mins at 140 °C. All procedures after this point were performed in an inertatmosphere glovebox. Solutions of Polymer:PCBM were prepared in chlorobenzene or chloroform and were stirred at ~  $70^{\circ}$ C for 24 hrs to ensure complete dissolution. Immediately prior to deposition, the solutions were passed through 0.45 µm PTFE syringe filters. The blend solution was applied to the substrate and spun at 1500 RPM for 60 s. The substrates were then placed in a resistive-heating evaporation chamber and held under vacuum  $(10^{-7} \text{ torr})$  for 8 h before evaporating 100 nm of Al through a shadow mask at a rate of 0.1-0.3 nm/s while rotating the substrates at approximately 1 Hz to ensure even electrode deposition. The configuration of the shadow mask afforded eight independent devices on each substrate. The mechanical removal of part of the organic layer allowed contact with the ITO, and adding conductive paste to the removed area to ensure electrical contact completed the device. Annealing was performed after Al deposition on a temperature-controlled hotplate. Devices were left to cool to RT before testing. Testing of the devices was performed under an argon atmosphere with an oriel xenon arc lamp with an AM 1.5G solar filter. I-V behavior was measured with a Keithly 236 SMU. Eight devices were averaged for each condition.

Transmission electron microscope images were obtained using a FEI TECNAI  $G^2$  with a 200 kV accelerating voltage. Samples were prepared by spin-casting films from either chloroform or chlorobenzene as used for device measurement onto freshly cleaved NaCl single crystal substrates at 1500 rpm for 60s. The films were floated onto water and placed onto a 600 mesh copper TEM grid (Electron Microscopy Science, Inc.).

Optical Microscope images were captured with Qcapture software using a Nikon TE200 Microscope with a 5 MP camera. Films were spin coated onto glass microscope cover slides from solutions that were 10 mg/ml in polymer.

#### REFERENCES

- (1) Günes, S.; Neugebauer, H.; Sariciftci, N. S. Chemical Reviews 2007, 107, 1324-1338.
- (2) Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. Advanced Functional Materials 2005, 15, 1617-1622.

