10-22-2014

Photophysical and Electronic Properties of Low-Bandgap Semiconducting Polymers

Evan Lafalce
University of South Florida, elafalce@mail.usf.edu

Follow this and additional works at: https://scholarcommons.usf.edu/etd

Part of the Physics Commons

Scholar Commons Citation
https://scholarcommons.usf.edu/etd/5424

This Thesis is brought to you for free and open access by the Graduate School at Scholar Commons. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of Scholar Commons. For more information, please contact scholarcommons@usf.edu.
Photophysical and Electronic Properties of Low-Bandgap Semiconducting Polymers

by

Evan Lafalce

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
Department of Physics
College of Arts and Sciences
University of South Florida

Major Professor: Xiaomei Jiang, Ph.D.
Randy Larsen, Ph.D.
Garrett Matthews, Ph.D.
George Nolas, Ph.D.

Date of Approval:
October 22, 2014

Keywords: Bulk-heterojunctions, Excitonic processes, Morphology, Charge Transport

Copyright © 2014, Evan Lafalce
I could not have achieved the work I present here without the blessing and support of God. I will be forever grateful towards my advisor, Dr. Xiaomei Jiang. I had essentially no experience with experimental physics when I joined her group and she has taught me a great deal since then. Not only did she serve as a mentor in my research, Dr. Jiang has introduced me to the scientific community and done all in her power to provide me with opportunities there. I would like to thank the Department of Physics, the Duckwall Foundation for sponsoring my industrial practicum, Fred L. and Helen M. Tharp for a summer fellowship in 2013, and New Energy Technologies, Inc. I acknowledge that the transient pump-probe spectroscopy, some electroabsorption measurements and the magnetic field-effect measurements were performed by Prof. Zev Valy Vardeny and his research group at the University of Utah. I am also indebted to Prof. Vardeny for many helpful discussions and proposed experiments. Much gratitude is extended to Dr. Cheng Zhang at South Dakota State University for supplying me with many of the materials used in this study. I am thankful towards Prof. Randy Larsen and his research group for transient photoluminescence measurements, Dr. Jianjun Pan for conducting neutron scattering measurements at Oak Ridge National Laboratory, and Prof. Dennis Killinger for lending me optics. Within Dr. Jiang’s group, I would like to thank Patrick Toglia for performing the AFM measurements and Dr. Jason Lewis for some training in lithography and device fabrication. Much of this work would not have been possible without the facilities available and the expertise of the personnel at the Nanotechnology Research and Education Center (NREC) at USF. Particular thanks there go to Richard Everly for assistance with cleanroom lithography and profilometry, and to Robert Tufts for assistance with X-ray diffraction. I thank Dr. David Rabson for his tutelage and mentorship when I was an undergraduate and first-year grad student. Thanks also to
Prof. Larsen, Prof. Paul Kim, Prof. George Nolas, and Dr. Garrett Matthews for serving on my committee. My family and their never ending support has been a pillar of strength for me during the last five years and more. Finally, I would like to thank Ali Sibiga for proofreading this manuscript and for putting up with my moods while I was writing it.
TABLE OF CONTENTS

LIST OF TABLES iv

LIST OF FIGURES v

ABSTRACT ix

1 INTRODUCTION 1

1.1 \(\pi\)-Conjugated Polymers and Organic Electronics 1

1.2 Fundamentals of \(\pi\)-Conjugated Polymers 3

1.2.1 Intramolecular Properties and Essential States 3

1.2.2 Effects of Conformational Disorder and Supramolecular Order 6

1.3 Organic Photovoltaic Devices 7

1.3.1 Basic Physics and Characterization of Solar Cells 7

1.3.2 Basic Operational Mechanisms of Organic Photovoltaics 12

2 EXPERIMENTAL METHODS 18

2.1 Photophysical Characterization Techniques 18

2.1.1 Absorption and Photoluminescence 18

2.1.2 Photo-induced Absorption (PIA) 21

2.1.3 Electroabsorption Spectroscopy (EA) 23

2.1.4 Transient Photo-induced Absorption 26

2.2 Device Fabrication Methods 26

2.2.1 Conventional, 2mm \(\times\) 2mm Diodes and OPVs 27

2.2.2 Inverted, 2mm \(\times\) 2mm Diodes and OPVs 27

2.3 Morphological Characterization 28

2.3.1 Grazing Incidence X-ray Diffraction (GIXRD) 28

2.3.2 Atomic Force Microscopy (AFM) 28
5.4 ImidePTV Bulk-heterojunction Blends .................................. 110
5.5 Summary ................................................................. 116

6 PTV-BASED OPV AND CHARGE TRANSPORT 120
6.1 Introduction .............................................................. 120
6.2 PTV Derivatives as Donors in OPV ................................. 123
6.3 Charge Transport of imidePTV ........................................ 128
   6.3.1 SCLC in Single Carrier Diodes ................................. 129
   6.3.2 Photoconductivity .................................................. 133
6.4 Summary ................................................................. 139

7 SUMMARY AND FUTURE WORK 140
7.1 Summary ................................................................. 140
7.2 Future Work ............................................................ 147
   7.2.1 Two-Photon Studies of the 21 A_g State in PTVs ............. 147
   7.2.2 Regioregularity Effect on Charge Transport in PTV-CR Series by FET .......................................................... 147

REFERENCES 149

APPENDIX 171
LIST OF TABLES

3.1 Various Vibronic Replicas in Absorption of PTV-0:10 at RT (300K) and Low Temperature (10K) .......................................................... 37

3.2 Summary of GIXRD Data for PTV-CR ........................................... 41

3.3 Summary of Fitting Results Using Equation 3 for Triplet band T ........ 52

3.4 Summary of Fitting Results Using Equation 3 for Polaron band P2 ...... 52

4.1 Solvent parameters and photophysical parameters of imidePTV in solvents and film, listed from least polar to most polar going from top to bottom. 67

4.2 Values extracted from empirical fitting of thin film PL spectra at various temperatures. ............................................................................. 76

5.1 Lifetime of various photoexcitations in PIA spectra of neat PTV and PTV/PCBM blend films. ............................................................... 109

6.1 Solar cell device parameters for three prototypical PTV derivatives of this work in a 1:1 wt. ratio blend of PCBM as photoactive layer. .......... 124
LIST OF FIGURES

1.1 Schematic illustration of regioregular and regiorandom conformations of side-chains for the prototypical example of poly(3-hexylthiophene). . . . 8
1.2 Simulated J-V of an ideal solar cell in the dark (black squares) and in the light (red circles). ................................................................. 9
1.3 Circuit model of solar cell including parasitic resistors. ................. 11
1.4 Schematic energy level band diagram relevant to OPV operation and common materials used. ......................................................... 14
2.1 Experimental apparatus for measuring the electroabsorption of conjugated polymer thin films. ......................................................... 25
3.1 Chemical structures of the polymers discussed in the introduction. . . 32
3.2 Synthesis scheme and molecular structure of C12-PTV-a:b (PTV-CR). . 33
3.3 Absorption spectra of PTV-CR derivatives in film and solution. ....... 34
3.4 Effect of temperature on the absorption spectra of PTV-CR films. ..... 36
3.5 Photoluminescence spectra of PTV-CR derivatives in film and solution. 38
3.6 Grazing incidence X-ray diffraction measured in the out-of-plane geometry for films of PTV-0:10 and PTV-5:5 drop cast from DCB. ......... 41
3.7 Effect of thermal annealing on the GIXRD scan of PTVs. ............... 43
3.8 GIXRD scans of PTV films cast from various solvents. ................. 44
3.9 PIA spectra of all six PTV-CR derivatives. .................................... 45
3.10 Doping induced absorption (DIA) spectra of three PTV-CRs with different regioregularities. ......................................................... 47
3.11 Pump intensity and frequency dependence of PIA of PTV of different regioregularities. .............................................................. 48
3.12 Temperature dependence of the PIA bands of the films for PTV-1:9 (triangles), PTV-3:7 (squares), and PTV-5:5 (circles). ................. 51
3.13 Electroabsorption spectrum of PTV-0:10. 

4.1 Absorption of imidePTV in various solvents and in film. 

4.2 Absorption of imidePTV at several different concentrations for five of the solvents (as labeled) used in this study. 

4.3 Cylinder model fitting to two sets of SANS data (green and brown circles) obtained from two instrument configurations for 5mg/mL imidePTV in DCB solution and GIXRD scan of a thin film. 

4.4 Normalized PL of imidePTV in different solvents. 

4.5 Absorption maximum of imidePTV in the various solvents used in this study versus the solvent polarizability. 

4.6 Transient PL and fitting results. 

4.7 Absorption spectra of a thin film of imidePTV at various temperatures. 

4.8 PL spectra of a thin film of imdePTV at various temperatures. 

4.9 PL of imidePTV dispersed in polystyrene. 

4.10 Temperature dependence of the vibronic peak energies and various ratios of peak intensities, FTIR and Raman spectra of a film of imidePTV. 

4.11 Electroabsorption spectrum of PTVimide at 10K. 

4.12 Energy level diagram of the most relevant states and processes discussed. 

4.13 PIA and the change in PIA and PL with applied magnetic field. 

4.14 Semi-log plot of the PL subtracted cw-PA at several different probe wavelengths. 

4.15 Log-log plots of the PL (a) and PL subtracted cw-PA (b) vs. incident laser power density, shown at several different probe wavelengths. 

4.16 Doping induced absorption spectrum of a film of PTVimide. 

4.17 cw-PA of imide PTV during oxygen exposure achieved by purging the chamber with high-purity oxygen gas. 

4.18 cw-PIA measured using different laser excitation energies. 

4.19 Vis/NIR Transient PA spectra of imide film at different time delays after the pump.
4.20 Decay dynamics of the PA from Figure 4.19 at the probe energies of 1.74eV (black squares) and 1.34eV (blue squares). .............................. 90
4.21 Transient IR-PA spectra shown at different time delays after the pump. .......................... 91
4.22 Background subtraction of transient IR-PA spectra shown in Fig. 4.21. ............................ 92
5.1 Absorption of the blend films PTV010 and PTV55 with PCBM. ................................. 100
5.2 The PL spectra of films of PTV010 (black circle) and PTV010:PCBM blend and PTV55:PCBM with 1:1 weight ratio. ................................. 102
5.3 Molecular structures of PCBM and PTV 55 (regiorandom); PTV010 (re-gioregular) and energy levels of PTV:PCBM blend. ................................. 103
5.4 GIXRD patterns of films of PTV010, PTV010:PCBM blend, PTV55 and PTV55:PCBM blend (red circles, open). ................................. 105
5.5 The AFM images of (a) PTV55, (b) PTV55:PCBM blend, (c) PTV010, and (d) PTV010:PCBM blend films on sapphire substrates. ................................. 106
5.6 PIA spectra of PTV010:PCBM blend and PTV-55:PCBM blend films and their frequency dependence. ................................. 108
5.7 Photoluminescence of a 1:1 blend film of imidePTV and PCBM (black circles) compared to the spectrum obtained from a film of neat imidePTV (blue circles). ................................. 112
5.8 PIA spectrum of a 1:1 blend film of imidePTV and PCBM compared to that of a neat film of imidePTV. ................................. 113
5.9 Pump modulation frequency dependence of the PIA features in a blend film of imidePTV and PCBM. ................................. 114
5.10 Pump intensity dependence of the PIA features in a blend film of imidePTV and PCBM on a log-log scale. ................................. 116
5.11 Normalized pump intensity dependence of the PIA features in a blend film of imidePTV and PCBM plotted on a linear scale. ................................. 117
6.1 JV curves of PTV-19:PCBM (RR-PTV, black squares) and PTV-55:PCBM (RRa-PTV, red circles) solar cells under AM 1.5 illumination. ................................. 124
6.2 J-V curve of an imidePTV:PCBM solar cell in the dark (black squares) and under AM 1.5 illumination (“light,” blue triangles). 125
6.3 External quantum efficiency (EQE) spectrum of an imidePTV:PCBM solar cell. 127
6.4 Schematic of the layer-by-layer structure of an imidePTV hole-only diode and the resulting band structure. 129
6.5 J-V curve of an imidePTV hole-only diode including a fit to the Mott-Gurney relation. 131
6.6 Schematic of the layer-by-layer structure of an imidePTV electron-only diode and the resulting band structure. 132
6.7 J-V curve of an imidePTV electron-only diode including a fit to the Mott-Gurney relation. 133
6.8 Internal photoconductivity action spectrum in an imidePTV photodiode as a function of incident photon energy. 135
6.9 The photoconductivity of an imidePTV photodiode versus the incident photon flux in units of photon density at various applied field strengths. 136
6.10 The dependence of the generation rate-mobility product, $g\mu$, on the square root of the field plotted on a natural log scale at various temperatures. 137
6.11 The dependence of the generation rate-mobility product, $g\mu$, on the square of the inverse thermal energy plotted on a natural log scale at various applied field strengths. 138
ABSTRACT

In this Ph.D. work, we investigate the optoelectronic properties of low-bandgap π-conjugated polymers and project the potential for employing these materials in electronic and photonics devices, with a particular emphasis on use in organic solar cells. The field of organic solar cells is well developed and many of the fundamental aspects of device operation and material requirements have been established. However, there is still more work to be done in order for these devices to ultimately reach their full potential and achieve commercialization. Of immediate concern is the low power conversion efficiency (<10%) demonstrated in these devices so far. In order to improve upon this efficiency, several routes are being explored. Because the optical bandgap of π-conjugated polymers is larger (≈ 2eV) than in inorganic semiconductors, one of the most promising routes currently under exploration is the development of low-bandgap materials. Using polymers with lower band gaps will allow more of the solar irradiance spectrum to be absorbed and converted into electricity and thus possibly boost the overall efficiency.

The bandgap of these semiconducting polymers is determined by the chemical structure, and therefore can be tailored through synthesis if the relevant structure-property relationships are well-understood. The materials studied in this work, a new series of Poly(thiénylenevinylene) (PTV) derivatives, posses lower band gaps than conventional π-conjugated polymers through a design that incorporates aromatic-quinoid structural disturbances. This type of chemical structure delocalizes the electronic structure along the polymer backbone and reduces the energy of the lowest excited-state leading to a smaller band-gap. We investigate these materials through a variety of techniques including linear spectroscopy such as absorption and photoluminescence, pump-probe techniques like cw-photoinduced absorption and transient photo-induced absorption, and the non-linear electroabsorption technique in order to interrogate the consequences of the delocalized
electronic structure and its response to optical stimuli. We additionally consider the effects of environmental factors such as temperature, solvents and chemical doping agents. During the course of these investigations, we consider both of the two primary categorical descriptions of structure-property relationships for $\pi$-conjugated polymers within the “molecular exciton model,” namely the role of inter-molecular interactions on the electronic properties through the variation of supermolecular order and the fundamental determination of electronic structure due to specific intra-molecular interaction along the backbone of the polymer chain. We show that the dilution of aromaticity in semiconducting polymers, while being a viable means of reducing the optical band gap, results in a significant increase in the role of electron-electron interactions in determining the electronic properties. This is observed to be detrimental for device performance as the highly polarizable excited state common to $\pi$-conjugated polymers gives way to highly correlated state that extinguishes both the emissive properties and more importantly for solar cells, the charge-generating characteristics. This situation is shown to be predominant regardless of the nature of interchain interactions. We therefore show that the method of obtaining low-bandgap polymers here comes along with costly side-effects that inhibit their efficient application in solar cells.

Further, we directly probe the efficacy of these materials in the common bulk-heterojunction architecture with both spectroscopy and device characterization in order to determine the limiting and beneficial factors. We show that, while from the point of view of absorption of solar radiation these low-bandgap polymers are more suited for solar cells, the ability to convert the absorbed photons into electron-hole pairs and generate electricity is lacking, due to the internal conversion into the highly correlated state and thus, the absorbed photon energy is lost. For completeness, we fabricate devices and verify that both the charge-transport properties and alignment of charge extraction levels with those of the contacts can not be responsible for the dramatic decrease in efficiency found from these devices as compared to other higher band gap polymers. We thus conclusively determine that the lack of power conversion efficiency is governed by the inefficiency of charge-generation resulting from the intrinsic “defective” molecular structures rendering
a low-lying optically forbidden state \(2^1A_g\) below the lowest optical allowed state \(1^1B_u\) that consumes the majority of the photogenerated excitons.

It is emphasized that our means of investigation allow us to truly access the potential of these materials. In contrast, the direct application of these systems in devices and interpretation of the performance is exceedingly complex and may obscure their true potential. In other words, poor performance from a device may be extrinsic in nature and the optimization process may be very costly with respect to both time and materials. The methods used here however, allow us to determine the intrinsic potential. Not only is this beneficial in terms of preserving the resources that would be used on the trial-and-error method for devices, but it also allows us to learn more on a fundamental level about the structure-property relationships and their implications for device performance. The benefits of this increased understanding are two-fold. First, by learning about the fundamental response of a material, a new application may be realized. For example, the rapidly efficient internal conversion process that renders the materials in this study as poor candidates for solar cells may make them useful for photonics applications, as optical switches, for instance. Secondly, this type of investigation has implications for the whole organic electronics community instead of just being limited to the particular material system and the primary application attempted. In this case, we are essentially able to determine a threshold for aromaticity necessary in a \(\pi\)-conjugated polymer structure that will preserve the stability of the ionic excited state \(1^1B_u\) that is useful for charge generation in solar cells.
1 INTRODUCTION

1.1 π-Conjugated Polymers and Organic Electronics

The π-conjugated polymers form a novel class of functional materials that have potential use in numerous applications in electronic and photonic devices. Interest in these materials dates back to 1978 when Alan J. Heeger, Alan G. MacDiarmid, Hideki Shirakawa, and co-workers discovered that polyacetylene (t-[CH]x), the simplest example of a π-conjugated polymer, could be doped by exposure to oxidizing agents such as AsF$_5$ or iodine, leading to an increase in the conductivity [1, 2, 3, 4]. These conductivities would eventually be pushed to metallic levels [5]. For that work, the three received the Nobel Prize in Chemistry in the year 2000. Interest was fueled by numerous achievements in employing these materials in diverse device applications throughout the years and in subsequent improvement in the performance of device characteristics. Examples of thin-film transistors (TFT)s [6] and electroluminescent devices [7] that led to the organic light-emitting diodes (OLED)s were demonstrated in the mid-to-late 80’s. The first organic solar cell (OSC) employing a π-conjugated polymer was achieved a few years later in 1993 [8]. In this Ph.D. work, OSCs, or organic photovoltaics (OPV)s, will be the application that garners the most attention, and more about the history of development and fundamental principles of operation will be discussed shortly. Meanwhile, it should be mentioned that the field of organic materials for opto-electronics applications extends unto a broader material class than just the π-conjugated polymers. It can in fact be divided into two general categories: organic small molecules, exemplified by the cyclic aromatic hydrocarbons, or -acenes, such as a tetracene, and the extended polymeric systems that are the focus of this dissertation. The interest in the former actually predates that in the π-conjugated polymers [9], and small molecules have vigilantly rivaled or
even surpassed \( \pi \)-conjugated polymers in many of the diverse scope of organic electronic applications. Indeed, the first OSC was realized using the small molecules [10].

The two sub-systems do not differ much in terms of their fundamental electronic properties. It is the means of fabrication and resulting structural order that provides the most striking distinction. Thin films of small molecules are generally fabricated by vacuum evaporation techniques and possess crystalline structural arrangements, while polymer films are processed from solution by means of various coating techniques. The fabrication methods are significant for organic electronics. One of the most sought-after characteristics of organic electronics applications is their potential cost-effectiveness. Such potential stems from the low material-weight of carbon-based materials and the ease of fabrication from techniques that readily lend to large-scale production such as spray-coating or ink-jet printing. The higher solubility of polymers relative to small molecules gives them an advantage in this regard. However, this advantage comes at the cost of reduced structural order that has a significant impact on the optoelectronic properties.

The origin of the electronic properties of \( \pi \)-conjugated polymers is rooted in their chemical structure. The “backbone” is composed of a linear chain of carbon atoms bonded together by \( sp^2 \)-hybridized orbitals. This entails three of the four valence electrons of each carbon atom contributing to the \( sp^2 \)-hybridized orbitals that form strong, covalent \( \sigma \)-bonds between two neighboring carbon atoms and one hydrogen atom. These \( \sigma \)-bonds render the molecules planar and serve the role of completely filled electronic bands. The fourth valence electron of each carbon atom resides in an un-hybridized p-orbital which participates in \( \pi \)-bonds with neighboring atoms. These \( \pi \)-bonds form the “conjugated” or delocalized quasi-one-dimensional (1-D) electronic structure and serve the role of a half-filled, valence electronic bands. For reasons discussed below, these materials are formally semiconducting, but it is this delocalized electronic structure that is responsible for the optoelectronics properties of \( \pi \)-conjugated polymers that make them viable for device applications. This is in stark contrast to the more common “saturated” polymers, where all four valence electrons are involved in the formation of \( sp^3 \) hybridized orbitals leading
1.2 Fundamentals of $\pi$-Conjugated Polymers

1.2.1 Intramolecular Properties and Essential States

The quasi-one-dimensional (1-D) electronic structure of $\pi$-conjugated polymers has significant consequences on the electronic properties. First, the strong orbital overlap along the chain and negligible overlap between chains means that intermolecular coupling is generally much weaker than intramolecular coupling and thus the electronic structure is localized along a single chain. Secondly, because screening is weak in 1-D, electron-electron interaction plays a significant role on the electronic structure of these semiconductors. This results in a dramatic difference between organic semiconductors and their inorganic counter-parts. In the latter, the strong screening leads to delocalized Wannier excitons with large electron-hole separations while in the former the excitons are tightly bound Frenkel excitons with electron-hole separations on the order of a few Ångströms. Third, the electron-phonon coupling in these materials is also strong. Because the electronic structure is determined by the degree of overlap, it is intimately tied to the nuclear degrees of freedom, including the equilibrium bond lengths, vibrational modes, and rotational modes. This results in a description of electronic transitions in terms of the Frank-Condon overlap factors within the context of the Born-Oppenheimer approximation[11].

Formally, the electronic eigenstates of a $\pi$-conjugated polymer are solutions to the Hamiltonian that includes all of the aforementioned couplings plus the kinetic energy terms for the electrons and nuclei:

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i\neq j} \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_i - \mathbf{r}_j|} + \sum_u \frac{P_u^2}{2M_u} + \frac{1}{2} \sum_{u\neq v} \frac{Z_uZ_v e^2}{4\pi\epsilon_0|\mathbf{R}_u - \mathbf{R}_v|} - \sum_{u,i} \frac{Z_u e^2}{4\pi\epsilon_0|\mathbf{R}_u - \mathbf{r}_i|}$$

(1.1)

where $e$ (m) is the charge (mass) of each electron, $Z_u e$ ($M_u$) the charge (mass) of the
$u$th nucleus, $p_i$ and $P_u$ the momentum of the $i$th electron and $u$th nucleus respectively, for the set of electron coordinates \{r\} and nuclear coordinates \{R\}. This can not be solved unless simplifying assumptions and approximations are made. The most common approximation is the Born-Oppenheimer approximation, which uses the fact that the electron-mass is much smaller than the nuclear-mass, so that the nuclear dynamics will be very slow compared to electron dynamics. In terms of Equation 1.1, this amounts to neglecting the nuclear kinetic energy term. It is convenient to express the Hamiltonian in the representation of second quantization. It can be shown that in this representation the simplified Born-Oppenheimer Hamiltonian is

$$H = \sum_{ij} t_{ij} (c_{is}^\dagger c_{js} + c_{js}^\dagger c_{is}) + \frac{1}{2} \sum_{ijklss'} V_{ijkl} c_{is}^\dagger c_{js}^\dagger c_{ls'} c_{ks} + \frac{1}{2} \sum_{u \neq v} \frac{Z_u Z_v e^2}{4\pi\epsilon_0 |R_u - R_v|}.$$ (1.2)

Here, $t_{ij}$ is known as the transfer integral and conceptually is the energy involved in the transfer of an electron from an orbital $\phi_i(r,s)$ to an orbital $\phi_j(r,s)$ (s labels the spin of the state) and thus includes the electron kinetic energy and the electron-nuclear coupling term, while $V_{ijkl}$ represents the electron-electron interactions. The most commonly explored models (the so-called $\pi$-electron models) involve further simplifications. Of these, two have been explored in detail. They are the Su-Schrieffer-Heeger (SSH) model and the Pariser-Parr-Pople (PPP) model [11]. The SSH model does not include electron-electron interactions, but considers electron-phonon coupling. In this model, the presence of electron-phonon coupling leads to Peierls dimerization of the lattice (alternating single and double bonds). The bond alternation manifests in a small variation in the equilibrium bond lengths between every other pair of carbon atoms ($\approx 1.37\,\text{Å}$ for the $\sigma+\pi$-bond, $1.41\,\text{Å}$ for the single $\sigma$-bond) and creates a gap in the otherwise metallic-like half-filled valence band [12]. Further, the electron-phonon interaction leads to self-localization of an optically generated electron-hole pair which decays into solitonic excitations, which are described as domain walls between two alternate variants of conjugated structure.
This model has been very successful at explaining the properties of t-[CH]$_x$. We mainly emphasize here that this is a “band model” and that the origin of the gap is bond alternation. The PPP model, on the other hand includes electron-electron interaction but neglects the electron-phonon coupling. In this case, the excitations are properly described as molecular excitons. This model also leads to an energy gap, but in this case, the origin of these effects is the electron-electron interaction.

From the molecular standpoint, π-conjugated polymers can be viewed as extended versions of linear polyenes. These small molecules have been thoroughly investigated both experimentally and theoretically [13, 14]. They possess $C_{2h}$ symmetry that leads to ground state of $A_g$ symmetry which comprises the highest occupied molecular orbital (HOMO) and a sequence of excited states of $B_u$ and $A_g$ symmetry [15]. Here, the states labeled B are anti-symmetric with respect to the symmetry operations of reflection in the plane of σ-bonded $sp^2$-hybridized orbitals and rotation about the two-fold axis, while the A states are symmetric with respect to these operations. Meanwhile, the subscripts “u” and “g” refer to states that maintain odd or even parity, respectively, with respect to the center of inversion symmetry. Optically allowed transitions can only occur between states of opposite parity due to the dipole operator governing this phenomenon. It is well documented for polyenes of length beyond a couple of double bonds, the lowest excited state is of $A_g$ symmetry [13, 14]. In the shortest polyenes, such as stilbenes, the $1^1B_u$ is below the $2^1A_g$ (the additional superscript “1” refers to the states as spin singlets) [13]. As the length and the number of electrons in the system increases, the $2^1A_g$ state is pushed lower in energy more drastically due to its sensitivity to electron correlation and exchange interactions [15]. This is due to the “covalent” nature of the $2^1A_g$ and the “ionic” character of the $1^1B_u$. Thus, the gap between the excited $1^1B_u$ and $2^1A_g$ states increases, and as the length of the molecule is extended to the polymer regime this ordering of states is expected to be preserved. This renders these materials weakly or non-fluorescent since absorption populates the higher ($1^1B_u$) state, which is followed by the rapid internal conversion to the excited $2^1A_g$ state below, thus quenching the fluorescence of the dipole allowed transition [16, 17, 18]. This explains why t-[CH]$_x$ is
non-fluorescent [19]. However, there exists a multitude of highly efficient emitting conjugated polymers that have made possible the commercialization of OLED-based lighting displays. How is this possible? As shown by Soos et al., when the dimerization contribution to the structure is significant, the electronic structure is more localized, the $1^1B_u$ is the lowest excited state and the material is fluorescent [20]. When the effective dimerization is decreased (such as in the extreme case of t-[CH]$_x$), the electron correlation terms become significant and push the $2^1A_g$ state lower in energy. Therefore, to properly describe the electronic properties of these materials, both the electron-phonon and the electron-electron interactions must be considered, and the luminescent properties can be generally rationalized by the degree to which each contributes to the band gap.

1.2.2 Effects of Conformational Disorder and Supermolecular Order

The electronic structure and properties of \( \pi \)-conjugated polymers are subject to variations in structural order, of which there are two types. The first is intra-chain torsional disorder that leads to localizing of the chromophore to a length that is smaller than the polymer chain length. This shorter length is referred to as the “conjugation length segment”. It describes the extent of electronic coherence amongst \( \pi \)-electrons along the polymer backbone. This coherence can be abruptly truncated by structural and chemical defects, but more subtly will be limited by the extent of torsional dislocations from planarity along the chain. This intra-chain disorder can be dynamic, as it would be in solution, or can be static, as would arise during the quenching of rotational freedom upon film formation. From the point of view of device applications, limiting this type of disorder is beneficial, as it allows for more delocalization of the electronic structure which leads to lower optical gaps and better transport properties.

Another significant effect of disorder arises from the structural conformation of an assembly of chains and the relative strength of interchain coupling. The primary factor influencing the mesoscopic structural arrangements in thin films are the side-chain substitutions. The primary use of side-chain substituents on \( \pi \)-conjugated polymers is to
enhance the solubility of these large molecules that are generally insoluble in common organic solvents without them. Alkyl or alkoxy side-chains are the most common types and various lengths are used, with the general trend that the larger the side group the more soluble is the resulting \( \pi \)-conjugated polymer. In addition, these side-chains may be attached in such a way as to promote the self-assembly of ordered super-molecular structures. This side-chain arrangement is termed the polymer’s regioregularity. Examples of regioregular (RR) and regiorandom (RRa) orientations are displayed schematically in Figure 1.1. When the chains are regioregular, they take on an alternating “head-to-tail” conformation, while regionandomness is characterized by “head-to-head” and “tail-to-tail” conformations. One can imagine that the latter two conformations promote torsional dislocations, while the RR conformation promotes planarity. Perhaps more significant though, is the observation that RR polymers will self-assemble into two-dimensional (2-D) lamellae structures during film formation [21]. Such lamellae allow the formation of crystal domains that include many polymer chains with enhanced electronic overlap (termed \( \pi-\pi \) stacking) between neighboring chains within these domains [22]. The consequence is that the photophysical and charge transport properties of RR polymers is vastly different from their RRa counter parts [23, 21, 24, 25], with generally beneficial implications for device applications.

