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CONJUGATED BLOCK COPOLYMERS AS MODEL SYSTEMS TO EXAMINE
MECHANISMS OF CHARGE AND ENERGY TRANSFER IN ORGANIC MATERIALS

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ABSTRACT

Organic electronics is an exciting field with applications already beginning to impact our everyday lives. The key advantage of organic electronics over conventional inorganic-based systems is the ability to define functionality at the molecular level. As it stands, we do not fully understand the physics of charge and energy transfer within organic materials; this greatly hinders material design for high-performance organic electronic devices. With a focus on organic photovoltaics, this dissertation demonstrates that donor-acceptor block copolymers are useful model systems to examine processes of charge and energy transfer in organic materials.

First, we establish block copolymers as model systems. Using steady state photoluminescence quenching experiments, we have developed a procedure to quantify intramolecular charge transfer within isolated block copolymer chains. We find that a small perturbation to the molecular structure disrupts intramolecular charge transfer and is ultimately responsible for a substantial decrease in photovoltaic performance.

Next, we use these materials to perform a fundamental study investigating the influence of the energetic offset between a donor and acceptor on exciton dissociation. We systematically tune the two energy levels that make up this energetic offset, the singlet excited state and the intramolecular charge transfer state. In isolated block copolymer chains, a significant driving force is required to achieve efficient exciton dissociation.

Lastly, we use block copolymers to examine the influence of conjugation length on charge transfer. We demonstrate that conjugated homopolymers, made up of identical repeat units, require a significant conjugation length to achieve efficient charge transfer. Conversely, push-pull polymers, made up of alternating electron-rich and electron-deficient units, eliminate this chain length requirement.
Altogether, this work demonstrates the use of conjugated block copolymers as model systems to elucidate mechanisms of charge and energy transfer within organic materials. By performing fundamental studies on isolated block copolymer chains in solution, we uncover structure-function relationships to help guide material design for organic electronics.
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**Scheme 2-2:** Synthesis of H/Br P3HT using KCTP. Adapted with permission from ref. 183. Copyright 2011 American Chemical Society.

**Scheme 2-3:** Reaction scheme commonly used to synthesize fully conjugated donor-acceptor block copolymers. KCTP is used to synthesize the first block \((A)_n\). The block copolymer \((A)_n-b-(BC)_m\) is formed in the second reaction on using a Suzuki or Stille polycondensation. This representative scheme depicts a Suzuki coupling reaction. Using this procedure, diblock copolymer is typically formed as the major product. Although, side products including donor and acceptor block homopolymers and multiblock copolymers can also be produced.

**Scheme 2-4:** Synthetic method used to synthesize P3HT-b-PFTBT. In practice, P3HT synthesis results in imperfect end group functionalization; H/Br, H/H, and Br/Br P3HT are present in the reaction product. The uncontrolled step-growth nature of Suzuki polycondensation used for PFTBT can result in a mixture of diblock copolymer, P3HT homopolymer, PFTBT homopolymer, and multiblock copolymer.

**Scheme 6-1:** Direct (hetero)arylation polymerization forms \(sp^2\) hybridized carbon-carbon bonds by coupling a non-functionalized aromatic core (A) with a dihalogenated aromatic core (B).

**Scheme 6-2:** Proposed synthesis scheme for macoragents 1, 2, and 3 utilizing DHAP. Only expected major products are shown.

**Scheme 6-3:** Proposed synthesis scheme for block copolymers PTB7Th-b-PNDIT, PTB7Th-Ph-PNDIT, and PTB7Th-bPh-PNDIT.

**Scheme 6-4:** Proposed synthesis scheme for P3HT-b-PCPDT-b-PPT6BT.
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Chapter 1

Introduction

1.1. Motivation for Organic Electronics

Enabled by virtually limitless possibilities for material design, organic electronics is an exciting field that is already beginning to impact everyday life. Organic electronic devices utilize conjugated polymers and small molecules as the active materials in electronic devices. Conjugated polymers and small molecules are made up of covalently linked aromatic building blocks. Significant overlap of $\pi$ orbitals generates a delocalized network of $\pi$-electrons, enabling charge transport and electrical conductivity. These materials are known as organic semiconductors.

Since their discovery in the late 1970s, organic semiconductors have been a topic of significant interest.\textsuperscript{1,2} The use of organic materials that can be dissolved in organic solvents may facilitate low-cost, solution-based fabrication techniques which could decrease costs of electronic devices. As it stands, organic electronic devices often fall far behind traditional inorganic electronics with respect to performance and industrial development, leaving room for significant improvement and further research opportunities.

Nevertheless, a more noteworthy characteristic, where organic electronics reign supreme, is the ability to define functionality at the molecular level. Small adjustments to the molecular structure of the active material can result in vastly different device performance. For example, an early study in the field demonstrated that small perturbations to the molecular structure at the interface between two conjugated polymers would facilitate either: 1) energy transfer followed by light emission, enabling devices to function as light emitting diodes, or 2) charge transfer followed by photocurrent generation, enabling devices to function as photovoltaic cells.\textsuperscript{3} Enabled by
synthetic chemistry, there are virtually infinite possibilities for material design and thus, applications of semiconducting small molecules and polymers for organic electronics.