- (3) Kim, K.; Liu, J.; Namboothiry, M. A. G.; Carroll, D. L. Appl. Phys. Lett. 2007, 90, 163511.
- (4) Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat Mater* **2005**, *4*, 864-868.
- (5) Mihailetchi, V. D.; Xie, H.; de Boer, B.; Popescu, L. M.; Hummelen, J. C.; Blom, P. W. M.; Koster, L. J. A. *Appl. Phys. Lett.* **2006**, *89*, 012107.
- (6) Sivula, K.; Luscombe, C. K.; Thompson, B. C.; Fréchet, J. M. J. *Journal of the American Chemical Society* **2006**, *128*, 13988-13989.
- Kim, Y.; Cook, S.; Tuladhar, S. M.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C.; Giles, M.; McCulloch, I.; Ha, C.; Ree, M. *Nat Mater* 2006, *5*, 197-203.
- (8) Schilinsky, P.; Asawapirom, U.; Scherf, U.; Biele, M.; Brabec, C. J. *Chemistry of Materials* **2005**, *17*, 2175-2180.
- (9) Hiorns, R. C.; de Bettignies, R.; Leroy, J.; Bailly, S.; Firon, M.; Sentein, C.; Khoukh, A.; Preud'homme, H.; Dagron-Lartigau, C. Advanced Functional Materials 2006, 16, 2263-2273.
- (10) Nguyen, L. H.; Hoppe, H.; Erb, T.; Günes, S.; Gobsch, G.; Sariciftci, N. Advanced Functional Materials **2007**, *17*, 1071-1078.
- (11) Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. Advanced Functional Materials 2005, 15, 1617-1622.
- (12) Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat Mater* **2005**, *4*, 864-868.
- (13) Shaheen, S. E.; Brabec, C. J.; Sariciftci, N. S.; Padinger, F.; Fromherz, T.; Hummelen, J. C. Appl. Phys. Lett. 2001, 78, 841.
- (14) Sivula, K.; Ball, Z.; Watanabe, N.; Fréchet, J. Advanced Materials 2006, 18, 206-210.
- (15) Beek, W. J. E.; Wienk, M. M.; Janssen, R. A. J. J. Mater. Chem. 2005, 15, 2985-2988.
- (16) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. Science 2002, 295, 2425-2427.
- (17) Koetse, M. M.; Sweelssen, J.; Hoekerd, K. T.; Schoo, H. F. M.; Veenstra, S. C.; Kroon, J. M.; Yang, X.; Loos, J. Appl. Phys. Lett. 2006, 88, 083504.
- (18) Bhattacharyya, S.; Kymakis, E.; Amaratunga, G. A. J. *Chemistry of Materials* **2004**, *16*, 4819-4823.
- (19) Kymakis, E.; Alexandrou, I.; Amaratunga, G. A. J. J. Appl. Phys. 2003, 93, 1764.
- (20) Kymakis, E.; Amaratunga, G. A. J. Appl. Phys. Lett. 2002, 80, 112.
- (21) White, C. T.; Mintmire, J. W. The Journal of Physical Chemistry B 2005, 109, 52-65.
- (22) Guldi, D. M.; Rahman, G. M. A.; Zerbetto, F.; Prato, M. Accounts of Chemical Research 2005, 38, 871-878.
- (23) Grossiord, N.; Loos, J.; Regev, O.; Koning, C. E. Chemistry of Materials 2006, 18, 1089-1099.
- (24) Coleman, J. N.; Khan, U.; Gun'ko, Y. Advanced Materials 2006, 18, 689-706.
- (25) Star, A.; Liu, Y.; Grant, K.; Ridvan, L.; Stoddart, J. F.; Steuerman, D. W.; Diehl, M. R.; Boukai, A.; Heath, J. R. *Macromolecules* **2003**, *36*, 553-560.
- (26) Ong, B. S.; Wu, Y.; Liu, P.; Gardner, S. *Journal of the American Chemical Society* **2004**, *126*, 3378-3379.
- (27) Wu, Y.; Liu, P.; Ong, B. S.; Srikumar, T.; Zhao, N.; Botton, G.; Zhu, S. Appl. Phys. Lett. 2005, 86, 142102.
- (28) McCulloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; MacDonald, I.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Wagner, R.; Zhang, W.; Chabinyc, M. L.; Kline, R. J.; McGehee, M. D.; Toney, M. F. *Nat Mater* **2006**, *5*, 328-333.
- (29) Liu, J.; McCullough, R. D. Macromolecules 2002, 35, 9882-9889.
- (30) Ong, B. S.; Wu, Y.; Liu, P.; Gardner, S. Advanced Materials 2005, 17, 1141-1144.
- (31) Goh, C.; Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Fréchet, J. M. J. Appl. Phys. Lett. 2005, 86, 122110.
- (32) Lei, S.; Wan, L.; Wang, C.; Bai, C. Advanced Materials 2004, 16, 828-831.
- (33) Star, A.; Stoddart, J. F.; Steuerman, D.; Diehl, M.; Boukai, A.; Wong, E. W.; Yang, X.; Chung, S.; Choi, H.; Heath, J. R. *Angewandte Chemie International Edition* **2001**, *40*, 1721-1725.
- (34) Bahun, G. J.; Wang, C.; Adronov, A. Journal of Polymer Science Part A: Polymer Chemistry 2006, 44, 1941-1951.
- (35) Lou, X.; Daussin, R.; Cuenot, S.; Duwez, A.; Pagnoulle, C.; Detrembleur, C.; Bailly, C.; Jerome, R. *Chemistry of Materials* **2004**, *16*, 4005-4011.
- (36) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *The Journal of Organic Chemistry* **1993**, *58*, 904-912.
- (37) Hou, J.; Huo, L.; He, C.; Yang, C.; Li, Y. Macromolecules 2006, 39, 594-603.
- (38) Goh, C.; Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Fréchet, J. M. J. Appl. Phys. Lett. 2005, 86, 122110.
- (39) Hata, K.; Futaba, D. N.; Mizuno, K.; Namai, T.; Yumura, M.; Iijima, S. *Science* **2004**, *306*, 1362-1364.

# CHAPTER 6: DESIGN OF SEMICONDUCTING POLYMER NANOPARTICLES FOR Electronic Thin Film Devices

### ABSTRACT

The polymer-based bulk heterojunction is an efficient photovoltaic architecture for many donor-acceptor pairs, but only when the formation of continuous, interpenetrating, nanoscale morphologies can be obtained through processing parameters such as thermal annealing or solvent evaporation rates. The ability to independently control the nanoscale size of the donor and acceptor domains before device fabrication would provide a universal route to proper bulk heterojunction fabrication with any donor-acceptor pair. A new method to form surfactant-free size controlled polymer nanoparticles is demonstrated. By controlling the physical parameters of the initial polymer, both the average particle size and degree of crystallinity can be independently tuned. The internal structure and electronic performance of a variety of semiconducting polymer nanoparticles is presented.