1.3 Organic Photovoltaic Devices

1.3.1 Basic Physics and Characterization of Solar Cells

The first practical solar cells were developed in the 1950’s with the emergence of semiconductor based electronics and, in particular, the p-n junction [26]. It is from this period that the basic understanding of the physics of solar cells originates. An essential element of all such devices is a built-in asymmetric potential that is characteristic of a diode.
Thus, all solar cells are diodes in the dark. At reverse bias, a diode has a flat current-voltage (I-V) response that is due to thermally generated minority carriers in the semiconductor bulk. In the simplest approximation, the absorption of light by the semiconductor results in a higher density of minority carriers. The light-absorbing/charge-generating layer is referred to as the “photoactive” layer. The asymmetric potential is necessary for the “sweep out” of the photo-generated minority carriers so that a short-circuit current ($I_{SC}$), which is the current through the circuit at zero applied bias, may be extracted. Since the current will depend on the area of the cell, as the latter will affect the amount of photons (per unit time) absorbed, the current density $J = I/A$, where $A$ is the active area, is usually considered instead. Formally, the current density in a solar cell can be accounted for by subtracting the short-circuit current density ($J_{SC}$) from the “dark” diode
current density:

\[ J = J_{\text{sat}}(e^{\frac{qV}{k_B T}} - 1) - J_{SC} \]  (1.3)

Here, \( T \) is the temperature and \( k_B \) is Boltzmann’s constant, while \( V \) is the applied bias, \( q \) is the fundamental electron charge and \( J_{\text{sat}} \) is the reverse-bias saturation current density.

In application, solar cells are operated at positive bias where they may deliver power to a load resistance. Therefore, a major quantity of interest is the maximum output power of the cell. This is the maximum product of the current and applied bias in the 4th quadrant of the J-V characteristic: \( P_{\text{max}} = A J_m V_m \) (Fig. 1.2).

Figure 1.2: Simulated J-V of an ideal solar cell in the dark (black squares) and in the light (red circles). The relevant characteristic parameters as explained in the text are shown.
The power conversion efficiency (PCE) is the ratio of $P_{\text{max}}$ to incident solar power density, $P_{\text{solar}}$. As the bias is increased, the dark current and photo-current will cancel each other out, resulting in zero net current at the open-circuit voltage, $V_{OC}$. Another characteristic parameter of a solar cell is the fill factor, FF, which quantifies the “square-ness” of the I-V curve in the 4th quadrant:

$$FF = \frac{J_m V_m}{J_{SC} V_{OC}}$$

(1.4)

With this definition we can write the PCE as:

$$\eta_{PCE} = \frac{(J_{SC} V_{OC} FF)}{P_{\text{solar}}}$$

(1.5)

So far, we have considered a simple electrical circuit model for a solar cell consisting of an ideal diode in parallel with a current source. In practice, actual devices show various deviations from this type of behavior. Without sacrificing too much simplicity, the performance of real devices may be understood intern of the model described above and the addition of two sources of parasitic resistance. This amounts to placing one resistor in series with the diode and current source, termed the series resistance, $R_s$, and another in parallel with the current source and diode which is known as a shunt resistance, $R_p$. The resulting model is displayed in Figure 1.3. A simple circuit analysis now leads to the modified equation for current in the solar cell:

$$J = J_{sat}(e^{\frac{q(V - JAR_s)}{k_BT}} - 1) + \frac{V - JAR_s}{AR_p} - J_{SC}$$

(1.6)

Clearly, the presence of a non-infinite shunt resistance will reduce the observed $V_{OC}$ as well as the fill factor through both the exponential and linear terms in Eq. 1.6. If the shunt resistance is very low (shorted device), it can even reduce the ideal $J_{SC}$. The series resistance will also lead to a decrease in the fill factor, as it affects the slope of the J-V curve in the vicinity of $V_{OC}$. Additionally, the smaller the shunt resistance the more dramatic the effect of the series resistance will be.
Figure 1.3: Circuit model of solar cell including parasitic resistors. $J_{SC}$ is the current due to solar illumination. $J_{dark}$ is the current through the device in the dark and in the absence of the parasitic resistance. $R_s$ and $R_p$ are the series and shunt resistors respectively.

Equation 1.6 is a non-linear transcendental equation that generally requires a computational least-squares regression to solve. A convenient estimate of these resistance values may be obtained, however, by taking the series resistance from the inverse slope of J-V curve at $V > V_{OC}$ and by taking the shunt resistance from the inverse slope of the J-V curve near $V < 0$.

The first generation crystalline Si cells, though high in efficiency (> 10%), are costly in terms of both materials and processing. The second generation thin film solar cells made from inorganic semiconductors (e.g., amorphous silicon, its various alloys and thin film Copper Indium Gallium Selenide (CIGS)) cells offer promise to bring the cost of solar cells down to more reasonable levels, however, they usually require vacuum technique manufacturing. Thin film solar cells based on organic semiconducting materials are inex-
pensive, lightweight, flexible and versatile, due to their possibility of being manufactured by roll-to-roll printing through solution.

1.3.2 Basic Operational Mechanisms of Organic Photovoltaics

The most fundamental difference between OPV and their inorganic counterparts is the nature of the primary exciton formed upon absorption of a photon. In inorganics, the large dielectric constants lead to delocalized Wannier excitons with small binding energies. These excitons can easily be dissociated by the thermal energy available at room temperature. Therefore, absorption leads almost directly to free carriers in these materials. In contrast, the excitons in organic materials are tightly-bound Frenkel excitons with binding energies in the range of 0.5eV to 1eV. This means that an additional step is required for OPV operation, namely the deliberate dissociation of the exciton. This is usually accomplished by the addition of a strong electron-accepting material in the device architecture. Derivatives of C\textsubscript{60} such as phenyl-C\textsubscript{61}-butyric acid methyl ester, (PCBM) have been the most widely used materials for this purpose. Thus, the terms charge generation and exciton dissociation are equivalent in discussing the operational mechanisms of OPV and involve the transfer of an excited \( \pi \)-electron from a \( \pi \)-conjugated polymer to C\textsubscript{60}. After this process, electron transport must occur in the bulk of C\textsubscript{60}, while the respective holes must travel through the bulk of the \( \pi \)-conjugated polymer. This will occur until these carriers reach their respective electrodes at the ends of the photoactive layer and can be delivered to a load to supply current, or meet some other fate such as carrier recombination or trapping. In summary, we consider the operational mechanism of OPV as a sequential four-step process involving: (i) absorption of a photon forming an exciton, (ii) dissociation of the exciton into an electron-hole pair at the donor-acceptor interface, (iii) asymmetric transport of photogenerated electrons and holes, and finally (iv) extraction of photocurrent. Each of these processes are discussed in more detail below.

Absorption The fundamental description of the band gap and optically allowed excited
states in $\pi$-conjugated polymers has already been discussed. A point that has not been made that is relevant to photovoltaic is that the band gaps of these materials are usually larger than the inorganic crystalline semiconductors ($\approx 2\text{eV}$, compared to $1\text{eV}$ or less in inorganics). This puts organics at a disadvantage because a significant portion of the solar emission spectrum lies in the infrared and will not be harvested. However, since the band-gaps of $\pi$-conjugated polymers are generally tunable through the chemical design this is an obstacle that may be overcome. A significant amount of research is currently invested in the development of these so-called low band-gap (LBG) polymers.

The dilution of the quinodal character of $\pi$-conjugated polymers is a general strategy for lowering the optical band-gap of the material [27]. Perhaps, the most significant contribution of this work to the OPV community is to demonstrate that this method is not viable as it leads to a $2^1A_g - 1^1B_u$ energy level crossing, however. When the $2^1A_g$ state is energetically below the $1^1B_u$, absorption of a photon will be succeeded by rapid internal conversion to the $2^1A_g$. While this state may be a precursor state to singlet fission (see Chapter 4) [15] and is known to be a useful in photosynthetic processes when participating in energy transfer [28, 29], this internal conversion represents a loss channel in the conventional model of organic photovoltaic conversion discussed below. This is because the “covalent” $2^1A_g$ is much less susceptible to forming charge-transfer states with the electron-acceptor PCBM in the well-known bulk-heterojunction organic photovoltaics (BHJ-OPV), than is the “ionic” $1^1B_u$. Avoiding this energy level crossing is therefore an important design criteria for polymers with potential in OPV operation. A clear-cut illustration of these elements will be provided in this work using the case of the $\pi$-conjugated polymer, poly(thienylenevinylene) or PTV.

**Exciton Dissociation** The exciton formed upon absorption of a photon in organic materials is tightly bound and will not lead free carriers directly. On the contrary, the strong binding energy of this exciton makes it useful for electroluminescent devices where light is emitted during the favorable exciton recombination process. Thus, OPVs have historically employed a donor-acceptor structure where the photo-excited donor molecule
transfers an electron to the acceptor resulting in an electron-hole pair where the hole is left behind on the donor. The success of this process is a result of the favorable energy level alignment between the two entities. Figure 1.4 shows a typical device band-diagram for a π-conjugated polymer:PCBM donor-acceptor heterojunction.

Figure 1.4: Schematic energy level band diagram relevant to OPV operation and common materials used. The blue arrows represent the direction of photocurrent flow in the conventional structure while the green arrows represent the same in the inverted structure. Abbreviations are as described in the text.

Even so, the short diffusion length of excitons in π-conjugated polymers will limit their dissociation. A striking example of this is the large boost in efficiency of the bulk-heterojunction device architecture compared to the planar heterojunction architecture. In the latter, the π-conjugated polymer film and PCBM film are stacked one on top of the other. Absorption occurs through the bulk of the film generating excitons, but only those generated within the exciton diffusion length of the interface will be dissociated into charge-carriers. In the bulk-heterojunction, the two materials are mixed homogeneously.
in solution and a blend film is cast from such a solution. The result is a film containing meso-scopic domains of π-conjugated polymer and PCBM. As excitons are generated in the polymer domains, excitons now only have to diffuse to the most near-by PCBM interface, and charge generation can occur throughout the entire film. As will be discussed shortly, the efficiency of charge transport is necessarily lower in the bulk-heterojunction architecture due to increased recombination, so the improvement of the overall device performance speaks to the significant enhancement of charge generation in these types of photo-active layers.

*Charge-carrier Transport* At the end of the charge generation step, a relatively free positive charge will be left in the donor polymer and likewise for the electron now residing in the PCBM bulk. Because the electronic coherence in π-conjugated polymers is localized along solitary polymer chains, hole transport in the bulk of a heterojunction blend used in OPV is dominated by thermally assisted hopping (see Chapter 6). This will also be the case among the localized $C_{60}$ molecules that provide the pathway for electron transport. The main parameter that determines the efficiency of charge transport is the carrier mobility, defined as $\mu = v_{dr}/F$ where $v_{dr}$ is the average drift velocity of carriers in the presence of an electric field $F$, and generally describes the carrier independent part of the conductivity $\sigma = en\mu$ (with $n$ the carrier density). In a solar cell, the field $F$ is to be associated with the built-in voltage of the diode. This hopping-type transport has been verified experimentally, particularly by the increase in the carrier mobility with temperature. In contrast to band transport where increase in temperature leads to a decrease in the carrier mobility through increased scattering events, temperature will increase the hopping mobility as it allows the carriers to explore more of the energetic landscape and escape shallow traps. The morphological ordering of these materials has a significant influence on the carrier mobility. The more disordered is the morphology of the film, the lower is the probability that a carrier will complete a hopping event and the more difficult for the carrier to traverse the film. Furthermore, a more ordered film will result in better electronic overlap between separate polymer chains, allowing the carriers to delocalize over a greater distance before needing to hop to another conjugated segment. A great
example of this was the drastically improved mobility observed in FETs fabricated using regio-regular poly(3-hexylthiophene) as compared to their regio-random counter parts [23]. In this case, the quasi-2D lamellae structure oriented along the direction of charge transport and led to mobilities on the order of 1 $cm^2/Vs$, approaching that of amorphous Si. It has also been noted that the crystalline order of vacuum deposited organic small molecules leads to better transport properties. FETs using the small molecule Rubrene have achieved mobilities of $\approx 50cm^2/Vs$ [30].

In OPV, transport is perpendicular to the plane of the film, due to the sandwich structure of the devices. In bulk-heterojunction organic photovoltaics, the improvement in charge generation comes with a cost of the charge transport efficiency. Since the domains of polymer and PCBM are now inter-mixed through the bulk of the film, holes that end up in polymer domains may be isolated from the anode, and the same for electrons in PCBM from the cathode. This means that many of the photo-generated carriers are destined to recombine. Much ongoing work is therefore concerned with the optimal morphology of bulk-heterojunction films to optimize the generation and transport efficiency product.

**Current Extraction** Essential to the functionality of photovoltaic devices is the use of a transparent electrode that can simultaneously transmit solar energy into the bulk of the device and carry the generated current into the external load. The state of the art material for this purpose is Indium Tin Oxide (ITO), due to its optimal combination of transparency in the visible to near-infrared and low sheet resistivity. ITO has conventionally been used as the hole-extracting (electron-injecting) contact, or anode, in OPV due to the proximity of its work function($\approx 4.7ev$) to the HOMO level of $\pi$-conjugated polymers (usually in the range of 5.0eV - 5.3eV). The remaining hole-extraction barrier of 0.3eV - 0.6eV will, however, induce a Schottky barrier at the interface that will inhibit charge collection. Thus, improvements in device performance were realized by inserting a thin, hole-transporting layer (HTL) in between the ITO electrode and the active layer. The conjugated polymer:ionic salt complex polyethylene dioxythiophene-poly styrene sul-
fonate (PEDOT:PSS) has been by far the most common HTL used in OPV [31]. This material will lead to p-type doping in the active layer and pin the work function of ITO to the HOMO of the polymer, thus eliminating the Schottky barrier [32]. In this geometry, a low work function electrode such as Al is then deposited on top of the active layer to serve as the electron-collecting (hole-injecting electrode, or cathode. The energetic requirement for this electrode is that its work function should form an Ohmic contact with the LUMO of PCBM. Similar to the case for the anode, device performance has been improved by inserting a thin, electron-transporting layer (ETL) in between the cathode and active layer. Calcium is a commonly used ETL, as is the ionic salt LiF [33, 34].

In a planar device structure, more light will be absorbed at the side of the transparent electrode than at the other. This means a higher density of charge carriers will be generated at this side as well. It is therefore, beneficial for the built-in field (depletion region) to reside at the side of the transparent electrode, to maximize the sweep-out of carriers. On the other hand, carriers have to diffuse to depletion region before the more effective drift current can be achieved. While the origin of the built-in field in OPV is still a subject of debate [35, 36], it is generally believed to occur due to contact between the polymer layer (essentially a p-type semiconductor) and the cathode (which acts as an n-type material) similar to the inorganic semiconductor p-n junction. This means that in principle it is more beneficial to have the transparent electrode to serve as cathode than anode. These so called inverted devices have been realized by means of inserting a ETL in between the ITO electrode and the active layer, effectively lowering the work-function of ITO [37]. Various ETL’s have been used for this purpose including $Cs_2CO_3$[37], ZnO [38, 39], $TiO_x$[40], and even other $\pi$-conjugated polymers [41]. In this case, a higher work-function metal such as Ag is often used as the back electrode together with the aid of a HTL. It has indeed been shown that when Ohmic contacts can be achieved in both geometries, the inverted structure leads to higher efficiencies than the conventional structure [41].
2 EXPERIMENTAL METHODS

2.1 Photophysical Characterization Techniques

2.1.1 Absorption and Photoluminescence

The absorption of π-conjugated polymer films and solutions is measured using a white light source (usually a Tungsten halogen lamp), a monochromator, and a solid-state photo-diode detector. The light is passed through the sample and subsequently dispersed by a Cornerstone 260 1/4m monochromator and collected by the photodiode. Amplifiers are used to convert the photodiode current into a recorded voltage signal. The transmission of light through a sample of thickness \( d \) is:

\[
T = \frac{I(1 - R)^2 e^{-\alpha d}}{1 + R^2 e^{-2\alpha d} - 2Rcos2\delta}
\]  

where \( I \) is the intensity of the incident light, \( \delta = \frac{2\pi nd}{\lambda} \) is the phase shift, with \( \alpha \) the absorption coefficient, \( R \) the reflectivity, and \( n \) the index of refraction at the wavelength \( \lambda \). The reflectivity of π-conjugated polymer films is generally low, and the non-uniformity of the surface of films cast from solution tends to cancel out interference effects such that the approximation:

\[
T = Ie^{-\alpha d}
\]  

can be made. When the optical density, \( \text{OD} = \alpha d \) is less than one, it is obtained from the formula \( \text{OD} = \frac{[T^{\text{ref}}] - [T^{\text{sample}}]}{[T^{\text{ref}}]}, \) where \( T^{\text{ref}} \) is the transmission obtained through a
transparent substrate for the case of film, and through a cuvette of solvent for the case of solution.

Photoluminescence (PL) measurements are performed by exciting the sample using a cw-laser source (Coherent, Ar⁺) where the energy of the incident photons exceeds the optical gap of the polymeric semi-conductor. A certain fraction of the incident laser photons will be absorbed and generate excitons, and a fraction of these excitons will recombine to the ground state by emitting a photon. The PL spectrum is detected by focusing the emission onto the entrance slit of a Cornerstone 260 1/4m monochromator using a concave mirror and collecting the resulting dispersed emission by a photodiode detector at the exit slit. A series of long pass filters at the entrance of the monochromator avoid the detection of scattered laser light and higher-order harmonics. A SR830 DSP Lock-In amplifier is used to collect the output from the photodiode after amplification by a trans-impedance amplifier. The reference frequency of the lock-in amplifier is provided by a mechanical chopper placed in the beam path of the laser light. The PL is thus collected in-phase with the laser excitation.

The lowest energy absorption band of π-conjugated polymers is due to a molecular exciton transition. This electronic transition will couple to the dominant vibrational modes of the the excited state in accordance with the Frank-Condon principle, which states that the oscillator strength of a transition is proportional to the square of the overlap (in momentum space) of the nuclear wave functions. Similarly, the transition from the exciton state to the ground state responsible for PL will couple to the dominant vibrational modes of the ground state. We therefore generally observe multiple peaks due to radiative transitions between one pair of electronic states (i.e. the ground state and 1^1B_u). We label these vibronic transitions accordingly with the 0-0 transition being the highest (lowest) energy transition for PL (absorption) and subsequently the 0-1, 0-2, etc. states for transitions of decreasing (increasing) energy.

Photoluminescence Quantum Efficiency (PLQE) PL quantum efficiency was measured using an integrating sphere technique [42]. The exit port of an Oriel Integrating Sphere
is coupled to the entrance slit of a Cornerstone 260 1/4m monochromator to obtain the emission and excitation spectra inside the sphere. The sample is mounted in the center of the sphere and the excitation source is directed at the sample through a small inlet port. The rest of the sphere is closed and the interior is coated with a BaSO₄ diffusively reflective coating that distributes any light source in the visible to near-infrared range uniformly throughout the volume of the sphere. The excitation source was the 488nm line from a Coherent Ar⁺ laser. The experiment is carried out in three parts using three experimental geometries. In geometry (a), the sphere is empty (contains no sample) and the laser is directed inside. The laser spectral profile is recorded and the integral of this spectrum is referred to as $L_a$. In geometry (b), the sample is placed in the sphere and indirectly illuminated by the laser, by directing the laser beam to strike the interior sphere wall before it strikes the sample. Both the laser profile and the sample emission spectrum are recorded. The integrals of these two signals are referred to as $L_b$ and $P_b$ respectively. In geometry (c), the sample is directly illuminated by the laser beam. Both the laser profile and the sample emission spectrum are recorded. The integrals of these two signals are referred to as $L_c$ and $P_c$ respectively.

PLQE is defined as the number of photons emitted by the sample divided by the number of photons from the excitation source absorbed by the sample. Experimentally, it is calculated according to the equation

$$PLQE[\%] = 100 \times \frac{P_c - (1 - A)P_b}{AL_a}$$

where $A = 1 - (L_c/L_b)$ is the absorption of the sample at the excitation wavelength. The factor $P_b$ corrects for absorption of the transmitted and diffusively reflected laser light in geometry (c), which can give rise to additional emission from the sample. All spectra are corrected for the response of the detector (Si photodiode) and converted into units of photon density before the integration is performed.
2.1.2 Photo-induced Absorption (PIA)

This technique uses two light sources, one as pump, the other as probe, to generate and detect long-lived photoexcitations in the material under study. The pump is a cw-laser beam of frequency larger than that of the lowest optically excited state. The probe light source is a Tungsten lamp, of which the transmission through a film is dispersed through a monochromator and collected using solid state detectors appropriate to the energy range of interest (Si, InSb). The use of a Stanford Research SR830 DSP Lock-In amplifier assures that only the transmission due to the pump excitation is detected. The reference frequency of the pump is set by use of a mechanical chopper. Thus, the chopper frequency sets the time scale of the process measured, namely, the non-radiative decay of photoexcitations. The modulation frequencies used in this work are from 100Hz to 20kHz, so that the characteristic lifetimes of the photoexcited species probed are in the range of milliseconds to microseconds.

The presence of the laser excitation gives rise to change in the transmission, $\Delta T$, which is related to the change in the absorption $\Delta \alpha$ through:

$$\frac{\Delta T}{T} = -\Delta \alpha d = \sigma n_{ph}d$$  \hspace{1cm} (2.4)

where $n_{ph}$ is density of photoexcitations and $\sigma$ is their optical cross section. Since the total density of electrons is conserved, changes in absorption must obey the sum rule:

$$\int_0^\infty \Delta \alpha(\omega) d\omega = 0$$  \hspace{1cm} (2.5)

which means that the spectral weight of induced absorption must be equal to the spectral weight of photobleaching of the ground-state absorption. The absorption of the laser leads to the generation of excitons. Some of these will recombine radiatively and give rise to PL. Thus, the incidentally collected PL signal is subtracted off after measuring
it separately with the probe beam blocked. Many excitons will recombine to the ground state non-radiatively, giving rise to a quasi-equilibrium of excitations that populate trap-states, \( n_{ph} \). It is the optical transitions from these trap states to higher states that are detected with the PIA method. In this way, charged excitations, such as polarones formed when excitons are dissociated at chain defects and through interchain-interactions, as well as neutral excitations, such as triplet excitons formed by intersystem crossing due to spin-orbit coupling, can be observed.

**Pump Frequency Dependence and Intensity Dependence**

The kinetics of the photoexcited species observed in PIA measurement can be accessed by means of modulation of the chopper frequency and thus the pump frequency. The rate of change of a photoexcited population is given by:

\[
\frac{dn_{ph}}{dt} = \eta g I - \gamma_{\beta} n_{ph}^\beta
\]  

where \( I \) is the laser intensity, \( \eta \) is the quantum efficiency for photogeneration of the species, \( g \) is the generation coefficient given by \( g(\omega) = (\hbar \omega d)^{-1}(1 - R)(1 - e^{-\alpha d}) \), \( \beta \) is the order of recombination, and \( \gamma_{\beta} \) is the recombination rate which will depend on the recombination mechanism. There exist two ideal types of the latter, namely, monomolecular recombination where \( \beta = 1 \), and bimolecular recombination where \( \beta = 2 \). These two scenarios can be distinguished experimentally by studying the dependence of the PIA signal with the pump intensity. For monomolecular recombination, a linear dependence on pump intensity is obtained. While for the bimolecular case, the signal will depend on the pump intensity with power 3/2 at low intensity and show a crossover to the expected square-root dependence at a high intensity. Even if the recombination order is known, the solution to Equation 2.6 for the whole frequency range of interest may require numerical computation subject to the appropriate boundary conditions. In any case, it has been shown for the assumption of a single lifetime \( \tau \) that \( \tau = (f^*)^{-1} \), where \( f^* \) is the pump modulation frequency at which the in-phase and quadrature PIA signals are equal in magnitude [43]. Thus, the modulation of pump frequency and pump intensity allows
for the determination of the recombination mechanism and lifetime of the photoexcited species in question. Furthermore, in the case that the PIA spectrum is a superposition of absorption features from multiple species, these analytical techniques may be used to distinguish them and thus aid in the identification of the features.

Temperature Dependence of PIA Every photo-excited species that gives rise to an optical transition in cw-PIA may be thought of as a trap state that prevents the excitation from returning to the ground state. It follows that during cw-excitation the population densities of these states will show a Boltzmann-like temperature dependence [44]. In particular, we note the steady state solution to Equation 2.6 yields:

\[ n_{ph}(T) = \left( \frac{\eta g I}{\gamma \beta} \right)^{\frac{1}{\beta}} \propto \left( \frac{1}{\gamma \beta(T)} \right)^{\frac{1}{\beta}} \]  

where in the last step we have assumed the generation rate \( \eta \) is independent of temperature over the experimental range \( T < 300K \). Usually a sum of Boltzmann factors can describe the temperature dependence of the recombination rate with characteristic “activation energies” which describe the trap depth (see equation 3.3). In general, the larger the activation energy and the lower the temperature the longer the photo excitation lifetime. As with the pump intensity and frequency dependence, in the event that multiple peaks due different photoexcited species are observed, temperature dependence of each PIA signal may distinguish them by the difference in their respective activation energies.

2.1.3 Electroabsorption Spectroscopy (EA)

Electroabsorption measures the change in transmission through a film by application of an electric field. This will, in principle, be described by a sum of field-induced changes in absorption and reflectivity. However, the changes in reflectivity are generally much smaller than the induced changes in absorption and to a good approximation can be neglected [45, 46]. Thus, the normalized change in transmission can be described as
arising solely from the induced absorption:

\[
\frac{-\Delta T}{T} = \Delta \alpha d
\]  

(2.8)

This induced absorption can be described through perturbation theory leading to the well
known Stark effect which describes the change in the transition frequency as [47]

\[
\Delta \omega = -\Delta \mu \cdot F - \frac{1}{2} F \cdot \Delta \tilde{p} \cdot F
\]  

(2.9)

where \(\Delta \mu\) is the change in the dipole moment and \(\Delta \tilde{p}\) is the change in polarizability
between the ground and excited state, and \(F\) is the electric field vector. For symmetric
molecules such as \(\pi\)-conjugated polymers, the linear term will be zero and only the
quadratic Stark effect will be observed. This term will lead to a feature that follows the
first derivative of absorption \(\partial \alpha / \partial \omega\), and is one of the two main features observed in the
EA spectra \(\pi\)-conjugated polymers. The second common feature observed will be induced
absorption to otherwise optically forbidden \((A_g)\) states, due to the field redistribution of
oscillator strength. This arises for \(A_g\) states that have strong dipole coupling to the optical
allowed \(1^1B_u\) exciton. This can be understood by realizing that more formally, the EA
signal is proportional to the imaginary part of the third-order susceptibility [45].

\[
\frac{-\Delta T}{T} = \Delta \alpha(\omega) d = \frac{4\pi\omega}{nc} \text{Im}[\chi^{(3)}(-\omega; \omega, 0, 0)] F^2 d
\]  

(2.10)

The two zero input frequencies in Eq. 2.10 are attributed to the quadratic field effect ,
while the third non-zero input frequency is from the optical field (because the frequency
of the field modulation is much lower than the optical frequency, it can be taken to be
zero). It has been shown that a four essential states model can be used to adequately
describe the EA of \(\pi\)-conjugated polymers [45, 46, 48]. They are the ground state \((1^1A_g)\),
the lowest optically allowed excited state \((1^1B_u)\), the state most strongly coupled to the
\(1^1B_u\) \((mA_g)\) and the next lowest \(B_u\) state \((nB_u)\) which is strongly associated with the
onset of continuum states [46, 48].
In the experiment, the field is applied by the use of a special substrate with lithographically-patterned interdigitated electrodes 20µm wide and 100nm thick, separated by 20µm gaps (Figure 2.1a). The films are deposited on this substrate and placed inside a Janis helium-exchange cold-finger cryostat equipped with electrical terminals and windows for optical access. Electrical contact is made between the substrate electrodes and voltage terminals by means of gold wire and Indium solder. The field is applied by means of a Stanford Research DS345 function generator in series with a step-up transformer leading to field strengths of up to $10^5$ V/cm. The transmission through the film from a Tungsten-halogen probe beam is dispersed by a Cornerstone 260 1/4m monochromator and collected by a Si photodiode. The signal is recorded by a Stanford Research SR830 DSP Lock-In amplifier set to the second harmonic of the field modulation frequency (no signal was observed at the fundamental) for $\Delta T$ and to a reference frequency set by a mechanical chopper for the unmodulated transmission. All experiments were performed with the sample temperature at 10K.

Figure 2.1: Experimental apparatus for measuring the electroabsorption of conjugated polymer thin films: (a) 20x optical microscope image of the lithographically-patterned EA substrate. (b) Schematic of the optical and electronic equipment set-up.
2.1.4 Transient Photo-induced Absorption*

For the transient PM spectroscopy in the mid-infrared spectral range we employed the
fs two-color polarized pump-probe correlation technique using a low-power (energy/pulse
\(\approx 0.1\) nJ), high repetition rate (\(\approx 80\) MHz) laser system based on Ti:sapphire (Tsunami,
Spectra-Physics), and an optical parametric oscillator (OPO; Opal, Spectra-Physics) that
spans \(\hbar \omega \text{(probe)}\) from 0.24 to 1.1 eV [49]. The pump beam (\(\approx 100\) fs pulse duration) was
frequency doubled to \(\hbar \omega \text{(pump)} = 3.1\) eV, and subsequently both pump and probe beams
were focused on the sample film to a spot of \(\approx 50\) \(\mu m\), with resulting photoexcitation
density \(\approx 10^{16}/cm^3\). For the transient PM in the visible/near-infrared spectral range we
used a high power (energy/pulse \(\approx 10\) \(\mu J\)), low-repetition rate (\(\approx 1\) kHz) fs laser system
with pump \(\hbar \omega \text{(pump)} = 3.1\) eV and \(1.3\) eV < \(\hbar \omega \text{(probe)}\) < \(2.5\) eV based on supercontinuum
white light generation [49]; in this case the photoexcitation density was \(\approx 5 \times 10^{17}/cm^3\).
The transient PM was obtained from \(\Delta T/T(t)\), the fractional change, \(\Delta T\) in transmission,
\(T\) using a phase sensitive lock-in technique, where negative PM is due to photoinduced
absorption (PA) and positive PM is due to photo-bleaching (PB). For retrieving the
ultrafast response below the system temporal resolution of \(\approx 150\) fs, we analyzed the
obtained PM transients using a convolution scheme of the transient response with the
pump/probe cross-correlation function [50].

* These measurements were performed by Prof. Zev Valy Vardeny’s research group at
the University of Utah.