# **6.1 INTRODUCTION**

Solution-processed,  $\pi$ -conjugated polymers and small molecules have garnered significant interest as alternative semiconductors, primarily for lightweight and inexpensive thin film electronic devices.<sup>1,2</sup> The thin film device performance can be significantly influenced by both the molecular and nanoscale polymer morphology, since intra- and intermolecular  $\pi$ -interactions control critical semiconductor parameters such as the band gap, charge generation and electron transport. In organic thin film transistors, polymer chain orientation and crystal packing is necessary for effective charge transport. For efficient organic light emitting diodes or photovoltaic cells, a nanoscale mixing between donor and acceptor molecules coupled with distinct conduction pathways must be formed. However, obtaining a desired nanoscale packing within a polymer thin film often requires extensive optimization procedures such as variations in solvent choice,<sup>3,4</sup> small molecule additives,<sup>5,6</sup> deposition technique<sup>7,8</sup> and post-fabrication annealing<sup>9</sup>. This process becomes even more involved, because the polymer primary structure (i.e. molecular weight, polydispersity index (PDI) and regioregularity (RR)) can also significantly alter the electronic performance of the field effect transistors or organic photovoltaics.<sup>10-14</sup> This complexity is particularly problematic for the development and implementation of new organic semiconductors, where improvements in the optical or electronic features of the polymer may be obtained, but device performance remains limited due to difficulties in generating appropriate morphologies.

Since most organic electronic devices are  $\leq 200$  nm thick and because of the localized excitonic nature of conjugated organics,<sup>15</sup> it would be advantageous to develop a general solution-phase strategy to form discrete nanoscale domains with controlled size and packing structure, prior to forming the associated thin films. A particularly attractive approach is the development of electronically-active organic nanoparticles with controlled diameters between 5 – 100 nm that are preformed from polymer semiconductors. The use of nanoparticles, whose size and solid state packing can be controlled and characterized in solution, would allow for the simple fabrication of favorable morphologies regardless of polymer choice and with less dependence on extensive optimization procedures.

Recently, there has been increasing interest in synthesizing semiconducting polymer nanoparticles for use in organic photovoltaics, light emitting diodes and field effect transistors.<sup>16-<sup>19</sup> In order to fully realize the inherent potential of these new materials, it is necessary to both understand and control the formation parameters that influence domain size, orientation, and packing structure in the resulting nanoparticle as these may be vastly different from the parameters used for thin films processed fromsolution. The surfactant-free, size-controlled synthesis and characterization of discrete, semi-crystalline polymer nanoparticles is described below. By controlling the physical structure (i.e. molecular weight distribution or regioregularity) and solution concentration of the polymers, a correlation of these parameters with molecular packing, nanoparticle morphology, and corresponding performance in organic field effect transistors (OFETs) can be achieved.</sup>

# **6.2 PROBING CONJUGATED POLYMER NANOPARTICLES**

# 6.2.1 MATERIALS

Commercial P3HT was obtained from Rieke Metals, Inc. and used as received. All other P3HT samples were synthesized, purified, and characterized according to published procedures.<sup>14,20</sup> All other polymers and materials were obtained from Aldrich and used as received unless otherwise noted. All sample preparation including nanoparticle synthesis was routinely conducted in a glovebox under nitrogen atmosphere at room temperature. All glassware was rinsed with Nanopure<sup>TM</sup> water (18.2 MΩ) and dried under a stream of nitrogen prior to use.

Polymer nanoparticles were synthesized using modified nanoprecipitation methodology. In general, nanoprecipitation methods require two fundamental components: dilute polymer solutions and miscibility of solvents.<sup>21</sup> Dilute polymer solutions are necessary to ensure that the solvent displacement interactions dominate nanoparticle formation, and that there are no predefined polymer aggregates when the solution is introduced into the polymer non-solvent. Solvent miscibilities are crucial in order to obtain a homogeneous colloid, as opposed to an emulsion or phase-separated state upon introduction of the polymer solution into the polymer non-solvent. Although alternative approaches to nanoprecipitation are possible, a "dropping" method was chosen where the polymeric solution is introduced dropwise into a stirring non-solvent phase. This approach avoids the time and product cost associated with other nanoprecipitation techniques such as dialysis, and also has been empirically shown to produce smaller diameter nanoparticles.<sup>22</sup>

In a typical experiment, 5 mg of a given polymer was dissolved in 1 mL of chloroform (CHCl<sub>3</sub>, anhydrous, 99%) and stirred overnight at room temperature. After complete dissolution, aliquots of this solution were diluted with CHCl<sub>3</sub> to produce 0.5 mg/mL and 0.05 mg/mL concentrations; all three concentrations are then used for synthesis. At the same time, ethanol (EtOH, 200 proof, molecular biology grade) was bubbled with nitrogen for 30 minutes and immediately transferred into a glovebox. Next, 500  $\mu$ L of the polymer solution is loaded into a syringe, and subsequently introduced dropwise (rate ~ 1 drop/s) into 5 mL of the stirring, degassed EtOH. Nanoparticle formation begins at the introduction of the first droplet, and is limited by the amount of polymer solution introduced.