2.2 Device Fabrication Methods

For both device structures below, fabrication began with a 1” x 1” piece of ITO coated
glass (Delta Technologies, Limited; sheet resistance \(\approx 10\Omega\) This was patterned into
four - 2mm \(\times\) 10mm rectangular electrodes using photo-lithographic techniques. The
patterned electrodes were then cleaned by rinsing with detergent and DI-water followed
by sonicating in Acetone then IPA for for 20min. each. These substrates were further
exposed to UV-ozone (NOVASCAN) treatment for 15 min. All subsequent steps were performed inside an MBraun glovebox in an inert nitrogen based atmosphere with < 50 ppm \(O_2\) content to prevent contamination during processing.

2.2.1 Conventional, 2mm \(\times\) 2mm Diodes and OPVs

PEDOT:PSS (Clevios) was passed through a 0.45 \(\mu\)m filter and then applied to the patterned electrodes by spincoating at 6000 rpm for 60 s. Samples were then baked at 120 \(^{\circ}\)C for 30 min to remove excess water. Active layer solutions were formed by dissolving the polymer in various organic solvents at various concentrations (typically between 5 mg/mL and 40 mg/mL). For OPVs, PCBM was added to these solutions at a 1:1 weight ratio with the polymer. About 80 \(\mu\)L of the active layer solution was then applied by spincoating in the range of 400 rpm to 1500 rpm, depending on the desired thickness, for 60 s. This layer was then allowed to dry for several hours and the edges of the substrate were wiped clean of excess material to provide for contact areas. Finally, Aluminum electrodes were deposited on top of the active layer film by Thermal Vapor Deposition (TVD) using an Ångström engineering TVD chamber inside the glovebox. These depositions were performed in vacuum at a pressure of \(\approx 10^{-6}\) Torr. Typical deposition rates were 2 \(\AA/s\). Four 2mm \(\times\) 10mm rectangular electrodes were formed by depositing the metal through a shadow mask, with orientation of these rectangular electrodes perpendicular to the ITO electrodes underneath. The resulting substrate then contains four 2mm \(\times\) 2mm devices as defined by the intersection between the ITO bottom electrode and the Al top electrode.

2.2.2 Inverted, 2mm \(\times\) 2mm Diodes and OPVs

Fabrication of inverted device structure was similar to that of the conventional structure but with the PEDOT:PSS HTL replaced by a ZnO ETL in order to functionalize ITO as a cathode. The ZnO layer was formed by the sol-gel precursor method following an
established procedure [38, 39]. The sol-gel precursor was formed by dispersing 0.6681g of Zinc acetate into 4.775mL of 2-Methoxyethanol with the aid of a magnetic hot-plate and stir-bar set at 60°C. After 1 hour of stirring, 0.225mL of ethanolamine was added, followed stirring at 60°C for an additional 2 hours. The sol-gel precursor was then applied by spincoating at 2000rpm for 60s. Films were then thermally converted into ZnO by baking the samples at 275°C, and allowed to cool to room temperature. Active layers were then deposited as described for conventional devices. Finally, gold electrodes were deposited on top in an identical manner to that for the Al deposition for conventional devices.

2.3 Morphological Characterization

2.3.1 Grazing Incidence X-ray Diffraction (GIXRD)

Grazing Incidence X-ray Diffraction (GIXRD) was performed on a Phillips X-ray Diffractometer with a 1.54 Å X-ray source. The incident angle was 1° and the 2θ scan was performed in the axis perpendicular to the plane of the film. Drop cast films on sapphire and Si(010) substrates were used for these measurements, after subtracting the background signal from the bare substrate (if any).

2.3.2 Atomic Force Microscopy (AFM)

AFM measurements were carried out utilizing a Veeco Dimension 3100 AFM. The AFM was set on tapping mode, the tip velocity of the cantilever was set to 20μm/sec and 10μm × 10μm Height (shows the surface profile) and phase (reveals the phase composition) images were generated. This size allowed us to view an ensemble of the topology of each sample.
2.4 Device Characterization and Charge Transport Studies

2.4.1 Current-Voltage Characteristic (J-V)

Current-voltage characteristics of diodes and photovoltaic devices was achieved using a Keithley 238 High Current Source-Measure unit. Voltage was the applied source and the current was measured. A voltage sweep was performed through automated computer interfacing using Labview. Contacts were made using alligator clips, sometimes aided by conductive silver paste.

For OPV characterization, J-V curves were measured in the presence of illumination from a Xenon arc lamp equipped with an AM 1.5 filter to mimic the solar spectrum irradiance distribution at the earth’s surface at an incident angle of 37°, calibrated to an intensity of 100mW/cm².

2.4.2 External Quantum Efficiency (EQE)

External Quantum Efficiency (EQE), also known as Incident Photon Converted Electron efficiency (IPCE) measures the spectral response of a photo-diode. To perform these measurements, monochromatic light was generated focusing light from either a Tungsten-halogen lamp or a Xenon arc lamp into a Cornerston 260 1/4m monochromator. The light emitted from the exit slit was then focused onto the device using a spherical lens while maintaining a controlled area smaller than the device area by means of an iris. The current was then measured as a function of the wavelength of incident light using a Keithley 196 multimeter. The resulting photocurrent spectrum is then normalized by the incident photon density to obtain the percent of electrons collected to the number of incident photons and at the wavelength $\lambda$ according to the equation

$$EQE(\lambda)[\%] = 100 \cdot \frac{\lambda I_{ph}(\lambda)}{1240 W_{inc}(\lambda)}$$

(2.11)
where $I_{ph}(\lambda)$ is the photocurrent in Amps, and $W_{inc}(\lambda)$ is the incident power density in Watts/cm$^2$ measured using a thermopile (.105 V/W) connected to a Ke2000 multimeter.

### 2.4.3 Temperature and Field Dependent Photoconductivity (PC)

Photoconductivity was measured from diodes fabricated according to procedures described in Section 2.2. Devices were illuminated through the transparent ITO electrode using a cw-laser source (Coherent, Ar$^+$) modulated by a mechanical chopper. The current was recorded as the voltage drop across a resistor of resistance that was small compared to the device series resistance by a Stanford Research SR830 DSP Lock-In amplifier referenced to the chopper frequency. Devices were mounted in a Janis helium-exchange cold-finger cryostat equipped with windows and voltage terminals for electrical contact. The applied voltage was from a Keithley 238 High Current Source-Measure unit and the field $F$ is calculated as $F = V/d$ where $d$ is the thickness of the active layer of the diode, as measured by a Dektak D150 profilometer.
3 PHOTOPHYSICS OF PTV-C12-CR SERIES

3.1 Note to Reader


3.2 Introduction

As mentioned in Chapter 1, various π-conjugated polymers have been successfully employed in optoelectronic device applications. Notably, poly(3-hexylthiophene) (P3HT), an alkyl substituted polythiophene derivative, has been successfully employed in organic photovoltaics (OPVs) [51, 52] and organic field-effect transistors (OFETs) [53]. Additionally, derivatives of poly(phenylene vinylene) (PPV) have been widely used in OPVs and organic light-emitting diodes (OLEDs).

Poly(thienylenevinylene) (PTV) is a non-degenerate ground state conjugated polymer with a structure which is considered similar to polythiophene or PPV (see Figure 3.1). It was recognized that the vinylene linkage between phenylene units as compared to the parent poly(para-phenylene) (PPP) led to a decreased band gap through a reduction in the aromatic resonance energy and enhanced electron delocalization [27]. In this regard, PTV may be considered the thiophene analog of PPV. It indeed exhibits a lower optical band gap than polythiophene derivatives and could thus provide a better match with the solar spectrum in OPV application [54, 55]. The oxidation potential of this polymer...
is low, in favor of stabilization of excitonic states [56]. Good hole mobility has been demonstrated in OFETs of PTV [57]. However, devices fabricated with this material so far have yielded very low efficiencies [58, 59, 60, 61, 62]. Electron transfer between these systems and $C_{60}$ fullerene molecules has been suggested [63], although a study in the ultrafast regime suggests this process may be quite inefficient [64]. It is currently unclear whether the low efficiencies observed in PTV based solar cells to date are due to poor charge transfer or other unknown reasons, and more detailed optical and structural investigations need to be conducted to realize the potential of this polymer.

Figure 3.1: Chemical structures of the polymers discussed in the introduction. The dashed rectangle shows the unit cell in each case. (a) Polythiophene (b) Poly-(para-phenylene) (c) Poly(thienylenevinylene) (d) Poly(pheneylenevinylene)

Regio-regularity (RR) has been shown to improve the crystallinity of solution cast films of poly(alkylthiophenes) with respect to their regio-random (RRa) counterparts [22]. This increases the strength of interchain interactions and results in higher mobility [23], and a lower optical band gap [24], both of which lead to improved performance in OPV application [65]. For the first time, a series of poly(3-dodecylthienylenevinylene) with controlled regioregularity (PTV-CR) were synthesized via a Horner-Emmons reaction using two isomeric co-monomers with molar ratios from 0:10 to 5:5 [54, 66].

Here, an optical investigation of PTV-CR, with controllable regio-regularity from regio-random PTV-5:5 (25% head-tail) to regioregular PTV-0:10 (100% head-tail) (see Figure 3.2), is presented as an attempt to obtain a better understanding of the photogenerated
excited states and their respective recombination mechanisms. By studying the regioregularity effect of this novel series of PTV, more can be learned about the microscopic arrangement and the subsequent balance of intrachain versus interchain coupling in π-conjugated polymer films. In particular, the photo-induced absorption (PIA) technique is employed to detect long-lived sub-gap states (see Chapter 2). Through analysis of the intensity, frequency and temperature dependence of the absorption associated with these states, much has been learned about the decay mechanisms for photo-generated excitons in this interesting material. Combined with doping induced absorption (DIA) and thermally modulated absorption (TMA), we hope to derive the regioregularity effect on the electronic levels in PTV-CR, and thus help to improve the performance of PTV based photovoltaic devices.

Figure 3.2: Synthesis scheme and molecular structure of C12-PTV-a:b (PTV-CR). The a:b ratio defines the regioregularity order, with 0:10 containing 100% head-to-tail coupling (regioregular, RR-) and 5:5 containing 25% head-to-tail coupling (regiorandom, RRa-).

3.3 Regioregularity Effect on the Photophysics of PTV-C12

3.3.1 Absorption and Photoluminescent Properties

In Figure 3.3a, the absorption spectra in films of the six PTV-CRs are shown together. The onset of absorption, or band edge, shows a blue-shift with increasing
Figure 3.3: (a) Absorption spectra of films of PTV-CR; (b) comparison of absorption spectra of films (line) and solutions in DCB (line+symbol) of PTV-0:10 (regular, red) and PTV-5:5 (random, black). Inset shows the shift of band edge in film and solution versus regioregularity.

regioregularity. The band edge occurs at 1.61eV for regiorandom PTV-5:5 and 1.70eV for regioregular PTV-0:10. This indicates that the effect of regio-regularity in PTV-CR is very different from the case for poly(3-hexylthiophene) (P3HT), where a significant
redshift of the absorption onset ($\approx 0.32$eV) from regiorandom (RRa-P3HT) to regioregular (RR-P3HT) was observed and explained by energy level splitting caused by the strong interchain interaction [25]. In the same case it was found that the peaks due to the vibronic levels of the excited states could only be resolved in RR-P3HT, whereas the broader distribution of conjugation length in RRa-P3HT smeared out such structures [24, 25, 21]. The vibronic levels are apparent in the spectra of all PTV-CRs, with no correlation to regioregularity. As a matter of fact, the spectrum shape is more broad and featureless for regioregular PTV-0:10, which might be from inhomogeneity in PTV-0:10 film morphology, since this polymer is the least soluble among the PTV-CR series [54, 66]. The poor solubility may also contribute to the blueshift of absorption onset. Measurement of HOMO-LUMO levels in PTV-CR reveals that PTV-0:10 (regioregular) has larger electronic band gap than that of PTV-5:5 (regio-random) by 0.06eV [66].

As the optical gap of $\pi$-conjugated polymers is considered to be directly related to the conjugation length, the average conjugation length in these films may be estimated by comparison with nTV oligomers [56, 67] It appears the conjugated segment extends to 10 to 12 monomers. It should be noted that this polymer’s absorption spectra largely resemble those of its corresponding oligomers of large $n$ [56]. The energetic spacing between the vibronic levels here is 0.18eV in all cases. Thickness measurements yield a value for the absorption coefficient of $\approx 10^5 \text{ cm}^{-1}$, which is similar to the absorption coefficient of P3HT [65].

Figure 3.3b shows the band edge shift, $\Delta_{\text{bandedge}}$ in PTV-0:10 (regioregular, red) and PTV-5:5 (regiorandom, black) upon going from film (line) to solution (symbol). In the case of PTV-0:10, $\Delta_{\text{bandedge}}$ is 0.07eV, whereas in PTV-5:5, $\Delta_{\text{bandedge}} = 0.17$eV to the blue. The inset of Figure 3.3b is the plot of $\Delta_{\text{bandedge}}$ vs. regioregularity (RR), and a trend of reduced $\Delta_{\text{bandedge}}$ with increased RR was observed, which means the more ordered arrangement of side chains prevents coils of polymer backbones in solution. The fact that the vibronic levels are as well resolved in film as in solution suggests most chains are well separated and ordered in these films.
The exception of PTV-4:6 is rather puzzling. At first, it was expected that this was due to aggregation, as this material shows poorer film morphology than the others, characterized by visible aggregates and surface roughness. However, the fact that we do not observe a reduced slope of the band edge in PTV-4:6 comparing with others indicates disorder alone cannot explain the resemblance of PTV-4:6 to PTV-0:10. In light of this, there exists the possibility of block copolymer formation during the synthesis, although the relative reactivity of the two monomers used are similar so efficient copolymer formation is not expected [66]. Perhaps the arrangement of the long alkyl-chain relative to the thiénylenevinylene unit assists in block copolymerization. Currently, investigations are underway to understand the strange behavior of this particular material.

Figure 3.4: (a) Thermally modulated absorption (TMA) of PTV-0:10 film (red solid circle) obtained by [T(RT) − T(10K)]/T(10K). Also shown is the absorption spectra at RT (black line) and 10K (red line); (b) A comparison of the TMA for all six PTV-CRs. The inset displays the variation of 0-0 transition at 10K versus regioregularity (peak position, black circle; peak intensity, red circle).
Table 3.1: Various Vibronic Replicas in Absorption of PTV-0:10 at RT (300K) and Low Temperature (10K).

<table>
<thead>
<tr>
<th>Temperature</th>
<th>0-0</th>
<th>0-1</th>
<th>0-2</th>
<th>0-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>low T (10K)</td>
<td>1.75eV</td>
<td>1.91eV</td>
<td>2.08eV</td>
<td>2.26eV</td>
</tr>
<tr>
<td>RT (300K)</td>
<td>1.85eV</td>
<td>2.03eV</td>
<td>2.21eV</td>
<td>2.39eV</td>
</tr>
</tbody>
</table>

The well-defined vibronic structure is further elucidated in Figure 3.4, where the thermal modulation of absorption (TMA) is shown. Figure 3.4a shows the absorption of PTV-0:10 at both 300K (room temperature, RT) and 10K, along with the resulting differential spectrum, which is calculated by \((T(RT) - T(10K))/T(10K)\). The band edge red-shifted 0.1eV as the sample was cooled down to 10K. The minima in the differential spectrum (black arrows) correspond with the vibronic peaks at room temperature (RT), whereas the maxima (red arrows) show these at 10K. The phonon energy which defines the vibronic levels in this polymer was 0.18 eV at room temperature, and slightly smaller (0.17eV) at 10K. Our result is consistent with a previous publication about PTV [68]. Table 3.1 lists these replica energies. In comparing the TMA of all PTV-CRs (Fig. 3.4b), it is seen that the minima are sharper and more easily resolved in the more regioregular polymers (PTV-0:10, 1:9, 2:8). Additionally, the magnitude of the 0-0 peak at 10K for the regiorandom PTV-5:5 (truncated in Fig. 3.4b) is much larger than for the others, indicating that this polymer is much more susceptible to thermal perturbation and has larger electron-phonon interaction, maybe due to the easier deformation of polymer backbones from less regular side chain arrangement. The inset of Figure 3.4b shows the variation of 0-0 peak versus regioregularity. As can be seen, while the peak position blue shifts, the peak intensity decreases, with increased regioregularity.

For the PTV-CRs studied here, only the regioregular PTV-0:10 has measurable PL in solid state, with photoluminescence quantum efficiency (PLQE) \(\approx 10^{-4}\). Figure 3.5a shows the PL of PTV-0:10 film at room temperature (300K) and low temperature (10K). Both PL contains one peak (0-0) at 1.38eV, and another peak (0-1) at 1.27 eV, as well as a broad shoulder around 1.52 eV. There is negligible variation of PL with temperature, meaning nonradiative recombination mechanisms such as phonon emission or disor-
Defects do not play an important role, as with most polymers. Nor was interchain interaction a factor, as in the case of P3HT. Other mechanisms such as oxidization of thiophene rings was invoked to explain the weak PL in PTV [71]. However, we have measured the PL of fresh and aged PTV-0:10, and found no significant change in terms of either spectra or PLQE.

Figure 3.5: (a) PL of PTV-0:10 (regioregular) film at room temperature (black line +solid square) and 10K (red line +solid square); (b) PL of four PTV-CRs in dilute dichlorobenzene solution (0.01mg/ml).

![Figure 3.5](image.png)

Figure 3.5b shows the PL of PTV-CR in very dilute dichlorobenzene solution (0.01mg/ml), and PLQE ≈ 2x10^{-4} for PTV-0:10 (regioregular), whereas PLQE < 10^{-5} for PTV-5:5 (regiorandom). Therefore the weakness of PL cannot be caused by the film quality [68],
but rather is intrinsic in nature. In order to explain the small PLQE in PTV within Kasha’s rule, the photogenerated \(1^1B_u\) exciton should undergo an internal conversion into a “dark” exciton with smaller energy [72]. According to the selection rules in \(\pi\)-conjugated polymers, the “dark” exciton should be an even-parity state \((2^1A_g)\) [48]. We thus conclude that the dark exciton in PTV-CR is in fact the \(2^1A_g\) state, which has been extensively discussed in the literature in relation with the photophysics of \(\pi\)-conjugated polymers and oligomers [63, 72, 48]. Particularly, electroabsorption of PTV synthesized by thermal conversion of precursor polymer gave supportive evidence of the \(2^1A_g\) exciton being below \(1^1B_u\) [45]. As a matter of fact, it is no surprise that the lowest lying exciton in PTV is the dark \(2^1A_g\). It turns out that any replacement of the C=C double bond in polyacetylene, the simplest conjugated polymer, by other groups (i.e., phenylene, thiénylene, triple bond etc.) will increase the overall dimerization of the polymers, and therefore increase the dimerization contribution to the optical bandgap compared to the electron correlation contribution [20]. For small dimerization contribution to the optical gap, the system is highly correlated and the \(2^1A_g\) occurs below the \(1^1B_u\). Conversely, for large dimerization contribution, one-electron theory begins to win and \(2^1A_g\) is above the \(1^1B_u\).

PTV and PT (polythiophene) are similar in the way that the replacement group is the same thiénylene, however, PTV has smaller dimerization contribution (alternate double bonds replaced by thiénylene) compared to polythiophene (all double bonds replaced by thiénylene) (see Fig. 3.2). It was reported previously that the \(2^1A_g\) is barely above the \(1^1B_u\), and the order can easily be reversed via, for instance, modification of intermolecular interaction [73]. Another interesting point is that PTV has the same small gap of trans-polyacetylene (1.6 eV) and even smaller gap than crystalline PTS-polydiacetylene [74]. Thus the occurrence of the \(2^1A_g\) below the \(1^1B_u\) is to be anticipated theoretically.

Comparing with film PL of PTV-0:10, the solution PL also contains two peaks, one (0-0) at 1.78eV, another (0-0) at 1.78eV (Fig. 3.5b). The blue shift of the 0-0 transition of 0.40 eV from dilute solution to film was expected, as the polymer chains go from isolated to close packed form, indicating the presence of energy transfer among segments of different conjugation lengths in the films. The Stokes shift for PTV-0:10, \(\Delta\), were 0.48eV for film
and 0.12eV for solution. The evolution of PL in solution with decreased regioregularity is very interesting. With reduced regioregularity, the relative oscillator strength of 0-0 peak was also reduced, which might be due to more chain coil shortening the effective conjugation length of the polymer, and more emission would come from shorter segment (at higher energy). PL completely vanished in the most random PTV-5:5, therefore we still observed the effect of disorder induced non-radiative recombination in PTV-CRs. Not only so, the formation of long-lived triplets was more pronounced in the more random PTV-CR, which further quenches PL, as will be explained in Figure 3.9.

### 3.3.2 Crystallinity of PTV-C12-CR

The effect of alkyl side group arrangement on the polymer chain packing in film has been investigated by Grazing Incidence X-ray diffraction (GIXRD). The results are displayed in Figure 3.6a for the most regular (0:10) and most random polymer (5:5). Similar results were observed for other derivatives studied here. The regular arrangement of polymer chains is evident from the large scattering signal collected as well as the appearance of multiple harmonics of the fundamental (100) peak. However, there is essentially no correlation between crystallinity and regioregularity (RR) as all the polymers studied here show diffraction peaks with similar spacings (Table 3.2). This is, again, in contrary to the case for poly(3-alkylthiophenes) (P3HT), where XRD peaks are significantly more prominent in RR-P3HT film [75]. The structural rigidity provided by the vinylene linkage of thiophene rings could be responsible for the crystalline order despite the randomly oriented alkyl chains. Regioregularity in PTV-CR is interesting for this reason, because even the random films show microscopic order. However, the subtle difference in GIXRD data still revealed the second order effect of RR, namely intra-chain ordering. The lattice spacing attributable to the (100) peak is 18.2 Å ± 0.5Å in all cases. This is comparable to what is expected from a 12 carbon atom alkyl chain (≈ 1.5Å per C-C bond).
Figure 3.6: Grazing incidence X-ray diffraction measured in the out-of-plane geometry for films of PTV-0:10 (black squares) and PTV-5:5 (red circles) drop cast from DCB. (a) The full measured range while the inset magnifies the range between 1.15 and 1.85 wave numbers (in Å\(^{-1}\)) (b) The data from PTV-0:10 in the range between 1.15 and 1.6 Å\(^{-1}\) fit to a sum of two Gaussians (solid red line) showing the methodology used to extract the peak center and width. The individual component Gaussians are shown as dashed red lines.

Table 3.2: Summary of GIXRD Data for PTV-CR

<table>
<thead>
<tr>
<th>PTV-C12- (a:b)</th>
<th>lattice domain spacing (Å) size (nm)</th>
<th>lattice domain spacing (Å) size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(100)(^a)</td>
<td>(010)(^b)</td>
</tr>
<tr>
<td>0:10</td>
<td>18.7 11.4</td>
<td>4.48 2.73</td>
</tr>
<tr>
<td>1:9</td>
<td>17.9 6.28</td>
<td>4.42 1.57</td>
</tr>
<tr>
<td>3:7</td>
<td>17.7 6.40</td>
<td>4.42 1.17</td>
</tr>
<tr>
<td>5:5</td>
<td>18.4 6.28</td>
<td>4.34 1.18</td>
</tr>
</tbody>
</table>

\(^a\) Extracted from (200) peak as determined by a Gaussian fit.

\(^b\) Extracted from a two Gaussian fit as described in the text.

Thus the lattice vector assigned to this peak extends along the direction of the alkyl group, perpendicular to the backbone axis and \(\pi-\pi\) stacking directions. Since the out-of-plane geometry of GIXRD is only sensitive to repeat structures oriented perpendicular to the substrate and parallel to the plane of the film, the strong contribution of peaks from the (100) lattice vector indicates a preferential alignment of alkyl groups perpendicular to the substrate. This is similar to what has been observed for poly(3-hexylthiophene) [76]. The interchain distances (Table 3.2) in PTV-CR are much closer together than those of
poly(3-dodecylthiophene) which has the same alkyl side chain, and is just slightly farther apart than those of poly(3-hexylthiophene) [75]. This is significant, as it indicates the lack of interchain interaction in this material cannot be accounted for merely by the long alkyl group length. As shown in the inset of Figure 3.6a, the fourth harmonic of the fundamental (400) is much broader than the other harmonics, which may result from overlap with another peak of a different origin. In Figure 3.6b we demonstrate the procedure for extracting the parameters associated with this additional peak by fitting this broad peak to a sum of two Gaussians for the case of PTV-0:10. The lattice spacing along this direction (4.4 Å) is similar to what has been observed for P3HT [23] in the π-π stacking direction (010) and is assigned to this lattice vector. Again, because the diffraction signal is almost entirely from structures with periodicity perpendicular to the film plane in this experimental geometry, the observation of this (010) peak is evidence of a minority of crystallite domains with the alkyl group and backbone axes in the plain of the film.

Various methods of altering π-conjugated polymer film morphology by means of processing techniques have been described in literature. Two of these, thermal annealing [51, 76] and solvent variation [77, 78, 79] have proven particularly successful. In contrast to the dramatic effect on poly(3-hexylthiophene) [51, 77, 76], we only found minor effect on crystallinity in regiorandom PTV by these common morphology running methods. Figure 3.7 shows the effect of annealing the samples at 120 °C for 30min. The (100) peaks are hardly affected by the thermal perturbation at all. In both cases of RR- and RRa-PTV, a small increase in the peak wave number (corresponding to a small decrease in the lattice spacing) is observed. This can be attributed to the formation of more close-packed chains from thermal relaxation. The most significant effect, as shown in the inset of Figure 3.7, is on the regiorandom PTV (010) peak, which is drastically reduced. This observation suggests that the side-chain disorder is responsible for the minority orientation of crystallites with π-π stacking direction perpendicular to the film plane. The thermal agitation allows the more favorable (with alkyl group direction perpendicular to the film plane) orientation to be adopted.
Figure 3.7: Effect of thermal annealing on the GIXRD scan of PTVs: PTV-0:10 as cast (filled, black squares) PTV-0:10-annealed(open, black squares), PTV-5:5-as cast (filled, red circles) and PTV-5:5-annealed (open, red circles). The inset magnifies the region from $1.15\text{Å}^{-1}$ to $1.85\text{Å}^{-1}$.

This is consistent with the effect of solvent variation on the crystal structure as shown in Figure 3.8. Films of regioregular PTV (PTV-1:9) cast from different solvents show no variation in crystal structure (Figure 3.8a), other than a variation in the intensity of the diffracted signal which can be attributed to variations in film thickness. Meanwhile for regiorandom PTV (PTV-5:5), it is observed that films cast from more volatile solvents such as chloroform ($\text{CHCl}_3$) show a stronger predominance of the (010) peak. Due to the much lower boiling point of chloroform, the film is formed faster and does not allow enough time for the chains to self-organize, therefore a more random distribution of crystallite orientations is formed.
3.3.3 Non-radiative Photo-excitations

The photo-induced absorption (PIA) spectra of PTV-CRs are displayed together in Figure 3.9a. The PIA spectra contain three main PA bands: $P_1$ (0.33 eV), $P_2$ (0.93 eV) and T (1.2 eV). $P_1$ is due to a transition from the highest occupied molecular orbital (HOMO) to a mid-gap state, where as $P_2$ is due to a transition between two mid-gap states (Fig. 3.9b). The higher energy peak, T, is attributed to the formation of long-lived triplet excitons by intersystem-crossing or by singlet exciton fission [25, 80]. $P_1$ and $P_2$ are correlated to each other since they show similar recombination dynamics, as verified by measuring their dependencies on the laser excitation intensity and modulation frequency (see Fig. 3.11). In contrast, the PIA band denoted T in Figure 3.9a does not correlate with $P_1$ and $P_2$; its spectrum is much sharper and is absent in the quadrature PIA spectrum, showing that it is much faster than $P_1$ and $P_2$. Also the PIA shoulder at the polymer band edge (1.6 eV) may be due to electro-absorption photogenerated charge excitations and thermal modulation (see Fig. 3.4). PB at $\hbar\omega$ (probe) $>$ 1.6 eV is photo-bleaching of the ground state absorption. Figure 3.9b shows the energy diagrams of the most important
excited states and related optical transitions in the neutral (triplet) and charge (polaron) manifolds.

Figure 3.9: (a) PIA spectra of all six PTV-CR derivatives. The excitation is the 457nm line from an Ar+ laser at an intensity of 100mW/cm². The sample is held at a temperature of 10K. (b) Schematic energy diagram of the most important excited states in PTV-CR and related optical transitions in the neutral triplet manifold, and charge manifold for a positive polaron.

Figure 3.9: (a) PIA spectra of all six PTV-CR derivatives. The excitation is the 457nm line from an Ar+ laser at an intensity of 100mW/cm². The sample is held at a temperature of 10K. (b) Schematic energy diagram of the most important excited states in PTV-CR and related optical transitions in the neutral triplet manifold, and charge manifold for a positive polaron.
At the band edge, a strong oscillatory behavior is observed which is most likely due to thermal modulation, of the kind discussed in Figure 3.4, induced by laser sample heating. Since the thermally modulated absorption is of order unity (Figure 3.4b), this would account for the large magnitude of these oscillations as compared to that of the PIA which is of order $10^{-4}$. However, a super-imposed Frank-Keldysh band edge oscillation due to the presence of the charged polarons on the chain cannot be ruled out [81]. Electroabsorption (EA) measurement was utilized to further study this feature (see Fig. 3.13).

To further identify the various PIA bands, we measured the doping induced absorption (DIA) by exposing the PTV films to iodine vapor [82]. In Figure 3.10, two DIA bands are observed for each polymer, which are accompanied by infrared-active vibrations (IRAVs), thus confirming that they are indeed due to charged excitations [83]. From the two DIA bands we conclude that the charge excitations in PTV-CR are polarons [84], and therefore identify $P_1$ and $P_2$ bands in the PIA spectrum (Fig. 3.9a) as due to long-lived polaron photoexcitations. The DIA bands appear at higher energies than $P_1$ and $P_2$ bands upon photoexcitation (Fig. 3.9a); this is due to “pinning” by the accompanying dopant ion having opposite charge [12]. In contrast, the band T in the PA spectrum is not correlated with the DIA bands, and is therefore due to long-lived neutral excitations; which we thus identify as triplet excitons. Recent work on oligothienylenevinylene (OTV) has confirmed the triplet absorption for a 12 unit OTV with a triplet state at 1.06 eV [63]. We therefore estimate the triplet $1^3B_u$ level for PTV is at 1.0 eV (Fig. 3.9b). Further experimental work is ongoing to determine the exact value of this state.

As for the assignment of the photoexcited species, not only does the sharper spectral shape of the 1.2 eV (band T) distinguishes it from the other two PIA bands ($P_1$ at 0.33 eV, $P_2$ at 0.93 eV); but in Figure 3.11a, we show that the dependence of the PIA of band T on pump intensity, I, indicates that its recombination dynamics is different from that of $P_2$. $P_1$ has similar dependence as $P_2$, therefore the data of $P_1$ is not shown here. Both polaron and triplet photoexcitations exhibit nearly square-root dependencies for pump intensity above 50 mW/cm$^2$ (fit using $\Delta T \propto I^m$, where the exponent $m=0.43$.
and 0.39 for triplets and polarons, respectively), but at low laser excitation intensity the polaron band is super-linear, whereas the triplet band shows sub-linear dependence. The deviation from linearity in the near steady state conditions (low modulation frequency) is a signature of a bimolecular recombination mechanism [43] For this reason, both types of photogenerated species in PTV recombine bimolecularly. Bimolecular recombination is not as common for triplets, but has been observed before and was interpreted as evidence of triplet-triplet annihilation [43, 85].

![Figure 3.10: Doping induced absorption (DIA) spectra of three PTV-CRs with different regioregularities. Polaron absorption bands (DP\textsubscript{1} and DP\textsubscript{2}) and correlated ir-active vibrations (IRAVs) were shown.](image)

In light of these assignments, it is notable that the formation of triplets is more efficient in the more random polymers PTV-3:7 and PTV-5:5 (again, PTV-4:6 behaves more like a regio-regular polymer). The reduced triplet formation in more regular PTV-CR is in consistency with photoluminescence quantum efficiency (PLQE, η) results. For the most regular PTV-0:10, η ≈ 2x10^{-4}, and η < 10^{-5} (the instrument limit) for the most random PTV-5:5. The results displayed here show the effect of side chain arrangement in film can be crucial to the fundamental properties (i.e. triplet formation) of π-conjugated polymers. In this case, the PIA spectra of random PTV-5:5 is similar to that of its
Figure 3.11: (a) The pump intensity dependence of PIA of PTV-1:9 measured at a modulation frequency of 30Hz. Filled triangles are for the triplet excitation, T; open triangles are for the polaron $P_2$. The lines indicating linear fitting of experimental data based on $T I^m$; (b) the frequency dependence of PIA of PTV-5:5 for $P_2$ (solid circles) and T (solid lines) measured both in-phase (black) and in quadrature (red). The laser intensity is 40mW/cm2. In both cases the sample is at 10K while under illumination with the 457nm line from an $Ar^+$ laser.

Parent polymer synthesized by thermal conversion of precursor polymers, where photoexcitations are expected to be of an intrachain character [68]. The strongest effect of
reorregularity observed in PTV-CR is the suppression of a triplet state which depends on the placement of the $1^1B_u$ and $2^1A_g$ levels. Such an effect does not even require an interchain interaction. This property of PTV-CR suggests RR will likely be necessary to aid in electron transfer with n-type fullerenes if it is to be useful in OPV application (Details will be discussed in Chapter 5). In Figure 3.11b the dependence of the PIA on the pump modulation frequency, $f$, shows that the long-lived photoexcitations in PTV-CR have lifetimes on the order of milliseconds, as extracted from the crossing point frequency of the in-phase and quadrature PIA signals [86, 43]. Although the lifetimes of $P_2$ and T are similar, they are not identical. The triplet has a lifetime 1.3 times shorter than that of $P_2$. In random PTV-5:5, these lifetimes are 2.4 ms and 3.2 ms, respectively; whereas they are 4.7 ms and 5.7 ms, respectively in regular PTV-0:10.

The longer lifetime of these species as the regio-regularity increases indicates a decrease in the density of recombination centers in the more ordered polymer.

Figure 3.12 shows the temperature dependence of the PIA bands, namely, $P_2$ (0.93 eV) and T (1.2 eV), for three PTV-CR films. The measurement was done with low pump intensity and slow modulation frequency $f$ ($\frac{1}{f} \gg \tau_T$ & $\tau_{P_2}$). At higher temperatures, the decay of the PIA is due to thermal depopulation of the defect states and can be related to the trap energy depth. The triplet (T) absorption (Figure 3.12a) decays monotonically with a plateau region at low temperature. For PTV-5:5, the decay is very fast, which confirms the thermal sensitivity of the most random polymer; the plateau extends out to 75K for PTV-3:7 and to nearly 100K for PTV-1:9. To further understand the triplet kinematics, the experimental data were fit using a thermal activation model for traps in polymers [44]. The lines in Figure 3.12 show the results of fitting. The density of long-lived photoexcitations $n_{ss}$ at steady-state condition ($\frac{1}{f} \gg \tau$, where $\tau$ is the lifetime of the photoexcitation) is expressed by

$$n_{ss} = \left( \frac{aG}{b} \right)^\frac{1}{2}$$

(3.1)
where G is the pump light intensity and a is the generation rate, usually a constant with constant G, b is the recombination (decay) rate and is dependent on temperature and light intensity. Under constant illumination of pump light, \( b = b(T) \) mainly varies with temperature T. \( \mu \) is between 1 (monomolecular recombination) and 2 (bimolecular recombination), and can be obtained by the dependence of PIA signal on pump intensity (Figure 3.11). Under pump intensity of 40 mW/cm², \( \mu \) was determined to be 0.64 for triplet (see Figure 3.11a). Under constant pump intensity, equation (3.1) can be written as:

\[
n_{ss} \propto b(T)^{-\frac{1}{\mu}} \tag{3.2}
\]

where \( b(T) \) is usually described by thermal activation behavior, with the activation energy \( E_T \) of the trap state extracted from a fitting using

\[
n_{ss}(T) = A(e^{-\frac{E_{T_1}}{k_BT}} + Be^{-\frac{E_{T_2}}{k_BT}} + C)^{-\frac{1}{\mu}} \tag{3.3}
\]

where A is a scaling factor, \( E_{T_1} \) and \( E_{T_2} \) are the thermal activation energies for two trap states with B representing the relative weight of the activated process, and C is the T-independent part of the decay rate. When B is set to zero, the fitting is done using only one activation energy. The fitting results were shown in Figure 3.12 as magenta solid line (two activation energies) and green broken line (one activation energy). For triplet T (Fig. 3.12a), a better fitting was obtained using two activation energies, i.e., one shallow trap (\( E_{T_2} < 50 \) meV), and one deeper trap (\( E_{T_2} > 100 \) meV) for all three PTV-CRs. It can be seen that at T < 100K, shallow traps dominate the recombination of triplets. At higher temperature, the deeper traps above 100 meV dominate the recombination. This is why using one activation energy resulted in increase of error at higher temperature (T > 120K). The parameter B was at the order of \( 10^3 \) to \( 10^6 \) for the three PTV-CRs, indicating a dominant influence from the deeper trap. The fitting does not show a correlation between regioregularity and the trap state depth (or activation energy). Table 3.3 gives a
Figure 3.12: Temperature dependence of the PIA bands of the films for PTV-1:9 (triangles), PTV-3:7 (squares), and PTV-5:5 (circles). The triplet exciton band, T, is shown in (a) while the polaron band, P2, is shown in (b). The fitting using equation (3) were shown as magenta solid line using two activation energies, and green broken line using one activation energy. The insets show the decay rate b(T) with shallow trap (black line) and deep trap (red line) for (a) triplet band T, and (b) polaron band P2. The blue broken line indicates the temperature independent part, C in equation (3).

detailed summary of the fitting results. However, the decay rate does show correspondence with regioregularity. The most random PTV-5:5 has the fastest decay, as indicated
by the shortest plateau region. We explain this by an increased non-radiative recombination due to defects such as chain kinks in the least structurally ordered PTV-5:5 film. The non-radiative decay further increases the decay rate of photoexcitations. This also explains the shorter lifetime of polarons and triplets in PTV-5:5 film (Figure 3.11).

<table>
<thead>
<tr>
<th>PTV-CR</th>
<th>$E_{T1}$ (meV)</th>
<th>$E_{T2}$ (meV)</th>
<th>C</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTV-1:9</td>
<td>7.4 ± 2.3</td>
<td>103 ± 16.0</td>
<td>0.91 ± 0.34</td>
<td>(2.5 ± 3.2) x 10^4</td>
</tr>
<tr>
<td></td>
<td>61 ± 9.7</td>
<td></td>
<td>(1.3 ± 1.3) x 10^-3</td>
<td></td>
</tr>
<tr>
<td>PTV-3:7</td>
<td>35 ± 5.0</td>
<td>227 ± 71.0</td>
<td>0.02 ± 0.01</td>
<td>(8.5 ± 3.8) x 10^3</td>
</tr>
<tr>
<td></td>
<td>63 ± 11</td>
<td></td>
<td>(1.4 ± 1.3) x 10^-3</td>
<td></td>
</tr>
<tr>
<td>PTV-5:5</td>
<td>12 ± 0.40</td>
<td>104 ± 21.0</td>
<td>0.02 ± 0.002</td>
<td>(2.5 ± 3.7) x 10^4</td>
</tr>
<tr>
<td></td>
<td>15 ± 1.2</td>
<td></td>
<td>0.01 ± 0.003</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.4: Summary of Fitting Results Using Equation 3 for Polaron band $P_2$.

<table>
<thead>
<tr>
<th>PTV-CR</th>
<th>$E_{T1}$ (meV)</th>
<th>$E_{T2}$ (meV)</th>
<th>C</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTV-1:9</td>
<td>12 ± 3.0</td>
<td>84 ± 22</td>
<td>0.70 ± 0.31</td>
<td>225 ± 266</td>
</tr>
<tr>
<td></td>
<td>31 ± 4.0</td>
<td></td>
<td>0.07 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>PTV-3:7</td>
<td>57 ± 19</td>
<td>442 ± 1843</td>
<td>0.03 ± 0.04</td>
<td>(1.7 ± 16) x 10^6</td>
</tr>
<tr>
<td></td>
<td>64 ± 12</td>
<td></td>
<td>0.02 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>PTV-5:5</td>
<td>7.5 ± 0.4</td>
<td>68 ± 37</td>
<td>0.33 ± 0.03</td>
<td>14 ± 29</td>
</tr>
<tr>
<td></td>
<td>8.3 ± 0.4</td>
<td></td>
<td>0.28 ± 0.02</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.12b shows the temperature dependence of $P_2$ (0.93 eV). Fitting of the experimental data using equation (3.3) is shown as a magenta solid line (two activation energies) and green broken line (one activation energy). Using two activation energies, the fitting of PTV-5:5 gives a good result, with a shallow trap at 7.5 meV, and a deeper trap at 68 meV.

However, the fitting results of PTV-1:9 and PTV-3:7 did not go very well with the experimental curves, especially in the low temperature region ($T < 100K$). In this region, the polaron excitation exhibits a very interesting feature for these two more regular polymers. An increase in the PIA signal with increasing temperature is apparent. PTV-3:7 shows a strong increase in the PIA signal until it peaks near 70K. On the other hand, PTV-1:9 shows a smaller increase about 20K and a plateau region at 70K. We think this increase in the low temperature region is due to thermally enhanced polaron generation.
In this process, the molecular resonance barrier is reduced as the temperature is raised and the chain becomes less resistive to the polaronic chain deformation. Noticeably, the temperature variation of triplet for PTV-1:9 and PTV-3:7 was much flatter in the low temperature region (Fig. 3.12a). The competing polaron generation gave way to the thermally activated recombination of polarons at temperature higher than 20K for PTV-1:9, and 75K for PTV-3:7. As a matter of fact, the super-linear increase in $P_2$ absorption with increasing pump intensity at low intensity region in PTV-1:9 (Fig. 3.11a) may also have a contribution from thermally enhanced polaron generation as increased pump fluence leads to sample heating. The thermally enhanced polaron generation was not observed with the most random PTV-5:5, since this polymer has much smaller activation energy for polaron (Table 3.4), the thermal perturbation likely annihilated the polarons. In addition, the disorder-related non-radiative decay might have cancelled out the enhancement at low temperature for this polymer. The inset of Figure 3.12b shows the decay rate, $b(T)$, of polarons with shallow (black line) and deep trap levels (red line). It can be seen that at $T < 150K$, shallow traps dominate the recombination of polarons. At higher temperature, the deeper trap above 90 meV dominates the recombination. Table 3.4 summarizes the detailed fitting results for polaron thermal decay. Overall, polarons have lower activation energy than triplets in this series of polymers, regardless of regioregularity.

### 3.4 Confirmation of State Ordering in PTV by Nonlinear Spectroscopy

Linear spectroscopy techniques can only be used to characterize the $1^1B_u$ excitonic state because this is the only excited state that is one-photon allowed and strongly dipole coupled to the ground state. Thus, the previous discussion in section 3.2 about the presence of the $2^1A_g$ state below the $1^1B_u$ was based on inference from the low PLQE. This inference shall be correct when the low PL yield is *intrinsic* in nature. However, there are other possible non-radiative pathways that could lead to a low PLQE that are
extrinsic in nature. For example, defects along the polymer chain and the formation of H-aggregates will reduce the PL yield significantly as well. While the former is not expected to be strong in these well-ordered materials and the latter is not expected to be responsible for the low PLQE in dilute solution, it is beneficial to confirm the energetic ordering of states by more direct means. In this section, we turn to the non-linear spectroscopic technique of electroabsorption (EA) to unravel the essential states and ultrafast transient pump-probe spectroscopy to follow the excitation dynamics in real time.

Figure 3.13: Electroabsorption spectrum of PTV-0:10. The derivative feature at low energy is assigned to the Stark shift of the $1^1B_u$ and the induced absorption at higher energy is assigned to the $mA_g$.

Figure 3.13 shows the EA spectrum of PTV-0:10. The measurement for PTV-5:5 produced similar results; this is expected because the arrangement of side chains should not affect the essential state ordering. The prominent oscillatory feature at low energy is
assigned to the Stark shift of the $1^1B_u$ exciton, which follows the first derivative of the linear absorption. The zero-crossing of this feature gives the $1^1B_u$ energy level (1.75eV). In this spectrum multiple vibronics can be observed, and the spectrum is pulled down to positive $\Delta T/T$ by the photobleaching of the ground state absorption feature. At higher energy, with a zero-crossing near 2.4eV there is an induced absorption peak that is not present in the one-photon spectrum and is thus assigned to an $A_g$ state. In particular, this feature is assigned to the $mA_g$ state that is commonly found to $\approx 0.6$eV above the $1^1B_u$ and is characterized by strong dipole coupling to the $1^1B_u$ [48, 87]. This strong coupling is the reason for its appearance in the third-order susceptibility as can be understood from perturbation theory in the sum-over-states approach. While $2^1A_g$ state could in principle be detected in a similar manner, it generally can not be resolved in EA due to cancellations in the $\chi^{(3)}$ summation in the presence of strong electron correlations [88].

The results presented are consistent with ultrafast dynamics of exciton decay in this material [89]. The transient PM spectra in regioregular PTV (PTV-0:10) film is dominated by two PA bands, namely $PA_1$ at $\approx 0.95$eV and $PA_2$ at $\approx 1.6$eV with broad tails at lower energies; as well as derivative-like feature showing an “isosbestic point” at $\approx 1.75$eV [89]. It is clear that the two PA bands do not share the same dynamics. Whereas $PA_1$ decays almost completely within $\approx \frac{1}{2}$ps, the decay of $PA_2$ is longer ($\approx 2.5$ ps) and contains a plateau that is evidence of a relatively stable photoexcitation [89]. Thus, the PA bands are not due to the same photoexcitation. $PA_1$ is instantaneously generated, whereas $PA_2$ is formed at a delay of $\approx 200$fs. Therefore, $PA_2$ is not from the primary photoexcitation in RR-PTV, but is formed during the decay of $PA_1$.

The band $PA_1$ is common to many $\pi$-conjugated polymers, and has been identified [49] as due to optical transitions from the photogenerated $1^1B_u$ exciton into the $m^1A_g$ [48]. Therefore the ultrafast decay kinetics of $PA_1$ indicate that there is another state at lower energy ($< E(1^1B_u)$), into which the photogenerated $1^1B_u$ decays; this should be the $2^1A_g$ exciton. As a check of this interpretation the PLQE from the $1^1B_u$ decay, and compare it
to the experimentally measured PLQE \( \eta \)-value. For this we use the relation: \( \eta = \tau / \tau_{rad} \), where \( \tau \) is the exciton lifetime and \( \tau_{rad} \approx 1 \text{ns} [90] \) is the \( 1^1B_u \) radiative lifetime. Using \( PA_1 \) lifetime of \( \approx 12 \text{ps} \) we estimate \( \eta(PTV) \approx 5 \times 10^{-4} \), in agreement with the measured \( \eta \)-value of \( \approx 2 \times 10^{-4} \). Within this decay scenario \( PA_2 \) is a transition from the \( 2^1A_g \) state. This optical transition is into an odd-parity exciton, namely the \( n^1B_u \), one of the polymer essential-states [48]. This state energy could not be determined experimentally from the EA spectrum, it is consistently found about one or two tenths of an eV above the \( mA_g \) state. The stabilization of \( PA_2 \) at later time (t>5 ps) into a plateau, shows some of the \( 2^1A_g \) excitons are trapped, similar to the case of the classic polymer t-(CH)_x [91].

### 3.5 Summary

In summary, we have investigated photo physics and crystal structure of a series of poly(3-dodecylthienylene vinylene) with varying degrees of regioregularity. We found, in contrast to the regioregular effect in pure polythiophene polymers, that regioregularity does not effect the supramolecular order in thin films of PTV-C12. This can be rationalized in terms of two peculiar features of PTV, one of them structural and the other electronic in origin.

Structurally speaking, the vinylene linkage of thiophene rings is expected to induce more backbone rigidity than simple coupling of thiophene rings. This leads to strong X-ray diffraction peaks independent of the alkyl-group arrangement. Consequently, the regio-random arrangement of side chains only allow for a degree of torsional disorder along the chain that is responsible for the smaller crystal domain sizes and the more pronounced sensitivity to thermal perturbation, as exhibited in the effect of annealing on crystallite orientation and temperature dependence of the PIA. This increased back-bone disorder is also responsible for the lower PL yield and more pronounced triplet population in PIA measurements comparing with the case of regioregular PTV. On the other hand, regioregularity in the side chains further promotes a planar, order backbone of PTV.
This then leads to larger crystallite domains, insensitivity to solvents used for processing (and concurrently, poorer solubility), as well as increased PL yield (though still extremely weak due to the ordering of excited states) and reduced triplet yield. The dependence of the steady-state triplet yield on intra-chain order may be point to the fact that they originate from the process of “singlet fission,” as will be discussed thoroughly in the next chapter.

Electronically, we expect that the role of interchain interaction that is so prevalent in regioregular polythiophene is effectively “shorted” by the sub-ps decay of the ionic $1^1B_u$ into the covalent, intrachain $2^1A_g$ state. This process essentially prevents exciton migration among different conjugated segments. Instead, there is a massive release of thermal energy in PTV that manifests itself as a propagating strain wave [89]. This is similar to the formation of a breather exciton in the wake of soliton motion in trans-polyacetylene [92]. In either case, the release of energy in internal conversion and subsequent non-radiative decay of the photoexcitation must manifest itself in vibrational forms. These energetics ultimately do not bode well for OPV device application potential. Such ultrafast dynamics do however, open potential avenues for photonic devices, particularly nonlinear optical devices.
4 PHOTOPHYSICS OF IMIDEPTV

4.1 Introduction

4.1.1 Emissive Properties and the Ordering of Excited States

The electronic properties of $\pi$-conjugated polymers are very sensitive to modifications in the chemical structure, incorporation of substituent groups and defects that occur during synthesis, as well as the local morphological conformation that is determined by the properties of solvents and methods used for processing of thin films. This sensitivity often leads to large variations in the optoelectronic characteristics of materials across seemingly modest changes in derivatives. This is attractive from the point-of-view of device application, since it allows for the potential to improve the figures of merit of a device by designing a material directly for that purpose. This can only be achieved, of course, if the structure-property relationships are very well understood. In the previous chapter we saw that the simple replacement of every other thienyl unit in polythiophene with a vinyl unit leads to an important energy level crossing, the consequence of which is a drastic reduction life time of the $1^1B_u$ exciton and subsequently the PL yield. In Chapter 5, it will be shown that this will have a similar effect on the photo-carrier yield in OPV application. This means that an attempt to improve organic solar cell efficiency by lowering the optical band gap of the donor polymer through extension of the conjugation length in this manner ultimately backfires. Such a surpassing observation highlights the need for continued fundamental characterization of $\pi$-conjugated polymers of various chemical structures in order to tailor their properties for the implementation of organic-based electronic devices and thus for future energy markets.

In this chapter, we look deeper into the structure property relationship that determine the
energy level ordering and resultant photo-physical processes. We investigate a novel PTV derivative that incorporates an electron-deficient imide group attached to a thienyl unit in the backbone and also involves a higher ratio of thienyl to vinyl units (see structure in the inset of Fig. 4.1). We refer to this polymer as imidePTV. Unlike the usual PTV which is nonluminescent, imidePTV shows observable PL in both solution and solid state. This has allowed us to investigate the role of the ordering of excited states in more detail. In Section 4.2, we will present strong evidence that in this material the $2^1A_g$ and $1^1B_u$ levels are much closer in energy, perhaps degenerate, which leads to a longer excitonic mean lifetime and larger PL yield. Furthermore, by studying the solvent dependence of the PL in solution and the temperature dependence of the PL in film, we observed a thermally activated emitting species in combination with the more commonly observed $1^1B_u$ emission, which shows a characteristic thermal disorder-induced decay. Quantitative analysis using the well-known “H-aggregate model” allows us to exclude the possibility that the changes in PL observed are merely due to the local morphology as is the case for regioregular poly(3-hexylthiophene), while a theory of $1^1B_u$-$2^1A_g$ state mixing put forth to describe the emissive properties of di-substituted polyenes provides insight to the order of states and energy separation. PL from imidePTV is a superposition of $1^1B_u$ emission normal of most $\pi$-conjugated polymers and emission from $2^1A_g$ which is made possible by an asymmetric perturbation such as Herzberg-Teller type vibronic distortion [93, 13]. We studied the PL in various morphological conditions to elucidate the effects of inter-chain and intra-chain order. The resulting picture that emerges provides further insight into the functional design of electronic polymers for device applications.

4.1.2 The Role of the $2^1A_g$ State and Prospects of Singlet Fission

Due to the large exchange coupling in organic systems, the energy of the lowest triplet exciton, $T_1$ can be substantially lower than that of the lowest energy singlet exciton, $S_1$. In many cases, this allows the ordering of excited states such that the splitting of $S_1$ into two triplets is energetically favorable. This process, singlet fission (SF), is currently
a subject of considerable interest [94, 95]. The coupled pair of triplets are a superpo-
position of quantum states with different overall spin multiplicities, some of which have
singlet character, and SF is therefore spin-allowed and hence much more efficient than
intersystem crossing by spin-orbit coupling. The potential for independently dissociating
the triplet excitons into electron-hole pairs would allow devices employing SF to yield
large currents and make efficient use of the high-energy portion of the solar spectrum,
thus providing a mechanism to overcome the Shockley-Queisser limit [96, 97]. The most
extensive studies of this process have been conducted on small molecules, in particular
single crystals and thin films of acenes such as tetracene and pentacene where SF is very
efficient [98, 99, 100, 101, 102, 103, 104, 105, 106, 107]. These studies have helped to elu-
cidate the energetics and dynamics of the process, and demonstrations of the applicability
to harvest more than one electron per absorbed photon have been made [108].

Although a great deal of progress has been made in understanding the fundamental as-
pects of SF with regards to optimal chromophore design, open questions remain. The
most pertinent question is how to design systems that possess the optimal coupling in
order to achieve a balance between maximizing yield of triplet-pairs formed by fission and
allowing the triplet-pairs to be separated into distinct excitations. The importance of the
latter is due to the desire, ultimately, to generate two independent electron-hole pairs.
A more limited number of reports have demonstrated that SF also occurs in polyenes
and π-conjugated polymers [109, 110, 111, 112, 80, 113, 114, 115, 116]. Accordingly, this
phenomenon is much less understood than in acene organic crystals and thin films. In
particular, the original proposition that the correlated triplet pair generated on a sin-
gle linear molecule can escape their mutual interaction by diffusion and result in two
separated triplets has recently been called into question [95]. It is now proposed that
intermolecular interaction is necessary to separate the pair, as is understood to occur
in acenes. Such concerns come to the heart of current open questions about the SF
process with an eye to maximizing the yield of photo-carriers and require further inves-
tigation.
In Section 4.3, we investigate the role of SF on the photophysics of the \( \pi \)-conjugated polymer imidePTV. First, we provide evidence that a correlated triplet pair is generated as a quantum superposition comprising \( S_1 \). Next, we show that variations in morphology do not lead to changes in the characteristics of the triplet-pairs. This allows us to aspect of singlet fission process is a purely intra-chain process. However, we need to emphasize two ambiguities in SF process as it is believed to occur in polyenes. The first involves the definition of SF. If the definition were considered to be a singlet exciton that results in the generation of two spatially distinct, electronically independent triplet excitations, then that is not what could be said to have occurred in imidePTV, or for that matter, what most likely has not occurred in many of the previous reports of SF in \( \pi \)-conjugated polymers, when the polymer chains were well isolated [110, 111, 116]. Instead, it appears that the triplet-pair state, which is an intermediate step in the more complete description of singlet fission, is what is observed in polyenes. This can be understood to result from the efficiency of the process, where the triplet-pair state is generated either in superposition with or less than a picosecond after the singlet exciton and is thus insensitive to changes in vibronic coupling that accompany a change in the chromophores local environment. Considering this, a second ambiguity arises in the difference between fission into a correlated triplet pair, and internal conversion of the \( 1^1B_u \) state to the \( 2^1A_g \) state, which has been theoretically described as a correlated pair of triplets [15]. There exists no experimental evidence to distinguish the two and there is no reason \textit{a priori} to do so. Even the case of an optically allowed superposition of singlet and triplet-pair does not distinguish SF, as excited state mixing of \( 1^1B_u \) and \( 2^1A_g \) states has been observed and extensively studied in polyenes. Furthermore, our observations of mixed \( 1^1B_u-2^1A_g \) emission in (Section 4.2), simultaneously with the superposition of \( 1^1B_u \) and triplet-pair absorption is consistent with the theoretical predictions.
4.2 Emission from the $1^1\text{B}_u-2^1\text{A}_g$ mixed state

4.2.1 Effect of Solvents on Absorption and Photoluminescence

The absorption spectra of imide PTV in several solvents are displayed in Figure 4.1. The room temperature (RT) film absorption can be seen to closely resemble that of dilute solution, particularly in lower polarity solvents such as Toluene and Hexane. The band edge does not shift much with the variation of solvents with the exception of the solvents with high polarity Pyridine and Dimethylformamide (DMF) (see Table 4.1), where a substantial blue shift that is proportional to the solvent dipole moment occurs. Also, in these solvents we note poor solubility with visible precipitation of solid imidePTV. As all solutions in this study were prepared at identical concentrations in range of 0.2mg/mL to 0.002 mg/mL, the observed precipitation means that the saturation limit for solubility in these two solvents is much lower than 0.002 mg/mL. This also indicates that the oscillator strength of the optically allowed transition is much stronger in these polar solvents, as the optical density at the resulting much lower concentrations is comparable to that in the less polar solvents. The lower energy shoulder structure apparent in the absorption spectra in film and in the lower polarity solvents is reminiscent of a signature feature of inter-chain interaction in $\pi$-conjugated polymers including in PTVs[117, 66]. However, the extremely dilute concentrations of the solutions make such interactions unlikely, and no shift of the spectrum was observed as the concentration was varied over a range of 0.2 mg/mL to 0.002 mg/mL in any of the solvents (Figure 4.2). Neutron scattering measurements also indicate that inter-chain interaction is not significant even at much higher concentrations (Figure 4.3).

To determine polymer conformation, different geometric models [118], including random coil, excluded-volume polymer, sphere, ellipsoid and cylinder were used to simultaneously fit two sets of SANS data obtained from two instrument configurations. The fitting procedure involved fixing the neutron scattering length density (NSLD) of DCB solvent
Figure 4.1: Absorption of imidePTV in various solvents and in film.

at $2.35 \times 10^{-6}/\text{Å}^2$, which was calculated from its density and molecular composition, while allowing parameters describing the polymer structure and its NSLD to vary. The random coil model fits poorly to the scattering data. Moreover, the only model that fits well, in terms of residual $\chi^2$, was the cylinder model. Specifically, the cylinder radius $r$ and length $L$ were determined to be 22.3 Å and 101.9 Å, respectively, and the NSLD of imidePTV was $1.85 \times 10^{-6}/\text{Å}^2$. Several interesting features can be discerned from the model fitting. The cylindrical conformation indicates imidePTV acts more like a rigid rod rather than a flexible coil, indicating steric type repulsive interactions dominate along the polymer chain.
Figure 4.2: Absorption of imidePTV at several different concentrations for five of the solvents (as labeled) used in this study. THF is tetrahydrofuran, DCB is dichlorobenzene.

In addition, the size of the cylinder radius, 22.3 Å, suggests the scattering object is most likely formed by a single chain, considering that each polymer chain is about 30 Å in diameter as extracted GIXRD measurements (inset to Figure 4.3) and allowing for some torsional disorder along the backbone. This suggests at 5 mg/ml concentration imidePTV does not tend to form large aggregates, thus supporting our assumption that at much lower concentration, 6.125 µg/ml, imidePTV mainly remains in monomer state.

Comparing the PL spectra of dilute solutions in different solvents (Figure 4.4) and film yields similar observations. As with the case of absorption, the PL spectra in highly polar solvents are blue shifted compared to the low polarity solvents, in terms of the most prominent peak. However, the blue-shift is only pronounced for Pyridine and DMF. In the other solvents there is a continuous relative enhancement of the low energy emission as the solvent polarity decreases, so there is a more pronounced low-energy vibronic
structure in the least polar solvents, again similar to absorption. In addition, the room temperature (RT) film PL is very similar to that obtained in dilute toluene solution.

Figure 4.3: Cylinder model fitting to two sets of SANS data (green and brown circles) obtained from two instrument configurations for 5mg/mL imidePTV in DCB solution. The inset shows the GIXRD scan of a thin film.