This approach produced stable, surfactant-free colloidal suspensions of P3HT nanoparticles of 0.5, 0.05, and 0.005 wt%, which could be used without need for further purification. Particle formation was carried out in a nitrogen glovebox to avoid potential photo-oxidation of the P3HT. The resulting PNPs are stable for more than two months when handled in or out of a glovebox with minimal agitation. However, because the nanoparticle solution contains no surfactants or stabilizing ligands there is little resistance to aggregation from either surfactant screening or charge-charge repulsion from a ligand shell. Therefore, care must be taken to prevent the particles from coalescing and eventually precipitating out of solution.

## 6.2.2 PNP SIZE CONTROL

Controlling the size domains of conjugated polymers in solution before thin film deposition potentially allows for a far finer control over the donor and acceptor domains sizes and device architecture dimensions. The size and uniformity of the PNPs were analyzed using transmission electron microscopy (TEM) and dynamic light scattering (DLS). Figure 6.1, shows a bar graph relating the average diameter of the PNPs. Comparing the polymer samples shows that the resulting nanoparticle diameter is largely influenced by the initial polymer concentration in chloroform, where lowering the concentration produces smaller average nanoparticle sizes. For semi-crystalline P3HT with molecular weights between 20-60 kDa, the difference in the P3HT polymer structure seems to have only a minor influence on the PNP size with the more regular polythiophene having a slightly shorter diameter. 0.5 wt% PNPs formed from the three other P3HTs also show almost identical particle sizes to the largest particles for Rieke P3HT and GRIM-P3HT. P3HT samples of 15 kDa and 100 kDa show much larger particles on average at all concentrations. Particles formed from PPV based materials, poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and poly[5-(2-ethylhexyloxy)-2-methoxycyanoterephthalylidene] (CN-PPV), follow the same concentration dependence as P3HT but form slightly smaller particles on average most likely due to their completely amorphous packing structure. P3HT PNPs were also used to encapsulate other organic molecules including PCBM and metallated phthalocyanines.



Figure 6.1 Bar graph showing the average size distribution of different polymer nanoparticles all made utilizing the same procedure, but with different starting concentrations.

### 6.2.3 CHARACTERIZATION OF P3HT PNPs

Nanoparticles were formed from three concentrations of the commercial P3HT (R1, R2, R3 formed from initial 0.5 wt%, 0.05 wt%, 0.005 wt% solutions, respectively), and compared to particles formed from 35kDa GRIM-synthesized polymer (G1, G2, G3 formed from 0.5 wt%, 0.05 wt%, 0.005 wt% solutions, respectively). The polymers were chosen because they have the most dissimilar primary structure. The Rieke polymer has the largest PDI and a low RR, while the GRIM-synthesized polymer has an extremely narrow PDI and RR greater than the detection limit of the NMR. In thin films spun from solution, P3HT with a narrow PDI and higher RR has a stronger driving force for crystallization and generally leads to larger more regular crystalline regions.

Transmission electron microscopy confirms the highly discrete nature of the PNPs in solution, and shows no evidence of solvated polymer chains (Figure 6.2). However, the solvent drying forces and the higher concentration of the large particles do lead to some population of aggregated PNPs during the sample preparation. Interestingly, the TEMs show that while R1 and G1 particles do not differ significantly in overall size they do exhibit different average colloidal morphologies. The samples of R–PNPs are composed of more spherical nanoparticles, while S-PNPs consist of more anisotropic shapes. The preferred packing structure of highly regular P3HT in the solid state is anisotropic crystalline nanofibrils with the  $\pi$ - $\pi$  stacking direction along the long axis of the crystal.<sup>23</sup> Thus, the differences observed in PNP shape are likely due to the differences in the polymer chain packing within the various nanoparticles as a result of the polymer structure.



Figure 6.2 TEM images of (a) R1-PNPs,  $d = 70 \pm 13$  nm (b) G1-PNPs,  $d = 55 \pm 10$  nm, (c) R3-PNPs,  $d = 30 \pm 10$  nm, and (d) G3-PNPs,  $d = 15 \pm 4$  nm cast directly from as-synthesized solution. Images show the influence of polymer sample homogeneity on the morphology of the resulting nanoparticles. Figure insets are individual nanoparticles, scale bar = 20 nm.

Figure 6.3 shows spectra of R1-3 and G1-3 PNP solutions compared to both P3HTs fully dissolved in chloroform. All PNPs formed are significantly red-shifted compared to the dissolved polymer. This evidence is consistent with the formation of unsolvated P3HT chains which exhibit a longer effective conjugation length.<sup>24,25</sup> The large red shift and pronounced phonon shouldering of G1-S3 indicates highly ordered polymer chains as well as an extended intermolecular  $\pi$ - $\pi$  stacking interaction.<sup>26</sup> The 0-0 and 0-1 vibrational peaks in R1-R3 are blueshifted and less resolved than those obtained from the S series of PNPs. These blue-shifted absorption features, which are due to the intrachain uniformity in the solid-state, indicate a reduction in the average conjugation length resulting from shorter or less planar polymer backbones. This could be a result of an overall decrease in the size of the crystalline region within the PNP or it could result from a higher density of crystal defects within the PNP due to steric twisting caused by more head to head couplings. The shorter conjugation length is also consistent with the more rounded colloidal structure observed for these particles by TEM and could be a result of either the larger PDI or smaller RR of the Rieke polymer as compared to the GRIM-synthesized sample. The reduced shoulder at larger wavelengths also suggests that the degree of intermolecular  $\pi$ - $\pi$  stacking is lower in the R-PNPs. This difference in crystallinity between R and G particles is consistent across all three of the size regimes tested with the G-PNPs always showing a more pronounced red-shift and shouldering than the R-PNPs.



**Figure 6.3** UV-vis spectra comparing the optical features of colloidal suspensions composed of nanoparticles made from synthesized (35 kDa) P3HT (bottom) and commercial P3HT (top) in ethanol. The black lines are spectra of the respective P3HT samples solubilized in CHCl<sub>3</sub>.

PNPs from polymer samples exhibiting very well-defined regioregularities and similar PDIs were also investigated., As the regioregularity of the starting polymer decreases the spectra for the resulting PNPs systematically blue-shifts and the shoulder at ~605 nm decreases in intensity (Figure 6.4). This highlights that while the RR is does not play a significant role in controlling the resulting size of the PNPs it directly influences the PNP crystallinity.



Figure 6.4 UV-Vis spectra of 5 different RR-P3HT PNPs. The blue shift in optical features and intensity is directly related to the reduction in polymer RR.

While the nanoparticle solutions from all of the polymers show size variation and packing differences which directly correspond to initial concentration and RR respectively, the PNP size and internal morphology shows no correlation with the PDI of the starting polymers. In addition, during PNP formation at the lowest initial polymer concentration (0.05 mg mL<sup>-1</sup>) the average distance between polymer chains is ~130 nm and shows no signs of intermolecular interactions as confirmed by the solution phase UV-Vis, which has no shouldering beyond 550 nm. Thus, during the synthesis at the lowest concentration the resulting PNPs are probably comprised of only a few polymer chains with most of them being made up of a single polymer (see Supporting Information for full calculation). If PDI influences the particle formation then there should be a marked difference between the optical features of the largest PNPs and the smallest. Examination of all polymer batches shows identical spectra suggesting no difference in structure, therefore confirming the lack of PNP dependence on polymer PDI.

Because the optical properties of P3HT arise from its crystalline structure, the UV-Vis spectra suggest that the different PNPs may have different internal structures. Two-dimensional grazing incidence x-ray diffraction spectra were taken of both R and S PNPs and compared to thin films of P3HT spun from chloroform. Line scans taken parallel to the substrate plane in Figure 6.5b show that both PNP samples contain crystalline regions with identical lattice spacings and , that these spacings are the same as the packing structure observed for thin films of P3HT (lattice parameters: a = 16.6 Å, b = 3.8 Å,). These lattice values are comparable to those obtained in previous works.<sup>27-29</sup> The one dimensional line scans indicate that while the overall packing may be different the crystal lattice of P3HT is unchanged even after being confined inside the nanoparticle.



Figure 6.5 GIXRD scans of a) R1-PNPs, c) G1-PNPs, and corresponding d) P3HT thin film. Each sample produces the same packing geometry as shown in the b) 1D line scans taken parallel to the substrate surface

The 2D-XRD spectra depict a difference in the crystalline orientation for the three samples. The thin film spun from chloroform (Figure 6.5d) exhibits a highly anisotropic crystalline orientation with the 100 direction favoring a perpendicular orientation to the substrate. This orientation is the most commonly observed orientation for RR-P3HT on silicon surfaces due to energetic interactions between the polymer chains and the surface chemistry of the substrate.<sup>27,30</sup> Counter to the substrate driven orientation for normal solution processed films, thin films formed from the PNPs show a slightly more isotropic orientation for the G1 particles and an almost completely isotropic orientation for the R1 particles (Figure 6.5c and Figure 6.5a respectively). Thse results match the PNP structure as seen by the TEMs. A film of irregular shaped particles whose crystal lattice has an anisotropic orientation as is the case with G1-PNP should give a more oriented two dimensional thin film when compared with a film comprised of spherical nanoparticles (R1 PNPs) which should exhibit no preferential orientation of the crystal lattice relative to the substrate. Thus, for the PNPs the orientation of the polymer crystal lattice relative to the substrate is likely a product of their colloidal nature, and has little input from substrate surface chemistry as is typically seen for P3HT spun from solution.