This supports the idea that the photo-physics in film is dominated by intra-chain interactions. The polarity dependent optical gap observed here signals the presence of dipole-dipole interactions between the solvent and solute. The blue-shift with increasing polarity is consistent with a larger dipole moment in the ground state than in the excited state. We note the imide substituent is electron-deficient, while the thiophene rings are electron-rich, which is expected to give rise to a larger ground state dipole moment than is possessed by most \( \pi \)-conjugated polymers. Dipole-dipole interactions do not explain the variation in the vibronic progression for the solvents of lower polarity than DCB, however, or the blue shift of the absorption maximum of imidePTV in Hexane as compared to film, for that matter, signaling that other solvachromic effects are at work here as well.
The PL quantum efficiency (PLQE) is also solvent dependent. The yield is near or above 1% in the most polar solvents while it decreases with decreasing polarity to 0.1% for Hexane, similar to the value in film. These values are summarized in Table 4.1 along with the relevant solvent parameters. Overall, however, the PLQE is very low, which may signal the presence of the optically forbidden $2^1A_g$ below the $1^1B_u$, as in PTVs studied in Chapter 3. In fact, it has been noted in polyenes of intermediate length, where the $1^1B_u$ and $2^1A_g$ states are nearly degenerate, that emission originates from both states, or perhaps, a hybrid state [119, 120, 121, 122, 123, 124, 125]. In this case, the solution PL
is observed to be sensitive to the choice of solvent, as is observed here. This sensitivity arises from perturbative effects on the energy levels through solvent-solute dispersion interactions that tune the extent the nearly degenerate states are mixed, and can even lead to inversions of state-ordering. The theory behind this phenomenon is explained below and the extent that it can be applied to imidePTV is discussed.

Table 4.1: Solvent parameters and photophysical parameters of imidePTV in solvents and film, listed from least polar to most polar going from top to bottom.

<table>
<thead>
<tr>
<th></th>
<th>(\epsilon(\epsilon_0))</th>
<th>(\alpha)</th>
<th>(\phi_{PL}) (± 0.001)</th>
<th>(E_{\text{abs max}}^{\text{abs}}) (eV) (± 0.02eV)</th>
<th>(E_{\text{onset}}^{\text{abs}}) /eV (± 0.02eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Hexane</td>
<td>1.88</td>
<td>.228</td>
<td>.002</td>
<td>2.25</td>
<td>1.72</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.38</td>
<td>.292</td>
<td>.004</td>
<td>2.33</td>
<td>1.74</td>
</tr>
<tr>
<td>THF</td>
<td>7.58</td>
<td>.246</td>
<td>.006</td>
<td>2.24</td>
<td>1.76</td>
</tr>
<tr>
<td>DCB</td>
<td>9.93</td>
<td>.319</td>
<td>.013</td>
<td>2.19</td>
<td>1.73</td>
</tr>
<tr>
<td>Pyridine</td>
<td>12.4</td>
<td>.299</td>
<td>.008</td>
<td>2.24</td>
<td>1.86</td>
</tr>
<tr>
<td>DMF</td>
<td>36.7</td>
<td>.259</td>
<td>.039</td>
<td>2.38</td>
<td>1.93</td>
</tr>
</tbody>
</table>

\(^a\) relative permittivity used to quantify the solvent polarity.

\(^b\) solvent polarizability calculated from \(\alpha = n^2 - 1/n^2 + 2\).

As discussed by Andrews and Hudson [93], solvent dependent PL in polyenes results from the energetic proximity of optically allowed and optically forbidden states. The Hamiltonian to be considered is the sum of the unperturbed solute Hamiltonian, \(H_0\), a solvent-solute perturbation \(H_{ss}\) and a Hamiltonian that induces the state mixing between the formally decoupled allowed and forbidden states, \(H_{\text{mix}}\). In the case of polyenes, this last term is usually assumed to arise for Herzberg-Teller type perturbation where the states are close enough that their vibronic potential surfaces intersect, and the optically forbidden \(2^1A_g\) state (gerade) can obtain a finite transition moment from the perturbation of coupling to an asymmetric vibrational mode (ungerade). The calculations are valid for any non-symmetric perturbation, however, such as the electric field due to the presence of a permanent dipole moment oriented along the axis of symmetry of the molecule.

The result of calculation is that to first order in the solvent-solute transition moment dispersion interaction, the nature and strength of the perturbation \(H_{\text{mix}}\) is unaffected, and changes only occur in the energy levels of the relevant states. Thus, the solvent affects
the radiative rate through the solvent polarizability $\alpha$, by shifting the energy levels of the states which are of the form:

\[
E_{2Ag} = E_{2Ag}^0 - \alpha P_{2Ag}, \tag{4.1.a}
\]
\[
E_{1Bu} = E_{1Bu}^0 - \alpha P_{1Bu} \tag{4.1.b}
\]

where $P_{2Ag}$ and $P_{1Bu}$ are the polarizabilities of the $2^1A_g$ and $1^1B_u$ states respectively. Subsequently, it can be shown that the radiative rate of the dipole forbidden state is given by:

\[
k_{2Ag} \propto \frac{\Gamma^2}{(\Delta E - \alpha \Delta P)^2} \tag{4.2}
\]

where $\Delta E$ is the difference between the gas phase energy levels ($\Delta E = E_{1Bu}^0 - E_{2Ag}^0$) of the $1^1B_u$ and $2^1A_g$, $\Delta P$ is the difference between the polarizability of the two states ($\Delta P = P_{1Bu} - P_{2Ag}$), $\alpha$ is the solvent polarizability and $\Gamma$ is related to the allowed transition moment between the ground state and $1^1B_u$, and the strength of the asymmetric perturbation, $H_{mix}$.

Since the dipole allowed $1^1B_u$ is of “ionic” nature, it is more sensitive to the polarizability of the environment than the “covalent” type $2^1A_g$. Therefore, changes in the solvent polarizability lead to variations in the energy gap between the $1^1B_u$ and $2^1A_g$ states. In other words, since $P_{1Bu} \gg P_{2Ag}$, an increase in polarizability will push the $1^1B_u$ state further down, increasing the mixing, and thus the radiative rate of the $2^1A_g$ state when $E_{1Bu}^0 > E_{2Ag}^0$, and can eventually lead to an inversion of the state ordering. This phenomenon is well documented in the $\alpha, \omega$-polyenes: diphenylhexatriene and dithienylbutadiene [119, 125, 121, 126, 127, 128].

The above theory applies to non-polar molecules in non-polar solvents, although the authors noted it also adequately described the emission of non-polar polyenes in polar solvents, because the interaction is second order in the perturbation. The same will not be true of polar molecules such as imidePTV. As discussed briefly by Longuet-Higgins
and Pople [129], solute-solvent interactions for both polar solvents and polar solutes involve several expansions involving the solute-dipole interaction with the unperturbed states of the solute, vice-versa, the interaction of permanent dipoles of both molecules in the ground state and in the excited state, as well as the dispersion interactions already discussed. We thus limit our discussion for the case of imidePTV to a qualitative level. We have already noted the blue-shift of the optical gap with increasing solvent polarity. This points to a larger dipole moment in the ground state than the excited state, such that the ground state energy is stabilized to a larger extent than the excited state, thus increasing the gap. Being dipolar in nature, the $1^1B_u$ is also expected to be pushed lower in energy by the interaction. This means that polarity is expected to have the same effect as polarizability on the energy levels of imidePTV. Additionally, we continue with the assumption that the $2^1A_g$ state is generally insensitive to its environment and is affected much less by these interactions.

Figure 4.5 shows the energy of the absorption maximum as a function of solvent polarizability for the solvents here. A general linear relation is obtained in accordance with Equation (4.1.b). The most clear deviations from linearity can be ascribed to the effect of solvent polarity that the theory of Andrews and Hudson does not account for. We thus use this theory to account for emissive properties of imidePTV below.

In the solvent with the lowest polarizability and lowest polarity, Hexane, the energy levels will be near the gas-phase values. In this case, the emission is extremely weak and dominated by the low-energy mode progression. As $\alpha$ and/or $\epsilon$ increase, as in Toluene and THF, the spectrum is similar to that in Hexane, but the relative weight in the low-energy modes decreases. Meanwhile, the PLQE increases, which is consistent with enhanced mixing between $2^1A_g$ and $1^1B_u$ and . Increasing the solvent polarity and/or polarizability even more as in DCB, Pyridine and DMF leads to a near vanishing of the low-energy component of the PL spectrum and a further increase in the PLQE. This indicates that in these polar solvents the ordering of the $1^1B_u$ and $2^1A_g$ energy levels nearly invert.
Figure 4.5: Absorption maximum of imidePTV in the various solvents used in this study versus the solvent polarizability. The redline is a linear fit to the data. Absorption in DMF, which is substantially blue shifted due to the strong polarity, has been excluded.

At this point the PL becomes predominantly $1^1B_u$-type, however the PLQE remains low, consistent with the adiabatic energies of the two states being equal to within less than $k_B T$. We note the presence of an emission component is observed above the primary peak at 1.74eV in the least polar solvents. This stems from above the band-gap and is termed “hot exciton” emission suggesting a thermal activation. Within the scenario described above, this could be due to thermal population of the $1^1B_u$ state from the lower $2^1A_g$ state as observed previously in diphenylhexatriene and dithienylbutadiene [119, 128, 130].

Thus, the enhanced emission with polarity and polarizability has been assigned to an increased transition moment of the $2^1A_g$ state in accordance with Equation 4.2. However, to be more accurate, it is the radiative rate that is proportional to the expectation value of the transition moment coupling for the two states. The radiative rate is the product of the quantum yield $\phi_{PL}$ and the experimentally determined emission rate, $k_{em}$, $k_{rad} = \phi_{PL} k_{em}$. In Figure 4.6, transient PL is shown. Figure 4.6a focuses on the early time dynamics of the PL for imidePTV in DCB at two different concentrations and in film
and shows the fitting to the equation

\[ I(t) = T(t) \otimes (A_1 e^{-\frac{t}{\tau_0}} + A_2 e^{-\frac{t}{\tau_1}} + A_0) \]  

(4.3)

where T(t) is the laser impulse function, \( \tau_0 \), the laser scattering time, and \( \tau_1 \) the radiative lifetime of sample, and \( A_0 \) is the background offset. Both sample and impulse functions were normalized. This is done because the intensities vary between samples and the laser scattering since the laser scattering is either off a glass cover slip (for film) or a solvent (for solution). Meanwhile, Figure 4.6b shows an additional long time component and a fitting using a bi-exponential function. As shown in the figure, the short time component was between 2ns and 7ns in all cases. For the long time dynamics, the first exponential decay was fixed at 2.5ns to reflect these early time dynamics. Importantly, we interpret the presence of two distinct lifetimes in the fluorescent decay dynamics as further evidence of a mixed-state emission, with the short time dynamics having a predominantly \( 1^1B_u \) character and the \( 2^1A_g \) character reflected in the long time dynamics. The longer \( \tau_2 \) time and the stronger contribution from this slow component in film as compared to DCB solution again support the notion that the film PL is predominantly of \( 2^1A_g \) nature. Furthermore, the shorter \( \tau_2 \) in DCB solution is in agreement with Equation 4.2 and thus, enhanced mixing of states as the \( 1^1B_u \) is pushed lower in energy and closer in proximity to the \( 2^1A_g \). Because the PLQE is based on the integrated spectrum, we can not separate the contributions from these two components. Thus, we do not attempt to quantitatively evaluate the adherence to Equation 4.2.

### 4.2.2 Temperature Dependent Absorption and Photoluminescence

Since the polarizability is inversely related to temperature, one would expect to see further evidence of environment dependent state mixing in the temperature dependence of the photo-physics of films. We first evaluate the temperature dependent absorption of a
Figure 4.6: Transient PL and fitting results. The broken line is the normalized laser impulse function, and solid lines are fitting for various samples. “Film” was for a drop-cast imidePTV film on sapphire, “Sol-50” a solution with concentration of 50µg/mL imidePTV in DCB, and “Sol-6” a 6µg/ml solution. (a) shows the fitting using Eq. 4.3 for the first 15 ns, and the fast component $\tau_1$ was extracted; (b) fitting based on a bi-exponential fitting with the short time constant fixed at 2.5ns, and the slow component $\tau_2$ was obtained.
thin film displayed in Figure 4.7. We observe a general trend of a red-shift with decreasing temperature. There are three vibronic peaks observed at all temperatures, and these were found to shift by 0.08eV upon cooling from 340K to 12.5K. Meanwhile, the vibronics become noticeably more resolved. These observations are consistent with the decrease in conformational disorder at lower temperature where vibrational and rotational modes are frozen out and a planar configuration is predominant.

![Absorption spectra of a thin film of imidePTV at various temperatures.](image)

Figure 4.7: Absorption spectra of a thin film of imidePTV at various temperatures.

The temperature dependent PL spectrum of a film of imide is displayed in Figure 4.8. There is a noticeable shift in energy and also a dramatic reorganization of the vibronic distribution as temperature is varied. To parameterize this dependence, a series of Gaussians constrained to identical widths were used to fit the apparent peaks. The values of the fitting are described in Table 4.2. The spectra reveal two temperature regimes where the values remain more or less constant. The low temperature regime is found below 90K. Indeed, the same parameters used to fit the 12.5K spectrum apply equally well to that at 90K, aside from a small decrease in the overall magnitude of the signal. The high temperature regime becomes apparent at 240K and remains up to 450K (spectrum not shown here). In this range, there is a continual blue-shift and modest broadening of the
widths that occurs as temperature is increased, consistent with thermally reduced con-
formational disorder, as well as a steady drop in the PL yield as non-radiative pathways
become increasingly efficient. The emission from both phases are characterized by three
dominant vibronic modes, which we indiscriminately refer to as 0-0, 0-1 and 0-2, with
decreasing energy.

Previous reports on the temperature dependence of PL of π-conjugated polymers have
focused on two governing physical processes: thermal reduction of the symmetry require-
ments in molecular aggregates, and temperature dependent activation and weighting of
vibrational modes through the Huang-Rhys (HR) parameter. The former phenomenon
has been well described by Spano and coworkers [131, 69, 132, 133, 134]. This theory has
explained the temperature dependent PL of many polymers where the structural packing
of polymer chains leads to the formation of H-aggregates [131, 133, 134], most notably
for regio-regular P3HT [131, 69, 135, 132]. The expectations in this case are that the
highest energy PL mode (0-0) is formally symmetry forbidden, and therefore grows in
intensity with respect to the other vibrational modes as thermal disorder increases and
reduces the symmetry requirements. This is experimentally tracked by measuring the
ratio of the 0-1 intensity to that of the 0-0 as a function of temperature, which should be
an decreasing function. While we do observe an decrease in this ratio with temperature
(Fig. 4.10b), we also have significant evidence against this interpretation. First, we have
already noted the similarity between both the absorption and PL at room temperature
to those observed in dilute solutions of Toluene (see Fig. 4.1 and Fig. 4.4), suggesting
that inter-chain interactions play a negligible role on the photo-physics in films of this
polymer. This is to be expected due to the bulky di-dodecyl side-groups attached to the
imide unit. Secondly, the symmetry requirements of H-aggregates should only result in
the suppression of the 0-0 peak while leaving the higher order vibronics unchanged. The
ratio of the intensity of 0-1 and 0-2 peaks should therefore be constant with temperature,
and the ratio of the 0-2 to the 0-0 should have the same temperature dependence as that
of 0-1 to 0-2. This is not what is observed at low-temperature (Fig. 4.10b).
Figure 4.8: PL spectra of a thin film of imdePTV at various temperatures. The spectra are offset for clarity. The solid lines show the result of the Gaussian fit for the 60K and 340K spectra. Additionally, the component Gaussians used to generate the sum are displayed for the 340K spectrum.

Meanwhile, at high temperature the temperature dependence is opposite of what is expected from the H-aggregate model as 0-1/0-0 is a increasing function of temperature (Fig. 4.10b). Additionally, we have measured the PL from a film of imidePTV dispersed in polystyrene at a 1:100 weight ratio in order to experimentally probe the role of inter-chain interactions (Figure 4.9). During these measurements the PL was observed to dynamically shift due to the effect of sample heating. Obtaining the emission at several different energetic positions as a function of time, we observed the thermally induced decay on a time scale of seconds. The kinetics are generally dominated by a single
Table 4.2: Values extracted from empirical fitting of thin film PL spectra at various temperatures.

<table>
<thead>
<tr>
<th>Temperature/K</th>
<th>$E_{0-0}$/eV</th>
<th>$E_{0-1}$/eV</th>
<th>$E_{0-2}$/eV</th>
<th>$\sigma$/eV</th>
<th>$A_0$</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$E_{0-0}$/eV</th>
<th>$E_{0-1}$/eV</th>
<th>$E_{0-2}$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.5</td>
<td>1.65</td>
<td>1.46</td>
<td>1.31</td>
<td>0.055</td>
<td>0.135</td>
<td>0.215</td>
<td>0.105</td>
<td>1.82</td>
<td>2.04</td>
<td>2.18</td>
</tr>
<tr>
<td>30</td>
<td>1.65</td>
<td>1.46</td>
<td>1.31</td>
<td>0.055</td>
<td>0.125</td>
<td>0.190</td>
<td>0.095</td>
<td>1.82</td>
<td>2.04</td>
<td>2.18</td>
</tr>
<tr>
<td>60</td>
<td>1.65</td>
<td>1.46</td>
<td>1.31</td>
<td>0.055</td>
<td>0.115</td>
<td>0.180</td>
<td>0.085</td>
<td>1.82</td>
<td>2.04</td>
<td>2.18</td>
</tr>
<tr>
<td>90</td>
<td>1.65</td>
<td>1.46</td>
<td>1.31</td>
<td>0.055</td>
<td>0.120</td>
<td>0.175</td>
<td>0.090</td>
<td>1.83</td>
<td>2.04</td>
<td>2.18</td>
</tr>
<tr>
<td>120</td>
<td>1.67</td>
<td>1.47</td>
<td>1.32</td>
<td>0.060</td>
<td>0.115</td>
<td>0.165</td>
<td>0.085</td>
<td>1.85</td>
<td>2.04</td>
<td>2.20</td>
</tr>
<tr>
<td>150</td>
<td>1.67</td>
<td>1.48</td>
<td>1.33</td>
<td>0.065</td>
<td>0.105</td>
<td>0.145</td>
<td>0.080</td>
<td>1.85</td>
<td>2.06</td>
<td>2.20</td>
</tr>
<tr>
<td>180</td>
<td>1.69</td>
<td>1.50</td>
<td>1.35</td>
<td>0.068</td>
<td>0.120</td>
<td>0.125</td>
<td>0.085</td>
<td>1.85</td>
<td>2.06</td>
<td>2.20</td>
</tr>
<tr>
<td>210</td>
<td>1.71</td>
<td>1.52</td>
<td>1.36</td>
<td>0.068</td>
<td>0.130</td>
<td>0.115</td>
<td>0.080</td>
<td>1.87</td>
<td>2.06</td>
<td>2.20</td>
</tr>
<tr>
<td>240</td>
<td>1.73</td>
<td>1.55</td>
<td>1.38</td>
<td>0.068</td>
<td>0.120</td>
<td>0.115</td>
<td>0.085</td>
<td>1.87</td>
<td>2.08</td>
<td>2.21</td>
</tr>
<tr>
<td>290</td>
<td>1.74</td>
<td>1.57</td>
<td>1.40</td>
<td>0.068</td>
<td>0.115</td>
<td>0.085</td>
<td>0.055</td>
<td>1.88</td>
<td>2.10</td>
<td>2.21</td>
</tr>
<tr>
<td>340</td>
<td>1.75</td>
<td>1.58</td>
<td>1.40</td>
<td>0.070</td>
<td>0.080</td>
<td>0.060</td>
<td>0.040</td>
<td>1.91</td>
<td>2.11</td>
<td>2.23</td>
</tr>
<tr>
<td>400</td>
<td>1.75</td>
<td>1.58</td>
<td>1.40</td>
<td>0.070</td>
<td>0.080</td>
<td>0.060</td>
<td>0.040</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>1.75</td>
<td>1.58</td>
<td>1.40</td>
<td>0.070</td>
<td>0.080</td>
<td>0.060</td>
<td>0.040</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
exponential decay, but at some positions there are rise kinetics convoluted with the decay owing to the thermo-chromic shift. By selecting the PL value obtained immediately after application of the laser, we are able to reconstruct a spectrum that very closely resembles the low-temperature phase PL of the neat film. A similar reconstruction at a later time shows a spectrum comparable that obtained at 150K. We conclude that the only effect of dispersing imidePTV through polystyrene is due to sample heating and thus that the effects of inter-chain interactions are absent in the neat film.

Turning then to the temperature dependence of vibronic modes, we can immediately make observations using the empirical fitting. It is evident that a single mode cannot be used to explain the temperature dependent spectrum. While energetic spacing between the 0-2 and the 0-0 remains a constant 0.34eV over the whole temperature range, the 0-1 is shifted from the 0-0 by 0.19eV at low temperature but moves continually closer to it as temperature increases, differing by less than 0.16eV at 450K (Figure 4.10a). Furthermore, a single HR parameter will not accurately describe the trio of peak intensities at any temperature (Figure 4.10b). In terms of fitting, invoking other modes requires adding more Gaussians to fit the same energy range. Without knowledge of the vibrational energies of separate modes in advance, these values become adjustable fitting parameters, as will be the distinct HR factors associated with each (which should then be allowed to vary with temperature). This procedure would result in so many fitting parameters that they would be deprived of physical relevance. The best procedure to remedy this issue would be to measure the temperature dependence of the Raman scattering spectrum. With this measurement unavailable, we must infer the possibility of a temperature varying HR parameter from the room temperature Raman spectrum (Figure 4.10c, green line). Due to the above band gap emission as noted earlier, the Raman signal is obscured by a broad luminescence background, on top of which only a few broad overlapping peaks may be discerned. The strongest of these are contained in a three peak band in the range of 0.19eV - 0.20eV, while another lower energy doublet appears with peaks at .175eV and .177eV. While the higher energy modes may be responsible of the 0-0 to 0-1 spacing at low-temperature, there appears to be no mode to be directly assigned to
smaller ($\approx 0.155\text{eV}$) 0-0 to 0-1 mode spacing in the high temperature phase PL spectrum. Furthermore, it has been shown by Wu et al. [136] that within the primary effect of temperature on the vibrational modes is increased damping, leading to a suppression of the low-frequency mode contribution to the PL. Thus, it is not expected that temperature dependent Raman measurements would be able to explain the decrease in the 0-0 to 0-1 spacing.

![Figure 4.9: PL of imidePTV dispersed in polystyrene. (a) The transient decay of PL after and during the application of the cw excitation at various probe wavelengths. (b) The reconstructed spectra at $t\approx 0.4\text{s}$ (black squares) and $t\approx 2.4\text{s}$ (red squares) after turning on the excitation, compared to the 90K (black dashed line) and 150K (red dashed line) spectra, respectively, from neat imidePTV film.](image-url)
Figure 4.10: Temperature dependence of the vibronic peak energies (a) and various ratios of peak intensities (b). (c) FTIR absorption (blue) and Raman scattering (green) spectra of a film of imidePTV at room temperature. The background of the Rama signal has been subtracted.

Another alternative is that the temperature of the film controls the degree of mixing between the $1^1B_u$ and $2^1A_g$ states. If emission is from the $2^1A_g$, it would be expected to couple to the asymmetric vibrational modes of the ground state, just as the $1^1B_u$ emission will couple to the symmetric modes. These modes may be obtained by FTIR
spectroscopy, the results of which are also displayed in Figure 4.10c (blue line). As can be seen, there is a rich structure of candidate modes to serve as the apparent modes in the PL spectrum. Within this scenario, the emission would change from predominately \(1^1B_u\)-type to predominantly \(2^1A_g\)-type as temperature increases, causing a similar switching in the nature of modes that contribute to the PL.

4.3 Non-radiative Processes and Prospects for Singlet Fission

Having established that the lowest energy singlet exciton, \(S_1\) in imidePTV is of mixed \(1^1B_u\)-\(2^1A_g\) nature, we now turn to the fundamental ordering of states through EA and the dynamics of exciton relaxation through transient pump-probe and (cw) PIA spectroscopies. We will show that the long-lived PIA features are due to triplet-pair states, that are instantaneously generated by singlet fission (SF). As mentioned in the introduction, there is no difference between the \(2^1A_g\) state, and the triplet-pair state and consequently no difference between the SF and internal conversion from the \(1^1B_u\) to \(2^1A_g\) in imidePTV and quite possibly in most polyene-type systems. In this section, however, we want to emphasize the spin-character of this state and its role as an intermediary in the currently hot topic of SF and will refer to it as the “triplet-pair state,” in contrast to the previous section, where the term \(2^1A_g\) state was used to emphasize its role in rendering imidePTV weakly luminescent.

4.3.1 Results

The electroabsorption spectrum in Fig. 4.11 shows a lineshape that follows the first derivative of the absorption spectrum superimposed on the photobleaching, and the three lowest energy vibronics are resolved. This feature is commonly observed in EA spectra of \(\pi\)-conjugated polymer and is due to the Stark shift of the \(1Bu\) exciton at 1.75eV. Beginning 2.35eV, there is an induced absorption that is attributable to the \(mAg\) (most
strongly coupled to the $1^1B_u$ exciton level, which is made optically allowed by the field induced transfer of oscillator strength. Just above the mA$_g$ in energy is a derivative feature that we interpret as arising from the Stark shift of the nB$_u$ (next highest B$_u$ state) at 2.55eV. The induced absorption at higher energies signals the presence of the higher lying A$_g$ states. From the above considerations we can construct an energy level diagram of the singlet manifold as shown on the left side of Fig. 4.12.

![Energy level diagram](image)

Figure 4.11: Electroabsorption spectrum of PTVimide at 10K.

The cw-PIA spectrum of a film at 10K (Fig. 4.13a) displays a broad absorption feature centered at 1.3 eV with an onset near 0.8 eV. At energies higher than the band gap, the spectrum shows a pronounced photo-bleaching of the ground state absorption. The photo-bleaching can be seen to ride on top of the broad photo-induced absorption that extends above the band edge at 1.8eV. Measurements at different pump intensities and
frequencies, as well as at different temperatures confirm that the entire absorption feature is due to one photo-excited species. At the modulation frequency of 3kHz the signal is almost entirely obtained in-phase with the pump, and the frequency dependence shows little or no decay of the species in the time resolution of the setup (Figure 4.14). From this we can determine that the lifetime of the feature is below the resolution of the setup of 9µs. The pump intensity dependence of the signal is linear from 10mW/cm² to 300mW/cm², as is the PL signal (Figure 4.15) thus allowing us to rule out exciton-exciton annihilation effects that are known to occur at high density[101, 80]. A linear dependence on pump intensity is usually interpreted as a sign of monomolecular recombination, but as will be discussed in detail shortly, is also consistent with bimolecular recombination of triplets formed by singlet fission [137]. From comparison to the doping-induced absorption spectrum (Figure 4.16), it is seen that the absorption feature due to the commonly observed charged species (polarons) are absent from the PIA (Fig. 4.13a) and we conclude that the observed feature is due to a neutral photo-excited species.

Figure 4.12: Energy level diagram of the most relevant states and processes discussed.
Figure 4.13: (a) In-phase (black) and quadrature (red) cw-PIA spectrum of a film of imidePTV at 10K, using a 2.54eV excitation amodulated at 3kHz. (b) Change in cw-PA at 1.2eV as a function of applied magnetic field. (c) Change in PL signal at 1.48eV as a function of applied magnetic field.

Furthermore, in Fig. 4.13b we show the effect of magnetic field on the cw-PA (MPA) probed at the energy of the peak (1.3eV). The figure shows a clear decrease in the PA with increasing magnetic field. This allows us to assign the long-lived PA to triplet excitons. Comparing this data to the magnetic field effect on the PL (MPL) in Fig. 4.13c, it is observed that there is an increase in the PL yield at the expense of the PA. The enhancement of the PL then results from a redistribution of the steady-state population between triplet and singlet excitons formed after photo-excitation as explained.
in the following section. Although triplets are commonly observed in the PA spectra of \(\pi\)-conjugated polymer, the spectrum in Fig. 4.13 is unique in two ways. First, it is much broader than expected, exhibiting a full-width half maximum of approximately 0.4eV, where as triplet absorption usually leads to much narrower bands due to their localized nature. Secondly, from

![Figure 4.14: Semi-log plot of the PL subtracted cw-PA at several different probe wavelengths. The data have been normalized to the maximum value for comparison. The decay is similar at all wavelengths, including for the photo-bleaching. This decay is consistent with the instrument limited decay time of 9\(\mu\)s.](image)

the frequency dependence of the PA we find that the characteristic lifetime of the species is shorter than the instrument response time of the setup (9\(\mu\)s). This short lifetime is uncharacteristic of isolated triplets in film at low temperature where radiative recombination to the singlet ground state is forbidden by spin conservation and non-radiative decay

84
isslow in the absence of available thermal energy, leading to lifetimes in the ms range. However, both characteristics are expected for correlated triplet pairs that result from singlet fission. The breadth of such triplet states is larger due to the interaction.

Figure 4.15: Log-log plots of the PL (a) and PL subtracted cw-PA (b) vs. incident laser power density, shown at several different probe wavelengths. The signal is linear at all wavelengths measured for both PL and PL subtracted cw-PA.
between the two triplets as has been noted and observed in previous reports [111, 116]. The shorter lifetime would also then be expected as a result of the mutual annihilation of the triplet-pair, that results in the formation of singlet exciton, excitation to a higher energy triplet (i.e., $T_2$) or provides an efficient non-radiative decay channel to the ground state (Fig. 4.12).

Figure 4.16: Doping induced absorption spectrum of a film of PTVimide.

A basic requirement for singlet fission is that the triplet energy is less than half of the singlet energy. While the triplet energy is not known precisely, we can set an upper bound of 1eV on its energy by noting that the PA is unaffected by the purging of the chamber with $O_2$ (see Figure 4.17). It is well known that the triplet state undergoes efficient
energy transfer to the singlet oxygen state as long as the energy of the triplet state above the ground state is 1eV or more [138]. While the sample was immersed in high-purity oxygen, no change in the PIA spectrum or the kinetics of the feature were observed. The slight decrease in the signal after 15min oxygen exposure can be attributed to the rise in temperature of the sample as the cryo-chamber cannot maintain the low temperature in the presence of room temperature, atmospheric pressure $O_2$. Furthermore, the empirical relationship of Monkman [139], as well as quantum chemical calculation on PTVs [140], leads to an estimate that the triplet energy is much less than 1eV in PTVs.