# 6.2.4 FIELD EFFECT TRANSISTOR PERFORMANCE OF P3HT PNPs

The charge carrier mobility in traditional solution processed P3HT OFETs is highly dependent on the solid state polymer packing and orientation as well as on the molecular weight and regioregularity of the polymer and its interaction with the dielectric surface chemistry.<sup>10,28,31,32</sup> To further investigate the structure and performance of PNPs for electronic device applications, bottom contact organic field effect transistors were fabricated and tested from R1 and G1 PNP films similar to those in the XRD films. Octadecyltrichlorosilane-functionalized transistors were spin-coated with P3HT either fully dissolved in chloroform or as PNPs from ethanol. A comparison of the transistor performance, tested inside an argon glovebox, can be seen in Figure 6.6 along with SEM pictures of representative channels filled by either PNPs or P3HT thin films. Both PNP films exhibited hole mobilities on the order of  $10^{-3}$  cm<sup>2</sup>/Vs ( $1.2 \times 10^{-3}$  cm<sup>2</sup>/Vs and  $1.4 \times 10^{-3}$  cm<sup>2</sup>/Vs, respectively). The thin film of Rieke P3HT gave  $\mu_h = 1.2 \times 10^{-3}$  while the more crystalline P3HT gave  $\mu_h = 1.6 \times 10^{-2}$  cm<sup>2</sup>/Vs. These values for the thin film devices are comparable to previously reported OFETs, which were fabricated in a similar manner with similar polymers.<sup>3</sup> The high mobilities obtained from the PNPs demonstrate that the electronic character of the semiconducting polymer is not degraded during nanoparticle formation or device fabrication and that there is sufficient electronic communication between particles after deposition without any need for any post-deposition annealing processes. The similarity in performance between both PNPs and the Rieke thin film also supports the use of PNPs as electronically viable alternatives to traditional thin film fabrication procedures.



**Figure 6.6** Field effect transistor scans (A, B) G1-PNP (D,E) S-P3HT thin film. (C) SEM of FET channel with G1-PNPs spun from ethanol and (F) S-P3HT thin film spun from CHCl<sub>3</sub>.

Interestingly, while our crystallographic characterization suggests that the PNPs made from the more regioregular polymer contain crystalline domains with fewer defects the OFET performance is similar to that of the less regioregular PNPs. This similarity is attributed to both a similar overall percent crystallinity as well as a lack of control over crystalline domain orientation in the FET channel. In the case of the preformed nanoparticles, it is expected that there is little influence of the substrate functionalization on crystal directionality as is typically observed when P3HT thin films are formed on alkyl functionalized SiO<sub>2</sub>. Since it is also unlikely that the forces involved during spin casting will result in a consistent in-plane nanocrystal orientation, and because charge conduction in an OFET is a highly directional process, the overall channel mobility is similar between the two particle types even though the crystalline

nature of the nanoparticles is different. These results demonstrate that the final device performance of the PNPs is less dependent upon the polymer structure, surface-polymer, or deposition conditions than is typically seen for P3HT field effect transistors.

### 6.4 MOLECULE ENCAPSULATION IN SEMICONDUCTING PNPs

The incorporation of electronically active small molecules into a conjugated polymer film allows for the combination or enhancement of optical or electronic properties compared to the native film. However, small molecules are often difficult to evenly disperse in semicrystalline polymer films during solution processing.<sup>14</sup> A unique and potentially useful route is the use of PNPs that have had the small molecule encapsulated during the nanoparticle formation process.

### 6.4.1 P3HT:PCBM NANOPARTICLES

P3HT blends with the small molecule fullerene derivative PCBM is the highest studied OPV system to date. The combination of strong light absorption from the polymer and high charge carrier mobilities in both materials can result in PCE of between 4-5%.<sup>6,9,33</sup> Control of the donor-acceptor morphology is the key requirement for achieving high photon-to-electron conversion efficiencies with the P3HT:PCBM system. Formation of the appropriate domains prior to film deposition would allow for a simplification of the solar cell processing and could lead to cheaper more uniform thin films.