We note also that the feature obtained is identical for pump energies employed in a range of 1.8eV to 3.4eV (Figure 4.18) at 10K. Thus, there is no need for activation from excess photon or thermal energy. In addition, isolated triplets distributed in space will lead to quadratic pump dependence of PL. The PL and cw-PA depend linearly on the pump

![Figure 4.17: cw-PA of imide PTV during oxygen exposure achieved by purging the chamber with high-purity oxygen gas. The time of exposure is indicated. The measurement was performed with the sample held at 100K before exposure to $O_2$.](image)
intensity (Fig. 4.15) and we expect that we are in the correlated triplet pair regime. Meanwhile, we observe no evidence of delayed fluorescence due to triplet-triplet annihilation leading back to the emissive singlet. This indicates that the sum of the energies of two triplets is less than that of the singlet, therefore the back-transfer to the singlet manifold is inefficient and needs some activation such as thermal perturbation, as discussed in section 4.2. As a result of these considerations, we propose that the non-radiative mutual annihilation of the triplet-pair, which is the dominant decay mechanism, results in the repopulation of the ground state. These energetic considerations are summarized in Fig. 4.12.

Figure 4.18: cw-PIA measured using different laser excitation energies. The laser power density was $10mW/cm^2$ in all cases.

In order to further investigate the generation mechanism of this unique triplet absorption feature, transient PA measurements were performed. A broad feature in the same energy range as the cw-PIA was observed in Fig 4.19; this feature is generated within the 100fs
rise time of the experimental setup (see the inset to Figure 4.20). This absorption then decays without spectral shift on a 100ps time scale and without generation of any other absorption feature, before reaching a plateau that persists into the ns range. As shown in Figure 4.20, the decay dynamics are similar over the whole spectral range.

The data could be fit by a bi-exponential function to extract the characteristic lifetimes. The long time dynamics were found to 145ps ± 5ps for both probe energies. We note that this is almost two orders of magnitude longer than those found in PTV-CR as described in Chapter 3. The early time dynamics were characterized by lifetimes of 10ps ± 5ps. In the IR range, the tail end of the triplet pair state is observed near 1.0 eV (Fig 4.21). Furthermore, the PA at 200ps also shows a magnetic field effect similar to the low temperature steady state PA. The similarity of ps-PA and the cw-PA spectrum as well as the lack of any other processes occurring in the sub-ns window lead us to conclude

Figure 4.19: Vis/NIR Transient PA spectra of imide film at different time delays after the pump. Delay times are indicated.
that they are due to the same species. This provides further support for the picture of singlet fission into correlated triplet pairs, as the time-scale for generation is too rapid to be accounted for by intersystem crossing due to spin-flip interaction, which occurs on a ns time scale. In addition there is another feature at lower energy, from 0.6eV to 0.9eV. This is more clearly observed by subtracting the background signal which is composed of the absorption from the long-lived triplet pair state (representing the transient-PA at $\approx 12$ns) as shown in Fig 4.22.
Using the energy levels determined from PL and EA spectra, this energy is consistent with a transition from the $1^1B_u$ singlet exciton level to the $mA_g$ commonly observed in transient PA of $\pi$-conjugated polymers and is the signature of the singlet exciton population. This feature is also generated within the pump duration of and shows an initial decay on the same time scale as the decay of the VIS/NIR transient features. We have thus shown that the generation of the singlet exciton the triplet-pair are simultaneous, and there appears to be no internal conversion from the singlet to the triplet pair state nor are their relaxation mechanisms distinct.
4.3.2 Discussion

We have already shown that the fluorescence lifetime is on the order of a few ns (early time dynamics extracted from Figure 4.6). The measured photoluminescence quantum efficiency (PLQE) of 0.01% in film then provides an estimate of the exciton lifetime on the order of a few ps consistent with the early decay dynamics extracted from Figure 4.20. The enhanced PL quantum yield in this material as compared to other PTVs is then

Figure 4.22: Background subtraction of transient IR-PA spectra displayed in Figure 4.21 (a) Comparison of the 0ps PA signal (black) to the background (red), which is recorded just before the pump beam arrives. (b) The result of

on the order of a few ps consistent with the early decay dynamics extracted from Figure 4.20. The enhanced PL quantum yield in this material as compared to other PTVs is then
explained by an approximately two order of magnitude increase in the exciton lifetime that results from the quasi-equilibrium between the singlet exciton and the correlated triplet pair state. These results taken together with the rise and decay dynamics of PA species suggest that the correlated triplet-pair state and 1Bu singlet exciton comprise a coherent superposition state. This observation is similar to what has been observed in pentacene and tetracence [107, 106] and also is consistent with a recent report on SF in PTV [116]. Most likely, this superposition occurs for the same reason that we observe mixed $1^1B_u - 2^1A_g$ emission from imidePTV, namely, an asymmetric perturbation of either Herzberg-Teller type or some other sort. If the energy of the $2^1A_g$ is lower than the $1^1B_u$, as was reasoned earlier, the 10ps exciton lifetime suggests the time at which internal conversion to the triplet-pair/$2^1A_g$ state is completed.

The effect of magnetic fields on SF and triplet fusion back into the singlet manifold have been investigated in detail [141, 142], most recently by Piland et. al [143]. The model is based on a two-step reaction pathway description of singlet fission:

$$S_1 + S_0 \rightleftharpoons (TT)^1 \rightleftharpoons T_1 + T_1$$

(4.4)

where $S_1$ and $S_0$ are the singlet excited and ground states of two neighboring chromophores respectively, $(TT)^1$ is the triplet-pair state of overall singlet character shared between the two chromophores, and $T_1$ is the isolated triplet state. Thus, going from left to right in Equation 4.4 describes the process of singlet fission, while going from right to left describes the reverse process of triplet fusion. To determine the effect of a magnetic field one has to consider solutions to the set of differential equations

$$\frac{dN_s}{dt} = -(k_{rad} + k_{fiss} \sum_{i=1}^{9} |B_i|^2)N_s + \sum_{i=1}^{9} k_{fus} |B_i|^2 N_{(TT)}i,$$

(4.5.a)

$$\frac{dN_{(TT)}i}{dt} = k_{fiss} |B_i|^2 N_s - k_{fus} \sum_{i=1}^{9} k_{fus} |B_i|^2 N_{(TT)}i,$$

(4.5.b)
where $N_s$ and $N_{(TT)i}$ refer to the population of singlets and in the $ith$ triplet-pair sub-level respectively, $B_i$ is the overlap factor between $S_1$ and $(TT)_i$, $k_{fiss}$ is the fission rate and $k_{fus}$ is the fusion rate (considering only the left side of the reaction described in Equation 4.4). $B_i$ describes the singlet character of the $ith$ triplet pair state; when this coefficient is non-zero, fission is possible. It should be noted that we have not included any spin-relaxation (redistribution of population between degenerate sub-levels) and that these equations are only valid after fission has occurred and there is appreciable population in the triplet pair manifold. However, the notion of a superposition between the singlet and triplet-pair renders this scenario applicable immediately upon photoexcitation and is thus expected to be valid here. Assuming a quasi-equilibrium such that $\frac{dN_s}{dt} \approx 0$, leads to an equilibrium constant between the singlet population and the total triplet-pair population, $N_{TT}^{tot}$,

$$\frac{N_s}{N_{TT}^{tot}} \propto \frac{k_{fus}}{k_{fiss}} \quad (4.6)$$

with a proportionality constant that increases with increasing magnetic field [143]. The effect of an applied magnetic field is thus to increase the singlet population at the expense of the triplet-pair population (specifically, by decreasing the number of non-zero $B_i$ from 3 to 2) [143]. The results shown in Figure 4.13 are consistent with the observation of enhanced prompt fluorescence at the expense of correlated triplet-pairs, since the magnetic field decreases the number of states of overall singlet character that the triplet-pair may assume.

The linear dependence of the cw-PIA feature on laser intensity is usually a signature of a monomolecular recombination process, such as PL or phonon emission. On the other hand, a sub linear dependence is characteristic of bi-molecular recombination, such as excitation collision and annihilation processes. This is because the generation rate of excitations is expected to be linear with pump intensity in linear materials such as the polymers studied here. For SF, however, the generation rate will be quadratic, since one photon will generate two triplet excitons. In the event that annihilation is the recombination mechanism, the quadratic pump dependence of generation is exactly canceled.
out the by the square root dependence of population through pair-annihilation processes. With this in mind, it is significant that there is no deviation from linearity at either high or low pump intensity (Fig. 4.15), which indicates that there is no threshold for annihilation consistent with the assertion that the triplet-pair remains correlated throughout its lifetime. This is expected if the pair is confined to a single chromophore, which is almost certainly the case with imidePTV, where the photophysics has already been shown to be dominated by intra-chain physics (see Section 4.2). We consider the results here as suggestive of the preconception that interchain interaction may be necessary to separate the triplets if they are to be independently harvested for photovoltaic application. This is shown schematically by the red-arrows with X’s through them in Figure 4.12.

4.4 Summary

In this chapter, a large amount of evidence has been presented to show that the $1^1B_u$ and $2^1A_g$ star in imidePTV are essentially degenerate in energy, with the consequence that they can be pertubatively mixed form a superposition state. This superposition state is reflected in the observation of dual-state, or mixed-state emission and also in the instantaneous generation of both the singlet exciton and triplet-pair state in upon optical absorption. The signature of the mixed state emission is a special solvent sensitivity as was described in Section 4.2.2. This solvent sensitivity arises from the dependence of the mixing of the two states on the their respective energetic proximity, such that subtle variations in these energy level positions through interaction with the solvent environment have dramatic effects on the nature of the lowest excited state, as viewed from linear one-photon measurements such as PL. Although this affect was well known in linear plyenes, the results presented here are different in that the role of solvent polarity over solvent polarizability were emphasized. This was not prevalent in highly symmetric molecules such as polyenes, but the electron-deficient imide moiety in combination with the electron-rich thienyl units in imidePTV result in a permanent dipole moment and thus a first-order dipole-dipole interaction with polar solvents. This fact was apparent in the
blue-shift in highly polar solvents showing that the ground state level was pushed lower in energy than the excited state by the interaction. Furthermore, it was shown to combine with the effect of solvent polarizability to enhance mixing between the lower lying $2^1A_g$ state. The mixed-state emission also manifested in the temperature dependent effects of the PL. In this case, a cross-over between a low-temperature and high-temperature vibronic progression could not be reconciled with the widely applied H-aggregate model of $\pi$-conjugated polymers, nor could a simple explanation based on the temperature dependence of symmetric vibrational modes be constructed. The two progressions were compatible, however, with a switch between symmetric to asymmetric vibrational modes as temperature was increased. This is expected in the case that temperature controls the relative contributions of the $1^1B_u$ state and $2^1A_g$ state to the mixed excited state.

These results in combination with those for PTV in Chapter 3 show a trend of state ordering that indicates that polythiophene is at the limit correlated limit of emissive polymers. Adding one vinylene unit for every four thiophene rings as in imidePTV leads to weak but measurable PL where as replacing every other thiophene ring with vinylene units leads to an almost completely “dark” polymer. This trend has recently been substantiated by the results of Speros et. al [144] who systematically tuned the of vinylene to thiophene ratio in PTV type polymers and subsequently systematically tuned the PLQE in accordance with the trend put forth here.

The role of singlet fission as a potential boon to photovoltaic efficiency led us to discuss its role in the photo physics of imidePTV. The occurrence of SF in linear polyene systems is intimately tied to the presence of the $2^1A_g$ state below the $1^1B_u$ state because of the energetic requirements. In particular, the $2^1A_g$ state is composed of a pair of triplet states, and thus occurs at twice the energy of the lowest triplet (isolated) excited state [15]. For fission to be an energy conserving process, the $2^1A_g$ must be below the optically allowed $1^1B_u$ state. While in principle these observations could have been made for PTV-C12-CR studied in Chapter 3, the coherent superposition has allowed us to investigate these features in more detail, because of the resulting stability of the relevant species.
that provides the longer lifetimes and larger signals in PIA and PL measurements. We have shown that instantaneously generated absorption features following photo-excitation is due to the presence of a correlated triplet-pair that reside on a single chromophore. The mutual interaction leads to a broader absorption feature for the triplet-pair than is generally observed for isolated triplets generated by the usual mechanism of intersystem crossing due to spin-orbit interaction, and is also responsible for the recombination on the nano-second scale, which limits the lifetime of the species as it is measured in cw-PIA. This again in contrast to isolated triplets, which have lifetimes on the order of ms in films, such as in PTV-C12-CR discussed in Chapter 3. Significantly, the fact that the triplets remain correlated until they recombine to the ground state means they are unlikely to be able to be harvested for photovoltaic application. We have proposed that a pair dissociating mechanism may be necessary for isolating the two triplets that comprise the pair state, and that interchain-interaction may be a possible mechanism. In light of the observations from Chapter 3 that the long-lived triplets are more efficiently generated in regio-random PTV’s than in regio-regular ones, it may also be possible that intra-chain disorder can isolate the triplets. In this scenario, the conformational distortion accompanying the triplet excitons in combination with static and/or dynamic torsional disorder can lead to fracture of the electronic coherence. However, since we are unable to experimentally control the amount of disorder along a chain of imidePTV, we are unable to test this hypothesis. We note however, that in other cases where similar observations were made, namely an exceptionally broad, sub-ps generate triplet absorption feature (attributable to a triplet-pair state), the material was composed of well-order and well-isolated chains [110, 111, 112, 116].
5 PHOTOPHYSICS OF
BULK-HETEROJUNCTION BLEND FILMS

5.1 Note to Reader

Portions of this chapter have been previously published and are reproduced with permission from “Photophysics and morphology of poly (3-dodecylthienylenevinylene)-[6,6]-phenyl-C_{61}-butyric acid methyl ester composite,” E. Lafalce, P. Toglia, C. Zhang, and X. Jiang, *Applied Physics Letters*, **100**, 213306, (2012). Copyright 2012, AIP Publishing LLC.

5.2 Introduction

A major motivation for this work is the determination of the viability of using PTV based \(\pi\)-conjugated polymers as donors in bulk-heterojunction organic photovoltaics. Of the four step process used to describe the basic working mechanism of OPVs in Chapter 1, the first step, namely the absorption of solar emission, along with the subsequent energy conversion and dissipation processes that occur immediately following absorption, have been discussed in some detail. In this chapter, we investigate the impact on the photo-physics of PTV derivatives when in the presence of the electron-acceptor PCBM. Blending PTV, or any other \(\pi\)-conjugated polymer, with PCBM is expected to have both structural (morphological) and electronic consequences. Thus, we employ Atomic Force Microscopy (AFM) and X-ray scattering to investigate the former and absorption, PL, and PIA to study the latter. In particular, we look for evidence of charge transfer between the donor and acceptor systems and look at the factors affecting the efficiency of this process.
One key signature of exciton dissociation by PCBM that may be obtained from PL studies is PL quenching. If blending a π-conjugated polymer with PCBM results in PL quenching, this indicates the radiative exciton recombination process has been preceded by another exciton quenching process, such as electron-transfer. Indeed, the first reported result that indicated this mechanism for dissociating excitons into charge-carriers in π-conjugated polymers was viable and efficient was the quenching of PL in the π-conjugated polymer MEH-PPV by $C_{60}$ [145]. Meanwhile, in PIA measurements evidence of charge-transfer arise from the appearance of a meta-stable charge-transfer excitations [146, 147]. The results have strong implications for the ultimate efficiency of PTV based OPVs. It is worth noting that using the methodology described here, we established the efficacy of the new polymer for application in OPV, without the need to separate bulk photo-excitation losses from transport and contact losses that occur in devices. In this sense, the ultimate device efficiency is more accurately studied in this way than by fabricating and characterizing actual PV devices. This is because of the many fabrication parameters that may affect device performance (such as active layer thickness, Schottky barriers at contact interfaces, parasitic resistances, etc.) that must be optimized before the full potential of the system can be realized in such a manner.

In Section 5.2, blends of PTV-C12-CR series, in particular the most regioregular (PTV-0:10) and the most regiorandom (PTV-5:5), with PCBM are investigated. We find that strong evidence of exciton dissociation in this system are lacking, and instead that other processes such as internal conversion from $1^1B_u$ to $2^1A_g$ in PTV and Förster energy transfer from PCBM to PTV are predominant. Our results are compared with two types of polymer:PCBM composites: one, composite of the non-luminescent polymer polydiacetylene (PDA) with PCBM; two, the regioregularity-controlled polymer P3HT with PCBM which has shown definite photoinduced charge transfer.

In Section 5.3, similar investigations are made into the imidePTV:PCBM composite system. In this case, we find that the near-degeneracy of $1^1B_u$ and $2^1A_g$ states and subsequent coherence described in Chapter 4 allow for excitons to be dissociated and for
charge-transfer to occur. This result indicates that the potential for imidePTV based OPVs is significantly higher than for polymers with pure PTV backbone structures such as the PTV-C12-CR series.

5.3 PTV-CR Bulk-heterojunction Blends

The absorption of a 1:1 blend of PTV and PCBM film is a linear combination of the absorption from the two component materials, with mainly the absorption from the polymer below 2.5 eV, and predominantly that of PCBM above 2.5eV (Figure 5.1). Therefore, there is no ground state charge transfer between these two constituents.

![Figure 5.1: Absorption of the blend films PTV010 (black) and PTV55 (red) with PCBM. The absorption of the pure component materials is also shown as dashed lines, namely that of PCBM (blue), PTV010 (black) and PTV55 (red).](image)

Figure 5.2 shows the PL of films of the two neat PTVs, namely PTV010 (regio-regular) and PTV 55 (regio-random), and their blends with PCBM with a 1:1 weight ratio. PTV is intrinsically non-luminescent influenced by the order \( E(2^1A_g) < E(1^1B_u) \) [89]. PTV010 film has very weak PL (Fig. 5.2a, black circle), whereas PTV 55 is not luminescent at all (Fig. 5.2b, black circle). However, even with such low PL from the host polymer,
it is evident that no PL quenching takes place in the PTV010:PCBM blend film (Fig. 5.2a, red circle). It is interesting to note, however, that upon addition of PCBM, the PL acquires a new feature at 1.7 eV which can be attributed to PCBM emission (Fig. 5.2a, red circle) \[148\]. The possibility of energy transfer from PTV010 to PCBM can be ruled out due to the smaller bandgap of the polymer (1.8eV) \[149\]. It is more likely that direct absorption by PCBM accounts for this emission as the two constituents have comparative absorption at the pump energy of 2.54eV. The PL of PTV010:PCBM blend (Fig. 5.2a, red circle) is a simple superposition of PL from PTV \[149\] and that of PCBM at 1.7 eV \[148\] as with absorption, again indicating a lack of electronic significant electronic interaction between these two systems.

Regardless of the favorable energy alignment between PTV and PCBM (Fig. 5.3b), there is no occurrence of photo-induced electron transfer. Similar observation was reported in another non-luminescent polymer polydiacetylene (PDA) blend with \(C_{60}\) \[150\], and was explained by the tightly bound excitonic state of PDA inhibiting electron transfer to \(C_{60}\). The exciton binding energy of PTV was measured by electroabsorption to be 0.6 eV \[89\] (see Figure 3.13), which is even higher than the value of PDA (0.5 eV). Therefore it seems to be consistent that we did not observe evidence of charge transfer in PTV/PCBM blend. However, these binding energy values are not significantly higher than in other materials where charge transfer has been observed, such as MEH-PPV and P3HT. Meanwhile, the lack of luminescence from both PDA and PTV studied here is a result of the lower energy optically forbidden \(2^1A_g\) state. Thus, it is more likely that the lack of charge transfer in these systems is due to efficient internal conversion to this state that is not easily ionized due to its “covalent” nature. Unlike the case with PDA/\(C_{60}\) system, where the addition of \(C_{60}\) had no effect on the weak PL of PDA \[150\], the addition of PCBM instead “brings out” PL in PTV55 film (Fig. 5.2b). This is explained by Förster resonant energy transfer from PCBM to PTV55. Figure 5.3 illustrates this process. The singlet exciton generated in PCBM recombines to give energy to PTV55, creating an exciton that recombines radiatively. In order to prove this scenario, we used UV excitation (3.7 eV) for the same PTV55:PCBM film, and the PL intensity was four times that of the PL when
Figure 5.2: (a) The PL spectra of films of PTV010 (black circle) and PTV010:PCBM blend with 1:1 weight ratio (red circle). The line through data points is fit using a modified Franck-Condon model (see text). (b) Same as in (a) but for PTV55 film and PTV55:PCBM blend film. As a comparison, the PL spectrum of PTV55:PCBM blend film excited by UV light (blue empty circle) was also shown. The arrow in (a) and (b) indicates the PL from PCBM. All the data were not corrected by the response of grating-si detector, however, all PL were normalized to the 0-1 band intensity for comparison.
excited by visible (2.5 eV) after normalizing to the pump intensity. Not only so, very weak PL from PCBM itself at 1.7 eV was observed (Fig. 5.2b, blue empty circle) [148]. Since PCBM has stronger UV absorption than PTV55, more PL is expected from PTV55 upon energy transfer from PCBM under UV excitation. Furthermore, the energy transfer creates excitons in PTV55 with excess energy ("hot" excitons) allowing for migration to the most ordered domains with narrower distribution of conjugation lengths. This explains the red-shift as well as the sharper peaks in PL as the pump energy is increased from 2.5eV to approximately 4eV where PCBM has appreciable absorption [148]. The excitons generated in PTV55 by energy transfer from PCBM could be more likely to emit as compared to those generated by direct absorption by PTV55, as the latter quickly decay to the dark $2^1A_g$ state [89], whereas the former are generated with a delay and could arrive on conjugation segments for which the $2^1A_g$ state is already saturated. In PTV010:PCBM blend, no increase in PL from PTV010 is observed. The reason energy transfer from PCBM is apparent only in regiorandom PTV55 is explained by the difference
in film morphology, as will be shown later.

We could fit the PL spectra using a modified Franck-Condon model that includes vibronic replica [69]:

\[
I(\omega) \propto (n_f \hbar \omega)^3 \left[ \alpha \Gamma(\hbar \omega - E_0) + \sum \left( \frac{S^m}{m!} \right) \Gamma(\hbar \omega - (E_0 - mE_p)) \right] \tag{5.1}
\]

In Eq. 5.1 S is the Huang-Rhys parameter which defines the electron-phonon coupling strength, m is the number of the vibrational modes involved in the transition; \(E_0\) is the PL onset at \(E(1^1B_u)\); \(E_p\) is the strongest coupled vibrational energy, which is taken to be 0.18 eV for C=C stretching vibration which is the most strongly coupled to electronic transition in thiophene backbone polymer [69]; and \(\Gamma\) is a Gaussian distribution function around \(E_0\) having width of \(\sigma\) due to the disorder in the film. \(\alpha\) is a parameter measuring the 0-0 “suppression degree” from H-aggregates in the film, with \(\alpha = 1\) for isolated chains emission in dilute solution [69]. Using 4 phonon modes \((m = 0, 1 - 3)\), the fitting of neat PTV010 PL spectrum using Eq. (1) yields \(E_0 = E(1^1B_u) = 1.55\) eV, \(\alpha = 0.30\), \(S = 1.65\), \(\sigma = 0.07\) eV. On the other hand, fittings for PTV:PCBM blend films gave different parameters: for PTV010:PCBM, \(E_0 = E(1^1B_u) = 1.51\) eV, \(\alpha = 0.45\); for PTV55:PCBM, \(E_0 = E(1^1B_u) = 1.47\) eV, \(\alpha = 0.59\). \(S = 1.1\) and \(\sigma = 0.08\) eV for both blend films. The value of \(\alpha\) is less than 1 in all cases, consistent with the high crystallinity of the polymers in both neat [149] and blend films observed in X-ray diffraction measurements (Figure 5.4, below). Meanwhile, larger \(\alpha\) in blend films shows more disorder in polymer chains, due to the interruption of PTV crystalline by PCBM molecules, as was demonstrated in AFM images in Fig. 5.5 and in XRD measurement in Fig. 5.4. Going from neat polymer to blend, the 0-0 transition energy \(E_0\) was red-shifted, indicating more contribution from aggregate emission due to the morphological change upon adding PCBM. The X-ray diffraction measurements shown in Figure 5.4 indicate that the crystallinity of the polymers is maintained in the blend films. The reduction in peak intensity and increase in peak width in PTV010:PCBM blend suggested less density and smaller crystalline
domains, consistent with the AFM results. In addition, there is a strong enhancement in the diffraction in the range of 1.1 Å\(^{-1}\) to 1.6 Å\(^{-1}\) and also broad contribution near 0.7 Å\(^{-1}\) that overlaps with the (200) peak from PTV. These contributions are assigned to the (311) and (111) Bragg peaks of C\(_{60}\) [151, 152] showing that the side-chain of PCBM has a negligible affect on the crystal packing structure in agreement with other reports [152, 79]. The lattice spacings and domain sizes of the PTV (100) peaks are the same in the blend films as they are in the neat films (≈ 115 Å in PTV010 and ≈ 65 Å in PTV55) and the domain sizes extracted from the PCBM (311) peak is the same in both blend films (≈ 30 Å, or between 5 and 6 repeat units).

The more complete energy transfer in PTV55:PCBM blend (complete lack of PL from PCBM) comparing with PTV010:PCBM was mainly due to morphological influence. As shown in Figure 5.5, the AFM image of PTV010:PCBM shows severe and large phase segregation between polymer and PCBM (Fig. 5.5d), and the film is much rougher.
compared to PTV55:PCBM (Fig. 5.5b). All these mean that the coupling between polymer and PCBM was much weaker in PTV010:PCBM blend, which is consistent with less efficient energy transfer from PCBM to PTV010 in this blend film.

Figure 5.5: The AFM images (left panel: topology; right panel: phase) of (a) PTV 55; (b) PTV55:PCBM blend; (c) PTV010; and (d) PTV010:PCBM blend films on sapphire substrates. The scanning range is 10µm × 10µm. Height bar (peak to valley) represents 500nm, and phase bar (contrast) represents 90°. The inset of (b) right panel is the phase image of a smaller scale (0° to 50°).

AFM images shown in Figure 5.5 indicate much better miscibility between PTV55 and PCBM, partly due to larger solubility of PTV55 than PTV010 in dichlorobenzene [66]. Very small contrast was observed in the phase image of PTV55:PCBM (Fig. 5.5b). This indicates that PTV55 and PCBM were well mixed, forming tiny domains. The inset of Fig. 5.5b shows the same phase image with smaller contrast range (50°), and the polymer region (lighter color) and PCBM regions (darker color) are distinguishable. On the other
hand, the separate domains in PTV010:PCBM are as large as microns. Since Förster energy transfer goes as $1/r^6$, the large separation of host (PCBM) and guest (PTV010) constituents would not be in favor of such phenomenon.

Figure 5.6a shows the PIA of PTV010:PCBM blend measured at low and high modulation frequencies of 340Hz and 3KHz. Comparing with the neat PTV010 (Figure 3.9) [149], the long-lived photoexcitations of the polymer, namely polarons ($P_1 \approx 0.31\text{eV}$, $P_2 \approx 0.96\text{ eV}$) and triplet (T $\approx 1.2\text{ eV}$), are preserved in the blend film. Two new spectral features are observed in PTV010:PCBM blend film, the first being a broad band centered around 1.56eV, and the second a shoulder at 1.3eV. Both features were enhanced at the high modulation frequency of 3kHz, confirming that they decay much faster than the original photoexcitations (polarons and triplet) from PTV010. The lifetime of both species is about $\tau_{T,PCBM} = 29\ \mu\text{s}$, which is consistent with a previous report about the triplet state of PCBM molecules [148]. Since these two peaks have similar frequency and pump intensity dependences, we assign the lower energy shoulder at 1.3 eV as the phonon replica of PCBM triplet absorption centered at 1.56eV. The observed PCBM triplet energy is lower than previously measured [148], and this is due to the aggregation of PCBM molecules into crystals [153]. The crystallinity of PCBM was confirmed by grazing incidence XRD measurements (Figure 5.4). Due to the distribution of PCBM crystal domain sizes, there was a distribution of triplet state energies, which explains why the observed band was also broader than previously reported in $C_{60}$ fine particles [154] and in low concentration PCBM:Polystyrene blend [155].

The superposition of the PCBM triplet absorption peak with the photo bleaching (PB) of PTV010 is also responsible for the blue-shift of PB onset in PTV010:PCBM blend film, comparing the PB onset in neat PTV010 film (Figure 3.9) [149]. Note that it is also plausible that the broad band was due to polaron-pairs (or charge transfer complex $P^+/C_{60}$) as previously reported in polymer-$C_{60}$ system [85], or a mobile polaron generated via two-step process from the charge transfer complex as recently reported in P3HT/PCBM system [156]. However, we assign the transition centered at 1.56eV to that
Figure 5.6: (a) PIA spectra of PTV010:PCBM blend films measured at two modulation frequencies, 340 Hz (filled circle) and 3kHz (solid line). Both in-phase (black) and quadrature (red) components were shown; Blue line is the PIA spectrum of PTV55:PCBM blend at 3kHz; The frequency dependence of the (b) PTV010:PCBM blend film, and (c) PTV55:PCBM blend film, for polaron (black, triangles) and polymer triplet (red, circles), and PCBM triplet (green, squares) measured both in-phase (solid) and in quadrature (empty). The laser intensity is 40mW/cm$^2$. In both cases, the sample is at 10 K while under illumination with the 488 nm (2.54 eV) line from an Ar+ laser.
of the PCBM triplet absorption mainly due to the much shorter lifetime (≈30\(\mu s\)) comparing with either the polaron-pair (comparable to polaron lifetime) [85] or the mobile polaron (≈100 \(\mu s\)) [156]. Furthermore, the much better mixing among PTV55 and PCBM would naturally boost the formation of \(P^+/C_{60}^-\), if the band at 1.56eV was indeed due to the polaron-pair. However, in the PTV55:PCBM blend studied here, this absorption band was suppressed (green line in Fig. 5.6a), which can be assigned to reduced triplet generation from competition of energy transfer to PTV55 from PCBM.

We did not observe the characteristic \(C_{60}^-\) anion absorption between 1.1 eV to 1.2 eV [157], although it is possible that the \(C_{60}^-\) peak overlaps with the triplet peak (1.2 eV) of PTV. Since the polymer spectral features are all maintained when 50% by weight PCBM is added, we conclude that charge transfer does not occur in the PTV/PCBM blend, regardless of the polymer chain orders. The tightly bound excitons in PTV and the intra-chain sub-ps decay of these excitons into \(2^1A_g\) state prevents the formation of charge transfer complex \(P^+/C_{60}^-\).

However, the lifetimes of the original photoexcitations in PTV were greatly shortened. Fig. 5.6b shows the frequency dependence of both in-phase and quadrature PIA signals for PTV 010 polaron (\(P_2\)) and triplet (T-PTV), as well as PCBM triplet (T-PCBM) in PTV010:PCBM blend film, and the lifetime derived from the cross point of the in-phase and quadrature components [43] yield \(\tau_{T,PCBM} = 29 \mu s\) which is consistent with previous reports on the PCBM triplet lifetime [155]. \(\tau_p = 0.2\)ms for the polaron and \(\tau_T = 40 \mu s\) for the triplet of polymer, compared to about 5.7 ms and 4.7 ms for the polaron and triplet lifetimes respectively, in neat PTV010 [149].

<table>
<thead>
<tr>
<th>Film</th>
<th>(P_2) (ms)</th>
<th>T (ms)</th>
<th>T-PCBM (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTV010</td>
<td>5.7</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>PTV010:PCBM</td>
<td>0.20</td>
<td>0.040</td>
<td>0.029</td>
</tr>
<tr>
<td>PTV55</td>
<td>3.2</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>PTV55:PCBM</td>
<td>0.057</td>
<td>0.066</td>
<td>0.009</td>
</tr>
</tbody>
</table>
We explain the shortening of lifetime for the polymer photoexcitations by two mechanisms: one, the reduced electron-phonon coupling might reduce the activation energies of both species; two, the PCBM molecules may act as non-radiative recombination centers for such species, thus reducing the lifetime. Fig. 5.6c shows the frequency dependence of polaron and triplet in PTV55:PCBM blend film. It is surprising that the lifetime of the polaron was only 59 µs, and triplet 66 µs in this blend film, whereas the lifetime of the PCBM triplet is about 9 µs. All lifetimes are faster than those in blend of PTV010:PCBM (see Table 5.1). We believe the much more efficient energy transfer in PTV55:PCBM plays a role in further reducing the lifetime of the PCBM triplet, while the intermixing of PCBM molecules with PTV55 chains results in the shortening of lifetimes of the polaron and triplet of PTV55. This explains why the reduction of the PTV010 polaron lifetime in blend films is much less than for the PTV55 polaron. In light of this, it is more likely that PCBM molecules acting as recombination centers is the dominant lifetime reducing mechanism at work. It is interesting to note that the reduction of the polymer triplet lifetime is over two orders of magnitude while the reduction of the polaron lifetime is only 25 times in PTV010:PCBM blend, comparing with neat PTV010. This might be due to the close proximity in energy of the polymer triplet at 1.2 eV and the phonon replica of the PCBM triplet at 1.3 eV, rendering it difficult to separate these two peaks. The measured polymer polaron absorption might also include a contribution from the tail of PCBM triplet absorption.

5.4 ImidePTV Bulk-heterojunction Blends

In Chapter 4, we saw that the $1^1B_u$ lifetime is an order of magnitude longer in imidePTV than in the alkyl-substituted derivatives with pure PTV backbone structures discussed in Chapter 3 in PTV-CR. The important consequence of the state ordering that gives rise to enhanced PL in imidePTV may then be expected to have an impact on the process of photo-generation of charged species in bulk-heterojunction blend films. As discussed in the introduction, a first test of efficient charge transfer between a donor
π-conjugated polymer and the electron accepting PCBM is the quenching of PL in blend films. Figure 5.7 shows a comparison of the neat film PL spectrum to that obtained from a blend (1:1 wt. ratio) of imidePTV and PCBM. In this case, the PL is clearly quenched, being reduced by a factor of approximately 50. This suggests that nearly 98% percent of the excitons available for emission in the neat film are dissociated by the presence of PCBM. This is a very different situation from what was observed for pure PTV in Section 5.2, where the weak PL from PTV-0:10 was unaffected by the addition of PCBM and an enhancement in the PL of PTV-5:5 was observed due to energy transfer. We interpret this difference as being due to the ability of the $1^1B_u$ exciton in imidePTV to participate in charge transfer with the $C_{60}$ molecules of PCBM, where as the $2^1A_g$ state in PTV-CR had negligible contribution to charge-transfer. This could be due to the lower energy of the $2^1A_g$ state making the electron-transfer process endothermic, or could also result from the spin-wave nature of the $2^1A_g$ state making it generally inaccessible to ionic-type reactions. We note that in other π-conjugated polymer-$C_{60}$ systems, the charge-transfer reaction was found to occur on a time scale of hundreds of femtoseconds, making it competitive with the 10ps thermalization between the the $1^1B_u$ and $2^1A_g$ states in imidePTV as determined in Chapter 4.

The fact that the quenched excitons do indeed result in the generation of charge carriers is demonstrated by the observation of polaron absorption features in PIA measurements. Figure 5.8 shows the spectrum acquired from the blend film and compares to the neat film PIA spectrum shown in Figure 4.13a. We observe significantly different features from the blend film, the most notable being the presence of polaron absorption ($P_1$) in the IR range ($\approx 0.4$eV) that was not observed in the neat film. The identification of this species as polarons can be made by comparison to the doping-induced absorption in Figure 4.16 for imidePTV and also by comparison to the spectral positions of polarons in PTV (Figure 3.9). As previously explained, we expect a second transition between the mid-level trap states ($P_2$) at $\approx 0.9$eV, and with similar magnitude as $P_1$. 

111
Figure 5.7: Photoluminescence of a 1:1 blend film of imidePTV and PCBM (black circles) compared to the spectrum obtained from a film of neat imidePTV (blue circles). The blend film signal has been multiplied by 10 to facilitate comparison.

This feature seems to be apparent in Figure 5.8 although it is difficult to resolve due to the presence of overlapping features, which are assigned to the residual triplet from imidePTV ($T_{iPTV}$) and the strong feature at 1.48eV which is assigned to the triplet of PCBM ($T_{PCBM}$) in accordance with literature and the similar observations discussed in Section 5.2. We clarify the presence of these three distinct features in the broad absorption of between 0.8eV and the band edge at 1.75eV in discussion that follows, with assistance from the intensity and frequency dependence of the PIA.

The frequency dependence of the states allows us to distinguish between the individual absorption features that overlap in the PIA spectrum. Figure 5.9 shows the variation of the in-phase and quadrature signals with frequency at three probe energies representative of the three features in the PIA spectrum. They are the polaron transition, $P_2$ probed at 0.91eV, the triplet of PCBM, $T_{PCBM}$, probed at 1.51eV (this energy is slightly higher than the peak observed in the PIA spectrum and was chosen to minimize overlap with the other features at lower energy) and the triplet-pair state population of imidePTV
(T_{iPTV}) probed at the peak energy determined from the neat film of 1.30 eV. It is not obvious from the PIA spectrum of the blend film that the latter feature is preserved from neat imidePTV. However, the polaron features apparent in the spectrum are fairly weak, and thus the efficiency of charge transfer is not expected to be very high. Most likely it is close to the PLQE in film and accounts for less than 1% of the fate of initially generated excitons. We expect that the large PCBM triplet signal thus obscures the

Figure 5.8: PIA spectrum of a 1:1 blend film of imidePTV and PCBM (in phase - black, quadrature - red) compared to that of a neat film of imidePTV (in phase - blue, quadrature - magenta) at 3 kHz modulation frequency of the 488 nm (2.54 eV) excitation from an Ar+ laser. The sample temperature is 10 K. The labels assign peaks for the blend film as discussed in the text.
remnants of the triplet-pair transition from the imidePTV component. This assumption will be justified in the analysis of the pump intensity that follows. In passing, we note that there is also the possibility of ionization of triplets in the pair by PCBM, however, we suggest that this is unlikely, due to the low-signal obtained from polarons, which should be exceedingly large if they originated from charge generation from triplet-pair dissociation.

Figure 5.9: Pump modulation frequency dependence of the PIA features in a blend film of imidePTV and PCBM. Both in-phase (solid symbols) and quadrature (open symbols) signals are shown, with the arrows indicating the crossover frequency from which the lifetime is extracted. Data from the imidePTV triplet (T-iPTV, triangles) at 1.30eV, imidePTV polaron (P2, circles) at 0.91eV and PCBM triplet (T-PCBM, squares) at 1.51eV are presented.

The data in Figure 5.9 display a variation of photoeciation lifetimes across the spectrum. The shortest lifetime extracted from the $T_{PCBM}$ is 9µs, identical to what was observed in PTV-55:PCBM blend in Section 5.2 and again consistent, although slightly shorter, than observed in previous reports on the lifetime of this species [155, 148], suggesting additional recombination mechanisms involving interaction with imidePTV. Meanwhile,
the lifetime extracted for the polaron peak $P_2$ is longer by a factor of two, 18µs. This is about three times faster than observed in the blend film with PTV-55 suggesting that the polarons may be bound as charge-transfer complex at the interface of polymer and PCBM and quickly recombine, without truly delocalizing in the imidePTV domains. The lack of crystallinity in imidePTV plays a role here. Since the chains are quite isolated, the polarons can not hop from one to another as efficiently as they might in a PTV-C12-CR crystallite. Therefore positively charged polaron cannot escape the local Coulomb attraction with the electron residing on PCBM. Finally, at the probe position assigned to $T_{iPTV}$ a lifetime of 12µs is obtained. In this case, we interpret this as a linear combination of the lifetimes of $T_{PCBM}$ and $P_2$ due to the overlap of those two absorption features at this energy. This is expected as the lifetime of $T_{iPTV}$ is below the resolution of the cw-PIA set-up in neat films and is only expected to be shorter in blend films. Thus, the presence of the longer lived neighboring species dominates the frequency dependence there and obscures the fast feature from the triplet-pair in neat imidePTV (see Ch. 4).

The intensity dependence also helps to distinguish these features from one another, and provides an explanation for the short lifetimes. The log-log plots of the PIA intensity versus pump intensity all show an approximately linear dependence up to at least 150mW/cm². For the $T_{PCBM}$, the species show a crossover above 180mW/cm² to an almost perfect square-root dependence, a sure signal of bimolecular recombination. Almost identical behavior is observed for the $P_2$ peak, although the power-law dependence is 0.65 instead of 0.56. This is most-likely due to overlap with the $T_{iPTV}$ peak which has already been shown to exhibit linear dependence over the whole experimentally accessible intensity range. This latter peak shows a much subtler decrease in power-law dependence (0.72) and also at a much higher intensity of 295mW/cm², both of which indicate that the triplet-pair state maintains its strict linear dependence on pump intensity, and only when the other features (predominantly the more close-by $T_{PCBM}$) become very strong does the experimentally measured intensity dependence deviate from linearity due to the overlap with other species. This is possible because the ratio of the generation rate to the recombination is highest for $T_{PCBM}$ compared to the other features, so that the
Figure 5.10: Pump intensity dependence of the PIA features in a blend film of imidePTV and PCBM on a log-log scale. Data from the imidePTV triplet (T-iPTV, blue triangles) at 1.30eV, imidePTV polaron (P2, green circles) at 0.91eV and PCBM triplet (T-PCBM, black squares) at 1.51eV are presented. Red lines are linear fits used to determine the recombination order.

absorption peak of PCBM triplets grows faster with pump intensity in the linear regime, as will be shown in Figure 5.11. This is due to the larger absorption coefficient of PCBM than that of imidePTV at the pump energy of 2.54eV. The triplet-pair state may also show sub-linear dependence due to annihilation events with polarons or PCBM triplets at the interface, but such occurrences are unnecessary to explain the data and unlikely for reasons discussed above.

5.5 Summary

The photovoltaic implications of the photo-physical properties have been demonstrated in this chapter through the analysis of the photophysical properties of bulk-heterojunction blend films with PCBM for the various PTV derivatives. In particular, it has been
shown that the PLQE of a π-conjugated polymer can be directly related to its ability to undergo charge-transfer with PCBM and thus to generate photocurrent in a bulk-heterojunction organic photovoltaics. This suggestion has not been put forth before to the author’s knowledge. In the past, the PLQE was related to a π-conjugated polymer’s potential for OLED applications. In fact, since emission is suggestive of a strong binding energy for the exciton, PLQE was expected to be inversely proportional to OPV efficiency. However, we have shown here that when a material is intrinsically non-luminescent, it will consequently also be a poor donor in bulk-heterojunction organic photovoltaics, because the lack of emission suggests that the relaxation pathways for photo generated excitons are inherently internal.

In PTV-C12-CR, it was determined that electron-transfer does not occur between these materials and PCBM, independent of the regioregularity. This was confirmed by the lack
of PL quenching in the blend films, and the observation of the competing process of energy transfer from PCBM to PTV-5:5 which actually enhances the PL yield. Furthermore, no strong evidence of a meta-stable charge-transfer excitation, such as a $C_{60}^−$ anion, was observed in PIA measurements. In fact, the observation of the PCBM triplet exciton absorption and the simple superposition of the PL from the two material components in the blend film spectrum indicate that the materials do not communicate electronically other than the energy transfer process. While the better solubility and random ordering of chains of PTV-5:5 allows for fine-scale mixing of the two materials, the severe phase segregation observed for 0:10 further limits the interactions between the two and inhibits even the energy transfer process.

In imidePTV, the PL was observed to be significantly quenched by the addition of PCBM. This fact, along with the observation of polaron absorption features in PIA that are absent from the neat imidePTV film PIA spectrum show conclusively that electron-transfer occurs between these two systems, leading to positive charges residing in the polymer domains. The good solubility and lack of crystallinity of imidePTV means we expect the morphology of the blend films similar to those of PTV-55:PCBM with fine-scale heterogeneous mixing. This explains the extremely short lifetime of the species since the identified bimolecular recombination mechanisms of both the imidePTV polaron and PCBM triplet make both polaron-polaron and polaron-triplet annihilation processes plausible. The lack of inter-chain interactions in imidePTV domains also limits the available landscape for polarons to sample, reducing entropically driven charge-separation and results in much shorter polaron lifetimes.

Although imidePTV is a better candidate for OPV than its pure PTV counterparts PTV-CR, it is still far from the ideal donor polymer. While it has a lower optical band-gap than poly(3-hexylthiophene), the band-gap had to be raised at least 0.1eV in order to help to stabilize the $1^1B_u$ exciton by reducing the quinoidal-aromatic structural disturbance compared to PTV-5:5 and similar materials. The gain is hardly worth it either, since the close energetic proximity still limited PLQE and the polaron yield in
the blend films. Furthermore, for the particular imidePTV studied here, the bulky side groups have restricted inter-chain interactions and therefore there is limited excitation diffusion. The adverse effects for OPV application due to this last characteristic are apparent in the exceedingly short lifetime of the resulting polarons in the blend with PCBM. Thus further improvements in the material series presented in this Ph.D. work would include reducing the inter-chain distance and increasing the inter-chain coherence through regio-regularity for imidePTV or other variants of PTV with more dilute vinylene content. Practically speaking, however, the effort is not worth the potential gain that such a material would be expected to surpass poly(3-hexylthiophene). This work has thus demonstrated that diluting aromaticity of \( \pi \)-conjugated polymers in order to lower the band gap has reached its practical limit for OPV application and the effort to establish other low-band gap polymers with high solar cell efficiency is better handled by other chemical strategies such as the donor-acceptor type \( \pi \)-conjugated polymers.
6 PTV-BASED OPV AND CHARGE TRANSPORT

6.1 Introduction

To complete our characterization of the viability of using PTV based $\pi$-conjugated polymers as donor polymers for photovoltaic application, we focus our investigation on the final two steps in the photovoltaic process, namely carrier transport and extraction. We have previously described the electronic characteristics of the materials in this Ph.D. work in the context of molecular exciton theory. It is the properties of these primary excited states that determine the characteristics of absorption and the possibility of charge generation ("free" electrons and holes). For instance, in a bulk-heterojunction organic photovoltaics, the charge transfer from a polymer to PCBM will leave a "free" electron in PCBM and "free" hole in the polymer. The nature of carrier transport in the respective materials will subsequently determine the charge extraction efficiency. An additional contribution will come from the contacts, specifically, the extent that they form Ohmic junctions with the energy levels of interest. These latter energy levels (termed "transport levels") are fundamentally different from the exciton levels because they are true single-particle states and not the quasi-particle states such as excitons and polarons previously discussed.

The transport levels are thus usually described as HOMO and LUMO levels. For example, in the above description the photogenerated hole is said to rest in the HOMO of the polymer while the photogenerated electron is said to rest in the LUMO of PCBM. This terminology is somewhat misleading, however, because macroscopic transport in these systems is inherently intermolecular, and consequently involves a distribution of
such single-particle states in phase-space. In this sense, the transport can be described in the language of conduction and valence bands. The density of states (DOS) characterizing these bands will be largely dependent on the conformation of molecules and their orientation with respect to each other. The DOS can vary, therefore, depending on the processing conditions. Charge transport in $\pi$-conjugated polymers is generally described by carrier hopping with a disorder-broadened Gaussian density of states (GDOS). The GDOS model developed by Bässler [158] presents the transport of a charge-carrier (polaron) in terms of a Miller-Abrahams type hopping [159], where the probability of a transition between transport sites $i$ and $j$ take a form:

$$
\nu_{ij} = \nu_0 \exp(-\Gamma_{ij} + \frac{E_i - E_j}{k_B T} \Omega(E_i - E_j)) \quad (6.1)
$$

where $\nu_0$ is an “attempt-to-jump” frequency prefactor, $\Gamma_{ij} = 2\beta_{ij}a_{ij}$ describes the overlap between sites $i$ and $j$ and is subject to site-to-site variation due to the distribution of inter-site distances $a_{ij}$ and conformations (described by $\beta_{ij}$), $E_i$ is the energy of the $i$th transport site, $k_B$ is Boltzmann’s constant, $T$ the temperature and $\Omega$ the unity-step function that declares the Boltzmann term to be unity for jumps that are downhill in energy. The variation in transport site energies $E_i$ is due to the variation in HOMO and LUMO levels of different conjugation length segments and is termed “diagonal disorder,” while the variation in $\Gamma$ is referred to as the “off-diagonal disorder.” These hopping events take place within the GDOS of the form

$$
g(E) = \frac{N_t}{\sigma \sqrt{2\pi}} \exp\left(-\frac{E_c^2}{2\sigma^2}\right) \quad (6.2)
$$

about some mean energy $E_c$. Here $N_t$ is density of transport sites and the width $\sigma$ includes both the diagonal and off-diagonal disorder. The main consequence of this type of transport is a charge-carrier mobility that depends on temperature and electric field, $F$, according to

$$
\mu(F, T) = \mu_0 \exp\left[-\frac{2\sigma}{3k_B T} + C\left((\frac{\sigma}{k_B T})^2 - \Sigma^2\right)F^{1/2}\right] \quad (6.3)
$$
where C is an empirical fitting parameter and Σ is the variance of Γ and is thus attributable to the off-diagonal disorder only. The hallmark of hopping transport within the GDOS is therefore a Poole-Frenkel type field dependence of the mobility that goes as $\ln \mu \propto \sqrt{F}$ and temperature dependence of the mobility $\ln \mu \propto (1/T)^2$.

In this chapter we investigate the photovoltaic device performance of bulk-heterojunction organic photovoltaics devices that contain the PTV derivatives discussed in this work as donors and subsequently analyze the contributions to the device performance results through an independent study of the transport properties. In Section 6.2, we turn to the direct evaluation of the OPV performance through fabrication and characterization of these devices. A caution is set out that these results may not reflect the best possible performance relative to any particular donor polymer. This is mainly due to the fact that, in principle, each polymer may be optimized with completely different processing conditions. The processing parameters that may be varied for such purposes include the architecture (conventional or inverted structure), the choice of the opaque electrode, the deposition rate of this electrode, the thickness of the active layer, the ratio of donor polymer to PCBM, the solvent(s) used to form solutions, choice of and processing conditions for interfacial transport layers, as well as any post-production treatments such as thermal annealing. Furthermore, each set of parameters should be tested a sufficient number of times such that variations in performance due to electrode quality, active layer film quality and contacts may be excluded. The definition of “optimal” processing conditions then may be stated in terms of the average or maximum performance achieved. Such an exhaustive trial-and-error investigation is not possible here, nor is it even expected that it would yield either impressive performance or interesting conclusions. This discussion highlights the benefit of the contact-free methods used to interrogate these polymers in the previous chapters. Considering these factors, our primary intentions in Section 6.2 are to sample the device performance of the three most prototypical polymers in this study, namely RR-PTV-C12 (PTV-1:9 is used here because the extremely poor solubility of PTV-0:10 presented significant challenges for device fabrication), RRa-PTV-C12 (PTV-5:5) and imidePTV, and to compare their performance using a consistent architec-
ture and fabrication parameters. Additionally, we wish to interpret the OPV results in terms of the conclusions already obtained using the photophysical methods in previous chapters, and in doing so, to validate our approach.

In Section 6.3, we evaluate the role of the carrier transport properties of imidePTV in limiting the efficiency of photocurrent extracted in OPV as well as on the other parameters governing the efficiencies of these devices. We specifically focus on imidePTV since it shows much better potential for OPV performance than the other polymers studied here, although the efficiency is still low. It is the specific aim of Section 6.3 to determine why this efficiency is low. We analyze J-V curves extracted from single-carrier diodes in terms of the space charge limited current (SCLC) model in order to determine the value of both the hole mobility and electron mobility of imidePTV. Secondly, we measure the illumination intensity, temperature and electric field dependencies of the photoconductivity to evaluate the charge transport properties of imidePTV within the context of the GDOS model. Additionally, the photoconductivity action spectrum is used to show the generation of electron-hole pairs by direct photoexcitation with excess incident photon energy in order to clarify the origins of photocurrent observed from OPV.

6.2 PTV Derivatives as Donors in OPV

As discussed in the introduction, the purpose of this section is to compare the OPV results obtained by employing the various polymers from this study as donors in otherwise identical device architectures. We choose the most common architecture and fabrication procedures in the field for this purpose, consisting of ITO electrodes coated with a thin layer (≈30nm) of PEDOT:PSS as anode (this is the conventional structure), an active layer (≈100nm) composed of a 1:1 weight ratio blend of the polymer and PCBM formed by spincoating from DCB solution, and capped with a 100nm Al cathode formed by thermal vapor deposition (TVD). The typical results obtained under solar simulation are displayed in Fig. 6.1 for two derivatives from PTV-CR series with different regioregularities and
for imidePTV in Fig. 6.2. While Table 6.1 displays the average and best performance in each of the main parameters describing solar cell behavior taken from the ensemble of devices tried for the three donor polymers.

Table 6.1: Solar cell device parameters for three prototypical PTV derivatives of this work in a 1:1 wt. ratio blend of PCBM as photoactive layer.

<table>
<thead>
<tr>
<th></th>
<th>$J_{SC}$ ($\mu$A/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>$\eta_{PCE}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RR-PTV(1:9)</td>
<td>56</td>
<td>94</td>
<td>0.39</td>
<td>0.44</td>
</tr>
<tr>
<td>RRa-PTV(5:5)</td>
<td>143</td>
<td>193</td>
<td>0.22</td>
<td>0.28</td>
</tr>
<tr>
<td>imidePTV</td>
<td>355</td>
<td>893</td>
<td>0.41</td>
<td>0.58</td>
</tr>
</tbody>
</table>

These parameters were obtained from the same device.

The most striking difference is the much higher short-circuit currents ($J_{SC}$) obtained for imidePTV, which in the best case is about an order of magnitude more than for RR-PTV and and almost a factor of 5 higher than that obtained for RRa-PTV. The fact that $J_{SC}$ is lowest for the most ordered polymer of the three (RR-PTV) indicates that carrier

Figure 6.1: JV curves of PTV-19:PCBM (RR-PTV, black squares) and PTV-55:PCBM (RRa-PTV, red circles) solar cells under AM 1.5 illumination.
transport is not a primary factor in the low current observed as the enhanced order is expected to lead to better transport properties. The higher currents in RRa-PTV based devices compared to RR-PTV based ones is most likely due to the lower bandgap (see Fig. 3.3) that allows this material to harvest more of the solar spectrum.

Figure 6.2: J-V curve of an imidePTV:PCBM solar cell in the dark (black squares) and under AM 1.5 illumination (“light,” blue triangles).

Note that RRa-PTV also holds this advantage over imidePTV as well. Furthermore, imidePTV is the most amorphous of the three, judging from the XRD measurements and is therefore expected to have the worst charge transport properties of the three. All of this taken together provides strong evidence that the charge generation properties of these materials effectively controls the $J_{SC}$. In turn, it is noted in Table 6.1 that the $J_{SC}$ also dominates the power conversion efficiency $\eta_{PCE}$, as the best efficiencies were obtained simultaneously in the devices the devices with highest $J_{SC}$. The dependence of $\eta_{PCE}$ on the other parameters, $V_{OC}$ and FF, were more subtle. In all cases, the values for both of these parameters were low, which may be due to the lack of optimization of
the device fabrication conditions. Though $V_{OC}$ is not the theoretically expected value for any polymers studied here [160], the expected trend is observed, namely, that $V_{OC}$ scales with HOMO of the donor polymer. The respective HOMO’s for RRa-PTV, RR-PTV and imidePTV were estimated to be 4.96eV, 5.03eV and 5.3eV by cyclic voltammetry measurements [66, 161]. The scaling of $V_{OC}$ with the difference between the HOMO of the donor polymer and the LUMO of PCBM is consistent with the observations of Scharber et. al [160] and is anticipated theoretically [35]. Finally, we note that the low $V_{OC}$ in general may be partially due to the low $J_{SC}$ itself, according to the expression $V_{OC} = k_B T \cdot \ln \left( \frac{J_{SC}}{J_{sat}} + 1 \right)$ that may be derived from Equation 1.3, though parasitic resistances almost certainly play a role as well. Such resistances are also expected to be responsible for the low FFs although a bit more explanation is warranted there. The large slope of the J-V curves is suggestive of a small shunt resistance (see Ch.1). However, the shunt resistance should be as noticeable in the dark J-V as in that observed during illumination. Since the dark J-V curve of imidePTV is flat under negative applied bias, it is more likely that photoconductivity (increase of the conductivity due to illumination) is responsible, as has been suggested for other OPVs [162, 163].

The external quantum efficiency (EQE) spectrum from an imidePTV:PCBM OPV is shown in Fig. 6.3 (red line). The efficiency is on the order of 1% in accordance with the estimate based on PLQE as discussed in Ch. 5. The low energy side of the spectrum follows the absorption of the blend film, which below 2.3eV is predominantly due to imidePTV. This fact indicates that the EQE spectrum below 2.3eV is due to photo-generated excitons in imidePTV that are dissociated at the interface of imidePTV and PCBM, which is the most common charge-generation process in OPV. Above 2.3eV, however, the EQE spectrum deviates significantly from the blend film absorption. The EQE at higher energy follows the neat imidePTV device external photoconductivity action (EPCA) spectrum also displayed in Fig. 6.3 (black squares). The EPCA measurement is similar to EQE but the absence of PCBM in this case means we expect charge generation to be low (note the difference in the y-axis scales).
Figure 6.3: External Quantum Efficiency of an imidePTV:PCBM (EQE) solar cell (red line). The external photoconductivity action (EPCA) spectrum (black squares) of an imidePTV only device and absorption spectrum imidePTV:PCBM blend film is shown for comparison.

It is useful however, in the determination of energy levels at which carrier generation occurs and the dependence of this process on the initial energy of the photoexcited state. In this case, we see that the photocurrent from imidePTV increases with increasing pump energy. This can be attributed to either “hot exciton dissociation” where the excess above-gap energy is quickly redistributed into the lattice providing the driving force for dissociation [164], or carrier generation from higher lying states such as the $nB_n$ [87, 165, 166], with the latter being more likely (see section 6.3). We conclude,
therefore, that a significant portion of the current in an imidePTV:PCBM OPV stems from direct photocarrier generation in imidePTV. The efficiency of current collected from direct photocarrier generation is three orders of magnitude higher in the blend film OPV EQE (≈1% or 10⁻²) than in the neat film photodiode EPCA (≈0.001% or 10⁻⁵). This is consistent with the much higher electron-mobility in PCBM than in imidePTV as will be discussed in the next section.

6.3 Charge Transport of imidePTV

It is clear from the previous section that the analysis of bulk-heterojunction organic photovoltaics device performance is quite complex, as the parameters extracted are not mutually independent and they may all be influenced by many physical aspects of the complete structure, such as contacts, blend morphology, and the excited state energetics of the donor polymer to name a few. In this Ph.D. work, we have therefore attempted to separate the operation of these devices into four fundamental steps so that the true potential of the donor polymers can be assessed. In this section, we conclude such analysis by investigating the charge-carrier transport properties of imidePTV. We specifically focus on imidePTV because this material has displayed better potential for application than other PTV derivatives, because of the longer 1¹Bₓ excitonic lifetime and resulting higher efficiency of charge transfer with PCBM compared with the other derivatives in this work. The highest efficiency achieved with imidePTV in this work, \( \eta_{PCE} = 0.12\% \) is still low compared to the standards of the field however, for instance the \( \approx 5\% \) achieved using RR poly(3-hexylthiophene) in identical device structures [51, 77]. We expect that this is a result of the inefficient charge transfer (although more efficient than in the PTV-CR series) due to the competing process of internal conversion and relaxation within the mixed 1¹Bₓ- 2¹Aₓ state as explained in Chapter 4. However, to be certain, we should rule out other factors such as low carrier mobility. The purpose of this section is to address this issue.
6.3.1 **SCLC in Single Carrier Diodes**

Space charge limited currents (SCLC) are a generic feature of transport in a poorly conducting material and provide a simple method to obtain the carrier mobility of both electrons and holes separately. The principle of SCLC is that at a high enough injected current density, the low mobility of the conducting material will cause charges to accumulate in the bulk leading to capacitance and a space charge field. When only one type of carrier is present such that bipolar carrier recombination can be ignored a set of simple analytic solutions to Poission’s equations describe the current-density [167]. Thus, to study the hole transport through SCLC we require contacts that will block electron injection and also provide Ohmic hole injection. To achieve this we apply a thin layer of PEDOT:PSS onto ITO before spincoating to serve as the hole-injecting contact and complete the device by application of a gold electrode on top by TVD. The large work function of gold will inhibit the injection of electrons.