P3HT:PCBM NPs were synthesized in a similar manner to the P3HT PNPs. A solution of 5 mg P3HT and 5 mg PCBM in 1 mL of chloroform was added drop wise to stirring ethanol generating a stable colloidal suspension. Composite NPs made in this way are about 50% larger than pure P3HT PNPs (see Figure 6.1). Figure 6.7 shows a close up TEM of a P3HT:PCBM nanoparticle. While also spherical the internal structure of the P3HT:PCBM NP appears to be different from that of the simple P3HT PNPs (Figure 6.2a). The distinct contrast difference between center and the edges is usually representative of a core-shell nanoparticle where the center of the particle has a different electron scattering cross-section. This is most likely due to a higher concentration of PCBM at the center of the particle. Further experiments will be necessary to definitively prove the internal structure of these biphasic NPs.



Figure 6.7 Transmission electron microscope image of a P3HT:PCBM core-shell nanoparticle formed using the same nanoprecipitation method.

### **6.5 CONCLUSION**

The control of nanoscale materials will provide a new generation of solutions for the technological challenges of today. These results demonstrate the surfactant-free formation and characterization of discrete, semi-crystalline all-polymer nanoparticles for use in thin film electronics. By controlling the basic physical properties of the polymer and varying initial polymer concentrations both the size and crystallinity of the resulting PNPs can be modulated. OFETs using P3HT PNPs produce good semiconducting devices with hole mobilities on the order of  $10^{-3}$  cm<sup>2</sup>/Vs. This method of forming PNPs is uniquely suited for the introduction of solution-processable, well-characterized nanoscale crystalline domains into organic electronic devices irrespective of many other fabrication conditions.

#### **6.6 EXPERIMENTAL**

Organic field effect transistors (OFETs) were fabricated using n-doped silicon wafers as the gate, and thermally oxidizing the surface to form a 1000 Å silicon dioxide dielectric layer. Substrates were cleaned successively in acetone and isopropanol while sonicating, and dried under nitrogen. After UV/ozone treatment for 15 minutes, each substrate was introduced to a solution of octadecyltrichlorosilane (OTS, 90%, 40 mM in hexadecane) for 2 hours. The substrates were then briefly sonicated in toluene (< 30 sec.), further dip-rinsed in toluene and dried under a stream of nitrogen. Functionalized substrates were transferred to a nitrogen-filled glovebox, and the semiconducting material was deposited on the functionalized substrates by spin-coating either polymer or nanoparticle solutions. The channels tested with this preparation had widths from 200-400 µm and lengths of 10 µm. Current–voltage (I-V) characteristics were measured in a nitrogen glove box using a Keithley 236 SMU at room temperature.

Transmission electron microscopy (TEM) was carried out using a FEI Technai G2 S-Twin electron microscope operating at 200 kV. Samples were prepared by dropcasting 10  $\mu$ L of assynthesized nanoparticle solution onto a 400 mesh Cu TEM grid that has been coated with an ultrathin carbon film on holey carbon support film (Ted Pella, Inc.). Scanning electron microscopy (SEM) was performed using a Zeiss Gemini Ultra-55 Analytical Scanning Electron Microscope operating at 5 kV accelerating voltage and an average working distance of 4.2 mm. Samples were prepared on either HOPG (Ted Pella, Inc.) or taken of field effect transistors channels directly on highly doped silicon. Dynamic light scattering (DLS) was performed using a Zetasizer Nano ZS (Malvern Instruments). Nanoparticle samples were measured at an optical density of 0.1 in EtOH, and measured in a 1 cm pathlength quartz cuvette. UV-vis-NIR spectra of nanoparticle colloids were taken using a Shimadzu 3600 spectrophotometer that was baselined to anhydrous ethanol. Samples were measured in 1 cm pathlength, quartz cuvettes. Grazing incidence x-ray scattering (GIXS) spectra were obtained at the Stanford Synchotron Radiation Laboratory on beamline 11-3. The sample was irradiated at a fixed incident angle (angle = 0.12°) and the GIXS patterns are recorded with a 2-D image detector (MAR345 image plate detector).

The X-ray energy was 12.72 keV ( $\lambda = 0.975$  Å). Samples were prepared by spin-casting multiple times the as-synthesized nanoparticles onto silicon substrates coated with a native oxide layer.