![Schematic of the layer-by-layer structure of an imidePTV hole-only diode and the resulting band structure.](image)

We plot the J-V curve on a log-log scale (inset to Figure 6.5) to determine the power of the dependence on voltage and obtain a linear relationship at low voltages before a crossover to a quadratic regime. The latter signals that the injected carriers are now larger in concentration than the intrinsic carriers and space charge accumulation occurs. Once these two regimes have been clearly identified, the linear part of the curve can be
fit to Ohm’s law \((J = \sigma F, \text{ for an applied field, } F, \text{ and the conductivity, } \sigma)\) while the quadratic part is fit to the Mott-Gurney equation [167],

\[
J = \frac{9}{8} \epsilon \epsilon_0 \mu V^2 \frac{d}{d^3} \tag{6.4}
\]

which allows us to extract the mobility, \(\mu\). More accurately we obtain the product of the material permittivity \(\epsilon\) and hole mobility \(\mu\). To a decent approximation \(\epsilon = 1\) for most polymers [168] and can be neglected. Furthermore, the role of shallow trapping has been neglected, for which a numerical factor that is less than 1 would be included in the Mott-Gurney equation. If shallow trapping is has occurred, the neglect of this factor leads to an under-estimate of the mobility rather than an over-estimate due to a higher permittivity.

The values obtained were \(9 \pm 0.7 \times 10^{-8} \text{ S/cm}\) for the conductivity and \(9.5 \pm 2.5 \times 10^{-5} \text{ cm}^2/\text{V-s}\) for the mobility, where the uncertainties listed are attributed to the uncertainty in the film thickness that was measured to be \(65 \text{nm} \pm 5 \text{nm}\) by profilometry for this device. Additionally, the crossover voltage, \(V_X\), at which the current transitions from the linear to the space charge limited regime here at about \(0.45 \text{ V}\), provides a means of evaluation of the intrinsic carrier density (intrinsic in this case should be taken to mean that they are not injected carriers) through the equation \(V_X = e \rho_0 / \epsilon \epsilon_0\) [167] and from this value in combination with the conductivity extracted from the linear fit, we can obtain the mobility independently through the equation \(\sigma = e \rho_0 \mu\). A carrier density of \(1.2 \pm 0.1 \times 10^{15} \text{ cm}^{-3}\) was extracted. Furthermore, that the same value for the mobility is obtained within the experimental uncertainty provides a validation of the SCLC model application. The extracted hole mobility is relevant to OPV device performance, as the polymer domains in a bulk-heterojunction film will be where photo-generated hole transport occurs.

The mobility obtained here for imidePTV is large enough that we don’t expect this to be the predominant limiting factor for solar cell performance upon comparison to the hole mobilities of other \(\pi\)-conjugated polymers that have achieved reasonable efficiencies
when used as donors in bulk-heterojunction organic photovoltaics. For instance, a hole mobility of $5 \times 10^{-7} \text{cm}^2/\text{V} \cdot \text{s}$ was reported for MDMO-PPV [169], a system that has achieved 2.5% $\eta_{PCE}$ in OPV despite of a higher bandgap than imidePTV [170].

Figure 6.5: J-V curve of an imidePTV hole-only diode including a fit to the Mott-Gurney relation (red dashed lines). The crossover between the linear and space-charge regimes is indicated by $V_X$ and the parameters extracted from the fit are displayed with $\mu$ the mobility, $\sigma$ the conductivity and $p_0$ the intrinsic carrier density. The inset shows the same data on a log-log scale to facilitate the identification of the linear (Ohmic) and quadratic (space-charge) regimes.

Although it is not the conventional transport property relevant to solar cells, we also used this method to determine the electron transport parameters in order to study the mobility
and conductivity anisotropy. To do this, we employ lower work function electrodes in order to block hole injection and allow for efficient electron injection. The top electrode was an Aluminum film formed by TVD, and the bottom ITO electrode was rendered a cathode by a ZnO sol-gel process that is a common method for fabricating inverted organic solar cells. It was necessary to increase the thickness of the imidePTV layer for these devices comparing to the hole-only diodes, in order to reduce the field strength. The thicker films were realized by the method of drop-casting.

![Figure 6.6: Schematic of the layer-by-layer structure of an imidePTV electron-only diode and the resuting band structure.](image)

Similar to the case for hole-only diodes, we obtain a quadratic current voltage relationship for electrons after a crossover from the Ohmic regime (inset to Figure 6.7). In this case, we extract a conductivity of $2\pm0.1\times10^{-11}$ S/cm from the linear fit, and a mobility value of $1.1\pm0.2\times10^{-6}$ cm$^2$/V·s from the Mott-Gurney equation, with a measured thickness value of 300nm ± 20nm for this device.

This mobility value is almost two orders of magnitude less than what was obtained for hole transport. Additionaly, from the crossover voltage $V_X$, the intrinsic carrier density of $5.9\pm1.0\times10^{14}$ cm$^{-3}$ is obtained, and we are able to independently obtain the same value for the mobility by plugging this value along with the observed conductivity into $\sigma = en_0\mu$. We find that the electron carrier density is less than the hole density by a
Figure 6.7: J-V curve of an imidePTV electron-only diode including a fit to the Mott-Gurney relation (red dashed lines). The crossover between the linear and space-charge regimes is indicated by $V_X$ and the parameters extracted from the fit are displayed with $\mu$ the mobility, $\sigma$ the conductivity and $n_0$ the intrinsic carrier density. The inset shows the same data on a log-log scale to facilitate the identification of the linear (Ohmic) and quadratic (space-charge) regimes.

A factor of 60, and thus the electron conductivity ends up being about four orders of magnitude less than that for holes.

### 6.3.2 Photoconductivity

In a photoconductivity experiment, we generate charge-carriers in the bulk by illumination and extract the current under applied reverse bias. The device geometry was identical to that used for the SCLC hole-only diodes, so that hole-extraction occurs.
This technique is very relevant to solar cell transport as the nature of carriers (photogenerated holes) is identical to that in OPV operation. This measurement is a spectroscopy technique, allowing the determination of energy levels at which carrier generation occurs and are dependence on the initial energy of the photoexcited state. We refer to this spectrum as the internal photoconductivity action (IPCA) spectrum or the efficiency for charge photogeneration \( \eta_{ph} \). In Figure 6.8 we display this spectrum and compare it to the film absorption. It can be seen that very little current originates from the excitonic absorption band. The measured quantum efficiency for photogeneration is on the order of \( 10^{-4} \). The large binding energy of the exciton formed upon absorption results in negligible electron-hole pair generation when absorption occurs into this band. The current generated in this spectral range is most likely due to exciton quenching that occurs at the electrode interface, and perhaps some contribution from field dissociation. At higher energies, the charge generation increases significantly. It can be seen that the sharp rise occurs above approximately 2.5eV, where no corresponding features in absorption can be claimed responsible. The onset of this enhanced charge generation is coincidental with the nB\(_u\) energy level determined by electroabsorption (see Figure 4.11). This is consistent with the theoretical interpretation of the nB\(_u\) state as marking the onset of continuum states, similar to a true conduction band in semiconductor language. We therefore conclude that charge generation occurs more efficiently from higher lying states upon direct photoexcitation than from the lower excitonic levels, though the efficiency for this process is still low.

In a complimentary form of photoconductivity measurement, a single excitation (pump) energy can was used to measure current as a function of illumination intensity, which is a proxy for carrier density, and also as a function of the applied field. The energetic position of the pump, 2.54eV, is denoted by the red arrow in Figure 6.8. The experiment was performed in a cryostat allowing the temperature of the sample to be varied. The DC (dark) current is excluded by measuring the signal with a lock-in amplifier set to the modulation frequency of the optical excitation, so that only the current arising from photogeneration of charge-carriers is observed. Figure 6.9 shows a plot of the current density
J, divided by the applied field F, which is the photoconductivity \( \sigma_{ph} \), versus the incident photon density. Since the photoconductivity is proportional to the photogenerated carrier density, the slopes of these data are proportional to the mobility.

Figure 6.8: Internal photoconductivity action spectrum (black circles) giving the efficiency for charge photogeneration \( \eta_{ph} \) in an imidePTV photodiode as a function incident photon energy. The data has been normalized by the absorbed number of photons. The absorption of imidePTV film (blue dashed line) is shown for comparison. Red arrow indicates the pump energy used in the study of photocurrent intensity dependence.

In particular, \( \sigma_{ph} = e n_{ph} \mu \) where the density of photogenerated carriers is \( n_{ph} = g \alpha \cdot I \), with I the incident photon density, \( \alpha \) the absorption coefficient and \( g \) the carrier generation rate (the number of electron-hole pairs generated per absorbed photon). Since we can not entirely separate the mobility from the carrier generation rate, a quantitative value of the mobility can not be obtained from this technique. However, the temperature and field dependence of the mobility can be examined in this way, since the carrier generation rate is expected to depend on these parameters much more weakly than the mobility, owing to the large binding energy of the excitons. The strictly linear dependence observed indicates
that in this range of carrier densities, bimolecular recombination is not a significant loss mechanism. The increase in the slopes in Figure 6.9 with increasing applied field \( F \), however, indicates that the carrier mobility increases with field. This behavior is expected for hopping type transport within the GDOS model as discussed below.

![Figure 6.9: The photoconductivity of an imidePTV photodiode versus the incident photon flux in units of photon density at various applied field strengths.](image)

Investigating the dependence on the electric field, we find a traditional Pool-Frenkel type relation where the mobility increases with increasing temperature and shows an electric field dependence according to

\[
\mu(F) = \mu_0 e^{\gamma \sqrt{F}}
\]  

(6.5)

where \( \mu_0 \) is the zero-field mobility and \( \gamma \) is a parameter that describes the field-activation of mobility. From the fits to the data in Figure 6.10, we obtain a temperature independent
value of $9.5 \pm 0.3 \times 10^{-3} \, (\text{cm/V})^{1/2}$ for $\gamma$ which is similar to values reported for other $\pi$-conjugated polymers [168, 171], although in those reports $\gamma$ was found to be weakly temperature dependent.

Figure 6.10: The dependence of the generation rate-mobility product, $g\mu$, determined from the slopes of photoconductivity vs. incident photon flux, on the square root of the applied field plotted on a natural log scale. Data from various device temperatures are shown.

In Figure 6.11 we show the dependence of the carrier-generation rate-mobility product on temperature at various applied field strengths. The GDOS model for $\pi$-conjugated polymers predicts that the mobility will depend exponentially on the square of the inverse temperature. As shown by the fits to this dependence, we also find the carrier transport of imidePTV to be qualitatively in agreement with this model. The fit provides an estimate of the width parameter of the Gaussian DOS of about 0.15eV, which corresponds to a zero-
field mobility $\mu_0$, with an thermal activation energy of $\approx 0.60\text{eV}$ [158]. Unfortunately this model is empirical and the parameter values do not lend much physical insight. They are useful however, in comparison with other $\pi$-conjugated polymers and similar systems, to which we find comparable agreement [168, 171, 169]. We therefore conclude that the transport properties of imidePTV are not significantly different from those observed for most $\pi$-conjugated polymers, being generally assigned to carrier hopping within a Gaussian density of states as is characteristic of disorder organic systems [158].

Figure 6.11: The dependence of the generation rate-mobility product, $g\mu$, determined from the slopes of photoconductivity vs. incident photon flux, on the square of the inverse thermal energy plotted on a natural log scale. Data from various applied field strengths are shown.
6.4 Summary

In summary, OPVs of the π-conjugated polymers in this study were fabricated and found to yield poor performance in comparison with the standards of the current field. The power conversion efficiency was shown to be strongly correlated with the short-circuit current, which is low because of the lack of charge-generation from excitons formed upon absorption. The longer exciton lifetime in imidePTV is responsible for the increase in $J_{SC}$ as compared to the PTV-CR series in an analogous way that this property leads to larger PLQE as discussed in Ch. 4. However, $J_{SC}$, and subsequently, $\eta_{PCE}$ in imidePTV:PCBM OPVs are still low. This is also in accordance with the observations from previous chapters, particularly that the $2^1A_g$ state still effectively competes with the $1^1B_u$ state for exciton population (which limits the PLQE) and the weak polaron formation in imidePTV:PCBM blend films. Therefore, the photocurrent in imidePTV:PCBM OPVs originating from exciton dissociation is comparable to that from direct electron-hole pair generation from higher lying states. That the primary reason for poor performance in imidePTV:PCBM devices is due to charge generation and not charge transport was confirmed in studies of the transport properties of imidePTV. It was shown that the hole mobility is actually higher than that in other polymers which have attained much higher $\eta_{PCE}$ in similar OPV architectures, namely MDMO-PPV[169, 170]. Meanwhile the mobility is not quite as high as in RR-P3HT due to the lack of interchain interactions in imidePTV[23]. Further studies of the transport properties confirmed the agreement of the temperature and field dependence of the mobility within the standard Gaussian Density of States model that has been widely applied to various π-conjugated polymers. Thus it was determined that the transport properties of imidePTV are typical for this class of materials and do not contribute to the order of magnitude lower efficiencies in photovoltaic devices, despite the lower bandgaps and resultant improved absorption efficiency.
7 SUMMARY AND FUTURE WORK

7.1 Summary

In this work, we have explored the fundamental operational mechanisms of organic photovoltaics with an aim to improve their prospects for commercialization and provide the world with a source of abundant, clean, renewable energy. Of the many proposed means of improving the efficiency of these devices, our efforts have focused on improving the collection efficiency of solar power by decreasing the optical bandgap of semiconducting polymers that are used as donors in the donor-acceptor bulk-heterojunction organic photovoltaics (OPV) architecture. Specifically, we examined the photophysical consequences of reducing the band gap of $\pi$-conjugated polymers by diluting the aromaticity via aromatic-quinoid structural disturbances. For the materials studied here, namely, a new series of Poly(thienylenevinylene) (PTV) derivatives, these disturbances are realized by the incorporation of vinylene units into thiophene backbone structures. These materials due indeed exhibit lower bandgaps compared to pure thiophene polymers and would thus be expected to be useful as light harvesting agents in OPV. However, because the donor polymers must not only absorb the sunlight but facilitate a charge-transfer process with the acceptor material phenyl-C$_{61}$-butyric acid methyl ester (PCBM), we found that this method of reducing the bandgap has severe adverse consequences for photovoltaic application. We investigated this phenomena in a range of different systems in order to determine the contributions from both intra-molecular and inter-molecular effects on the electronic structure. We studied the properties of both neat films and in bulk-heterojunction blends with the acceptor PCBM to directly probe the efficacy of charge-transfer. Finally, we fabricated and characterized devices, and were able to interpret the results based on our fundamental insight into the electronic properties gained...
through our spectroscopic investigations.

Using continuous-wave-photoinduced absorption (cw-PIA), doping induced absorption (DIA) and thermally modulated absorption (TMA), the optical properties of poly(3 dodecyl thiylene vinylene) with controlled regioregularity (PTV-CR) in the broad spectrum range from UV to near IR have been studied. We found that regioregularity affects photophysics of PTV-CR in a different way than that with poly(3-alkylthiophene). The optical bandgap increases with regioregularity from 1.65 to 1.75 eV for the most random PTV-5:5 (head-tail ratio of 25%) to regular PTV-0:10 (head-tail ratio of 100%). We found that PTV-CR is intrinsically dark with very small PL quantum efficiency ranging from $10^{-5} - 2 \times 10^{-4}$, from most random PTV-5:5 to regular PTV-0:10. We attribute the nonluminescent property to the existence of the dark excitonic state ($2^1A_g$) which lies below the bright excitonic state ($1^1B_u$). The phonon level in all PTV-CRs is about 0.18 eV, and exhibits temperature invariance. The side-chain arrangement seems to have little influence over film morphology, as indicated by the GIXRD results of crystallinility and domain size. There is no correlation between structure order and regioregularity in PTV-CR, in contrast with the case of poly (3-alkylthiophene). The measured cw-PIA and doping induced absorption spectra confirm that the long-lived charged and neutral photogenerated species are polarons and triplet excitons, respectively; and thus PTV-CR is a unique non-degenerate ground state $\pi$-conjugated polymer which is intrinsically non-luminescent. Through the measurements and the analysis of the PIA signal dependency on pump intensity, frequency, and the temperature of the sample, the respective recombination and generation mechanisms of polarons and triplets were characterized. Our studies of side-chain organization effect on films of PTV-CR provide a new perspective into regioregularity as a means of improving optoelectronic properties of $\pi$-conjugated polymers for device applications. Since very little to no evidence of interchain interaction, despite the fact that the polymer chains are reasonably close together as shown in GIXRD, has been observed even in the most regioregular polymers, subtle effects of chain organization on intrachain, one dimensional (1-D) excitations have been revealed. The results here suggest that regioregular self-assembly may not only improve mobility
and photon harvesting, as observed elsewhere, but may also be necessary for quenching dissipative channels that will inhibit electron transfer in heterojunction type OPVs in the case of novel polymers such as low band gap PTV-CR. We have shown, however, that the ultrafast response of regioregular-PTV (RR-PTV) is dominated by the fast decay of the photogenerated $1^1B_u$ excitons into the “dark” $2^1A_g$ exciton with lower energy; this limits the PLQE to $2 \times 10^{-4}$ and also limits charge transfer in OPV. From the PL, transient PM and EA spectra we determined the essential states in this NDGS polymer. We conclude that these polymers with intrinsic weak PL may be used in nonlinear optical applications because of their ultrafast photoresponse, as well as transducers for spectroscopic studies due to their ultrafast energy release.

Based on the results from the first stage of work here, our collaborating chemist Dr. Zhang has synthesized imidePTV, with the aim of reversing the order of dark and optically allowed states to “seal off” the ultrafast dissipative channel of photo generated excitons. An amide side-group was attached to the thiophene backbone, and the relative quinoidal element was reduced through the increased ratio of thienylene to vinylene units. In imidePTV, the PLQE is two orders of magnitude larger than in PTV-0:10, because of the closer energetic proximity of the $1^1B_u$ and $2^1A_g$ states in imidePTV. This occurs because of the higher ratio of thienylene units to vinylene units in the backbone structure. Because of this near degeneracy of states, emission from imidePTV was assigned to originate from a hybrid state of mixed $B_u$ and $A_g$ character. The mixing between the states is perturbative in nature arising from the asymmetry of vibrational modes coupled to the electronic transition as documented in the polyene case and may have a contribution from the permanent dipole moment in imidePTV due to the electron-deficiency of the amide group. The mixed state emission has shown the characteristic sensitivity to solvents in solution and to temperature in film, but unlike in the non-polar polyenes, the dominant contribution in this case was from the solvent polarity, and was more weakly dependent on the solvent polarizability in imidePTV. In the temperature dependence of the PL in film, we found that temperature controlled the vibronic progression of the hybrid state emission through variation of the contributions from the $1^1B_u$ and $2^1A_g$ state couplings to
the ground state. The hybrid nature of the excited state in imidePTV was also shown in PIA measurements on both ultrafast timescales and in the steady-state. We observed an instantaneously generated state with a verified triplet spin signature that persists onto a time scale of at least 100’s of ns. We assigned the triplet state to a correlated triplet pair which is in fact the $2^1A_g$ state in accordance with theoretical descriptions. The triplet-pair that comprises the $2^1A_g$ state give it a much broader absorption bandwidth due to this mutual interaction between them and determines their mechanism of recombination through mutual annihilation, thus giving this triplet state a much shorter lifetime than the isolated triplets in the PTV-CR series. We related this phenomenon with the hot topic of singlet fission, where two triplet states are generated by the absorption of one-photon due to splitting of the singlet state, and noted that the proposed mechanism of this process in linear conjugated systems is intimately tied to the ordering of the $1^1B_u$ and $2^1A_g$ states due to energetic considerations. That the triplet-pair excitation resides upon a single chromophore and makes it unlikely that it can be dissociated into two distinct triple excitations and be converted into two electron-hole pairs such as would be beneficial for photovoltaic application. That is, of course, unless interchain-interaction may be built into a similar system to serve as a triplet-pair dissociating mechanism.

We have conducted steady-state photophysics study of PTV-CR blended with the electron acceptor PCBM. Our results showed that exciton dissociation does not occur regardless of regioregularity, which was in contrast with the well-studied P3HT:PCBM blend. Förster energy transfer was observed in the well-mixed, electronically-coupled regiorandom PTV55:PCBM blend, however, not in the regioregular PTV010:PCBM blend, due to the morphological variation that resulted from polymer chain order. There were no new spectral features in PIA indicating the formation of a charge-transfer complex, or separate charge species. All long-lived photoexcitations (i.e., polaron and triplet) in neat polymers were preserved, however, with much reduced lifetime (as much as two orders of magnitude). We explain the shortening of lifetime by energy transfer and increased trapping by the addition of PCBM. The ultrafast decay of excitons to the lower $2^1A_g$ state precedes the possible charge-transfer between PTV and PCBM, and the tightly bound excitons
(binding energy exceeds 0.6 eV) in PTV also inhibit photoinduced electron-transfer to PCBM. Our results are consistent with recent report on very small electron transfer rate between oligo(thienylenevinylene)/fullerene composite [64]. These results have helped to explain the poor performance of OPV devices based on PTV and its derivatives, as the formation of PCBM triplet is detrimental to device efficiency and long term stability. Meanwhile, for imidePTV:PCBM blends, electron-transfer was clearly observed. The quenching of the photoluminescence shows that the excitons are dissociated before they can thermalize and radiatively recombine to the ground state. The cw-PIA showed an additional feature attributable to the presence of charged polarons that result from the charge transfer process. However, the polaron signal is very weak, indicating that much of the energy absorbed by imidePTV is still lost to internal conversion to the $2^1A_g$, consistent with the improved, but weak low PLQE ($\approx 1\%$) in this material compared to the PTV-CR series. Furthermore, the lifetimes of the species observed in PIA measurements were comparable to those in the PTV-55:PCBM blend, which indicates that the intrachain disorder in both cases leads to rapid recombination of polarons and triplets (originating from both the polymer and PCBM), as the excitations are not delocalized enough to escape the recombination centers and annihilation processes.

When photovoltaic devices were fabricated in the bulk-heterojunction architecture using these materials as donors, the short-circuit currents were comparable within the PTV-CR series, while they were almost an order of magnitude higher using imidePTV. This scaling follows the PLQE of the materials, thus confirming our predictions based on the photophysical studies. This scaling can be attributed to stability of the $1^1B_u$ exciton population, which governs both the efficiency of emission and that of charge-generation in the bulk-heterojunction films. The overall device performance depends on additional factors but is most strongly correlated with the $J_{SC}$. This means that in addition to other material parameters such as the carrier mobility and the positions of the transport levels (such as the highest occupied molecular orbital of the (HOMO) level of the donor polymer), the PLQE and exciton decay dynamics can be used to evaluate the viability of a $\pi$-conjugated polymer for use in bulk-heterojunction organic photovoltaics. We have
further shown that the charge transport properties of the polymer that achieved the highest efficiency, imidePTV, is not dramatically worse or qualitatively different from that observed for most π-conjugated polymers, including in particular those that have achieved much larger $J_{SC}$ and power conversion efficiency in OPV. We therefore conclude, that the predominant efficiency limiting factor in imidePTV is still the charge-generation efficiency. This explains why PTV based donor polymers have consistently achieved lower efficiencies than other materials despite the lower band gap and thus improved absorption efficiency. Extrapolating these results to the broader category of π-conjugated polymers this helps us to understand why non-luminescent polymers such as polyacetylene and polydiacetylene have not been successfully employed in solar cells despite their low bandgaps and delocalized excitonic structures, and high potential for conductivities.

Particular emphasis was placed on understanding the electronic characteristics of π-conjugated polymers since this knowledge will enable both the realization of the optimal conditions for a specific application and the development of new materials with improved properties. The majority of techniques used to characterize these properties are non-contact, spectroscopy based methods. While this may seem removed from the practical implications for device applicability, it is this very attribute that makes these techniques so valuable. Optimization of device performance is a slow and deliberate process requiring much trial and error. From the outside-in, realization of optimal performance requires defect free electrodes, Ohmic contacts between the electrodes and the photoactive layer (which in itself usually requires optimization of the processing of interfacial transport layers as well as the processing of the photoactive layer), and development of the ideal morphology for the photoactive layer through fine-tuning of the many processing parameters. For instance, the initial performance of poly(3-hexylthiophene):PCBM OPVs only achieved about 1% efficiency, and only years later was the full potential realized through the development of optimal processing and fabrication procedures. Meanwhile, the impressive (at the time, unparalleled) performance these devices would ultimately reach could have been predicted from the observations from more fundamental characterizations of strong red-shifted absorption (compared to other π-conjugated polymers),
pronounced crystalline order, delocalized neutral and charged excitations and good hole mobility. Similarly, in this work, our characterization of PTV based \( \pi \)-conjugated polymers and their blends with PCBM lead us to conclude the lack of efficiency in devices is intrinsic, and does not require thorough device fabrication and characterization trial and error based investigations that are costly in terms of time and materials.

Additionally, understanding the properties at a fundamental level also allows for progress to be made in the field of OPV despite the lack of success found for this particular class of \( \pi \)-conjugated polymer. This progress manifests itself in the form of a caution sign for a pitfall in the attempt to decrease the optical band gap of \( \pi \)-conjugated polymers through aromatic-quinoid structural disturbances and essentially establishes a threshold for electron delocalization in the backbone of a polymer, that can lead to lower band gaps while simultaneously allowing for a stable, ionic excited stated (\( 1^1B_u \) exciton) that will lead to charge-generation within the conventional model of bulk-heterojunction organic photovoltaics operation. Thus, researchers in the field can now discard this method for achieving low-band-gap polymers and focus on alternative routes such as alternate donor-acceptor polymers that maintain aromatic stabilization. Alternatively, this work suggests that a new method of charge generation is necessary for the utilization of highly delocalized electronic structures such as those of PTV, t-[CH]x, and PDA. This would require some means of dissociating the \( 2^1A_g \) exciton before the rapid internal conversion to the ground state occurs. While this is conceptually difficult to achieve, if discovered, such a process would be a tremendous breakthrough for the OPV community, as this latter class of materials generally possess lower band gaps than those of the donor-acceptor copolymer variety.
7.2 Future Work

7.2.1 Two-Photon Studies of the $2^1A_g$ State in PTVs

Perhaps the largest lingering open question at the end of this work is the location and nature of the elusive $2^1A_g$. Although this state has been central to the interpretation of many of the experiments in this work, its presence and role in the photo physics of these materials is ultimately determined by indirect means. This is because the optical investigations in this work are all one-photon processes, from which the $2^1A_g$ state is unaccessible. Although we were able to observe this state’s contribution to the PL of imidePTV due to the near degeneracy and perturbative mixing of this state with the formally allowed $1^1B_u$, still the exact location of this state is unknown. Also, in that analysis the assumption that the $2^1A_g$ state is insensitive to environmental interactions was made and is expected on theoretical grounds, but has not been verified experimentally. Therefore, an investigation of these materials using two-photon spectroscopy such as two-photon absorption and two-photon photoluminescence. This would allow for the direct determination of the $2^1A_g$ state as well as its dependence on external parameters such as solvent polarity and polarizabilities for solution measurements and temperature in film. These measurements would be particularly interesting considering the role of the $2^1A_g$ state in the process of singlet fission as described in Chapter 4. This is because the role of the $2^1A_g$ state as a precursor for singlet fission has been called into question despite the theoretical support for this concept [116].

7.2.2 Regioregularity Effect on Charge Transport in PTV-CR Series by FET

Because the role of regioregularity in the PTV-C12-CR series was observed to be vastly different from its more well-known effects in RR-P3HT, it would be very interesting to study the effect of regioregularity on the field-effect mobility in this series. The FET geometry would be the most relevant means of studying the effect of transport on these
polymers, because we have already shown the preferential conformation of alkyl-group alignment perpendicular to the plane of the film. This means that the $\pi$-$\pi$ stacking will be parallel to the film plane, which is the direction of current flow in a thin-film transistor. Therefore, the measurement of carrier mobilities in the FET geometry may lead to interesting observations about the role of regioregularity in the formation of 2-D lamellae in PTV.
REFERENCES


[128] T. Itoh and M. Yamaji, “1^1B_u (S_2) and 2^1A_g (S_1) Fluorescence and the 2^1A_g State of α,ω-Dithienylbutadiene and α,ω-Dithienylethylene,” Journal of Physical Chemistry A, vol. 112, pp. 13413–13418, 2008.


APPENDIX

In this appendix, the permissions obtained from publishers for the use of previously published materials are displayed.
Title: Generation and Recombination Kinetics of Optical Excitations in Poly(3-dodecylthienylenevinylene) with Controlled Regioregularity

Author: Evan Lafalce, Xiaomei Jiang, Cheng Zhang

Publication: The Journal of Physical Chemistry B

Publisher: American Chemical Society

Date: Nov 1, 2011

Copyright © 2011, American Chemical Society

Quick Price Estimate

Permission for this particular request is granted for print and electronic formats, and translations, at no charge. Figures and tables may be modified. Appropriate credit should be given. Please print this page for your records and provide a copy to your publisher. Requests for up to 4 figures require only this record. Five or more figures will generate a printout of additional terms and conditions. Appropriate credit should read: "Reprinted with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society." Insert appropriate information in place of the capitalized words.

I would like to... 
 reuse in a Thesis/Dissertation

Requestor Type 
 Author (original work)

Portion 
 50% or more of original article

Format 
 Print and Electronic

Select your currency 
 USD - $

Quick Price 
 Click Quick Price

To request permission for a type of use not listed, please contact the publisher directly.
Permission for the reuse of a published article for my dissertation

AIPRights Permissions <Rights@aip.org>
To: Evan Lafalce <elafalce@mail.usf.edu>

Wed, Oct 1, 2014 at 3:41 PM

Dear Dr. Lafalce:

Thank you for requesting permission to reproduce material from AIP Publishing LLC publications.

Material to be reproduced:

“Photophysics and morphology of poly (3-dodecylthienylenevinylene)-[6,6]-phenyl-C61-butyric acid methyl ester composite”


For use in the following manner:

Reproduced in your dissertation.

Permission is granted subject to these conditions:

1. AIP Publishing LLC grants you non-exclusive world rights in all languages and media. This permission extends to all subsequent and future editions of the new work.

2. The following copyright notice must appear with the material (please fill in the information indicated by capital letters):

“Reproduced with permission from [FULL CITATION]. Copyright [PUBLICATION YEAR], AIP Publishing LLC.”

https://mail.google.com/mail/u/0/?ui=2&ik=f4162e933f&view=pt&search-inbox&msg=148cd3aee533a8b0&siml=148cd3aee533a8b0