# REFERENCES

- (1) Thompson, B. C.; Fréchet, J. Angewandte Chemie International Edition 2008, 47, 58-77.
- (2) Horowitz, G. Advanced Materials 1998, 10, 365-377.
- (3) Chang, J.; Sun, B.; Breiby, D. W.; Nielsen, M. M.; Solling, T. I.; Giles, M.; McCulloch, I.; Sirringhaus, H. *Chemistry of Materials* **2004**, *16*, 4772-4776.
- (4) Surin, M.; Leclère, P.; Lazzaroni, R.; Yuen, J. D.; Wang, G.; Moses, D.; Heeger, A. J.; Cho, S.; Lee, K. J. Appl. Phys. **2006**, 100, 033712.
- (5) Lee, J. K.; Ma, W. L.; Brabec, C. J.; Yuen, J.; Moon, J. S.; Kim, J. Y.; Lee, K.; Bazan, G. C.; Heeger, A. J. *Journal of the American Chemical Society* **2008**, *130*, 3619-3623.
- (6) Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat Mater* **2005**, *4*, 864-868.
- (7) Wang, G.; Swensen, J.; Moses, D.; Heeger, A. J. J. Appl. Phys. 2003, 93, 6137.
- (8) Liu, S.; Wang, W. M.; Briseno, A. L.; Mannsfeld, S. C. B.; Bao, Z. Advanced Materials 2009, 21, 1217-1232.
- (9) Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. *Advanced Functional Materials* **2005**, *15*, 1617-1622.
- (10) Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Liu, J.; Frechet, J. M. J.; Toney, M. F. *Macromolecules* **2005**, *38*, 3312-3319.
- (11) Zen, A.; Pflaum, J.; Hirschmann, S.; Zhuang, W.; Jaiser, F.; Asawapirom, U.; Rabe, J.; Scherf, U.; Neher, D. *Advanced Functional Materials* **2004**, *14*, 757-764.
- (12) Schilinsky, P.; Asawapirom, U.; Scherf, U.; Biele, M.; Brabec, C. J. *Chemistry of Materials* **2005**, *17*, 2175-2180.
- (13) Barta, P.; Cacialli, F.; Friend, R.; Salaneck, W.; Zagorska, M.; Pron, A. Synthetic Metals 1999, 101, 296-297.
- (14) Woo, C. H.; Thompson, B. C.; Kim, B. J.; Toney, M. F.; Fréchet, J. M. J. Journal of the American Chemical Society **2008**, 130, 16324-16329.
- (15) Gregg, B. A. .
- (16) Moulé, A. J.; Meerholz, K. Advanced Materials 2008, 20, 240-245.
- (17) Moulé, A. J.; Allard, S.; Kronenberg, N. M.; Tsami, A.; Scherf, U.; Meerholz, K. *The Journal of Physical Chemistry C* **2008**, *112*, 12583-12589.
- (18) Ong, B. S.; Wu, Y.; Liu, P.; Gardner, S. Advanced Materials 2005, 17, 1141-1144.
- (19) Li, J.; Qin, F.; Li, C. M.; Bao, Q.; Chan-Park, M. B.; Zhang, W.; Qin, J.; Ong, B. S. *Chemistry of Materials* **2008**, *20*, 2057-2059.
- (20) Watanabe, N.; Mauldin, C.; Fréchet, J. M. J. Macromolecules 2007, 40, 6793-6795.
- (21) Fessi, H.; Puisieux, F.; Devissaguet, J.; Ammoury, N.; Benita, S. *International Journal of Pharmaceutics* **1989**, *55*, R1-R4.
- (22) Hornig, S.; Heinze, T.; Becer, C. R.; Schubert, U. S. J. Mater. Chem. 2009, 19, 3838-3840.
- (23) Kim, D. H.; Han, J.; Park, Y.; Jang, Y.; Cho, J.; Hwang, M.; Cho, K. *Advanced Materials* **2006**, *18*, 719-723.
- (24) Inganäs, O.; Salaneck, W.; Österholm, J.; Laakso, J. Synthetic Metals 1988, 22, 395-406.
- (25) Zhokhavets, U.; Erb, T.; Gobsch, G.; Al-Ibrahim, M.; Ambacher, O. *Chemical Physics Letters* **2006**, *418*, 347-350.

- (26) Brown, P.; Thomas, D.; Köhler, A.; Wilson, J.; Kim, J.; Ramsdale, C.; Sirringhaus, H.; Friend, R. *Phys. Rev. B* 2003, 67.
- (27) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. *Nature* **1999**, *401*, 685-688.
- (28) Jimison, L. H.; Toney, M. F.; McCulloch, I.; Heeney, M.; Salleo, A. Adv. Mater. 2009, 21, 1568-1572.
- (29) Joseph Kline, R.; McGehee, M. D.; Toney, M. F. Nat Mater 2006, 5, 222-228.
- (30) Kim, D. H.; Jang, Y.; Park, Y. D.; Cho, K. Langmuir 2005, 21, 3203-3206.
- (31) Kline, R. J.; McGehee, M. D. Polymer Reviews 2006, 46, 27.
- (32) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W. Synthetic Metals 2000, 111-112, 129-132.
- (33) Backer, S. A.; Sivula, K.; Kavulak, D. F.; Fréchet, J. M. J. *Chemistry of Materials* **2007**, *19*, 2927-2929.