A few promising applications that may yield high-performance organic electronic devices include: organic light-emitting diodes (OLED), white OLEDs, solar fuels, and organic photovoltaics (OPV). OLEDs can be used to make thin, lightweight, high-quality displays; they are one of the applications within the field that has successfully been commercialized.²⁴⁻¹¹ OLED displays are employed in high-end smartphones, smart watches, and televisions sold by well-known technology companies including Samsung and Apple (Figure 1-1a). The basic structure of an OLED includes an organic electroluminescent active layer sandwiched between two electrodes. When a voltage is applied between the electrodes, charges are injected into the organic material. Light is emitted when the injected charges recombine and decay radiatively to the ground state. Current challenges include the development of blue-emitting materials with long-term stability and preventing material degradation in the presence of oxygen and moisture.¹²

White OLEDs have potential to be used as a source of lightweight, energy-efficient solid state lighting.¹³⁻¹⁸ In 2015, lighting accounted for approximately 17% of total electricity use in the United States.¹⁹ Increasing the efficiency of lighting could generate savings in terms of cost and energy consumption. The operating principle of a white OLED is analogous to that of an OLED. To generate white light, multiple emissive materials can be combined; collectively their emission generates white light. In principle, a single material with broadband emission can also be used to produce white light; development of such a material is a current challenge in the field. Research efforts in the field of white OLEDs are also focused on improving relatively low external quantum efficiencies.

Solar fuels convert light into free charges which then participate in redox reactions to yield chemical fuels.²⁰⁻²³ Solar fuels can be used to produce hydrogen from water splitting. Light absorption is followed by a photoinduced electron transfer to produce free electrons. This is
followed by a redox reaction to produce hydrogen from water. This process may also be applied to
the capture of carbon dioxide from the atmosphere, which can then be reduced to carbon-based
fuels. Again, this is accomplished through light absorption followed by photoinduced electron
transfer and then a redox reaction to produce more reduced carbon compounds from carbon dioxide.
The structural regularity and chemical versatility of metal-organic frameworks could be useful in
this process.\textsuperscript{23} One main challenge in the field is development of new organic materials that can
efficiently generate free charge carriers to participate in this process.

OPVs convert solar energy into electricity. Typical device architecture incorporates an
active layer, composed of a molecular electron donor and a molecular electron acceptor,
sandwiched between two electrodes. After light absorption, free charges are generated by a
photoinduced electron transfer reaction, followed by transport of electrons/holes to the
cathode/anode, generating current.\textsuperscript{24-30} OPVs have the potential to become a source of efficient,
low-cost, low environmental-impact, renewable energy. Furthermore, due to the semitransparent
nature of most conjugated polymers, OPVs could possibly be integrated into the windows of
buildings as an aesthetically-pleasing energy source. Different molecular building blocks allow for
tailored optical properties which may enable building-integrated OPVs with customized colors
(Figure 1-1b). A significant challenge in the field is the rational design of new materials with well-
understood intra and intermolecular properties that facilitate efficient charge generation when
incorporated within devices.
Across these developing organic electronics applications, two important themes are evident: 1) the operating mechanism relies on efficient charge and/or energy transfer within organic materials; 2) challenges include the development of new materials for a desired function, namely efficient charge and energy transfer. Unfortunately, processes of charge and energy transfer within organic materials are not fully understood. A lack of concrete structure-function relationships renders rational material design challenging. To improve performance and overcome limitations of organic electronic devices, it is critical that the governing physics behind material performance is more thoroughly understood. This can be accomplished through the use of model systems; linking simple interactions between individual molecules to solid state morphology to device performance will aid in the development of high-performance devices.

**Figure 1-1:** Examples of organic electronic devices. (a) The “S8” smartphone by Samsung, which is commercially available, incorporates an active-matrix OLED display. Image obtained from Samsung.com. (b) A cartoon of building-integrated OPV windows on an office building. Image obtained from solarpowerworld.com. (c) A cartoon of a “solar tree” that uses solar energy to produce H₂ and hydrocarbons from water and carbon dioxide, respectively. Image obtained from solar-fuels.org. (d) Photograph of a laboratory white OLED device. Reprinted with permission from ref.³¹ Copyright 2013 John Wiley and Sons.
1.2. Intramolecular Electron Transfer in Donor-Acceptor Systems

Electron transfer within covalently linked donor-acceptor molecules has been studied for many years. In the 1950s, application of transition state theory to electron transfer reactions led to the development of Marcus theory.\(^ {32}\) Marcus predicted:

$$k_{eT} = A \exp \left( -\frac{\Delta G + \lambda}{4 \lambda k_B T} \right)$$

Where \(k_{eT}\) is the rate constant of electron transfer, \(A\) is a pre-exponential factor that depends on electronic coupling, \(\Delta G\) is the change in free energy of the reaction, and \(\lambda\) is the reorganization energy.\(^ {33}\) \(\lambda\) is the energetic cost of nuclear geometric changes of both the solvent and donor/acceptor that occur as a result of the electron transfer reaction. An important consequence of \(\lambda\) is the counterintuitive “inverted region”, in which the rate of electron transfer decreases as the change in free energy increases. In order to study electron transfer in very simple model materials, between a single donor and a single acceptor, many fundamental studies have been performed on covalently-linked donor-acceptor dyads.\(^ {34-47}\) Significant efforts have been applied to understanding intramolecular electron transfer in solution.

One particularly significant study examined the effects of \(\Delta G\), donor-acceptor distance, and stereochemistry on the rate of electron transfer.\(^ {34}\) Studies were performed on a series of molecules incorporating a biphenyl electron donor and various electron acceptors joined by rigid, saturated hydrocarbon spacer groups. Pulse radiolysis was used to generate negative biphenyl anions. Subsequent electron transfer to the acceptor moieties was monitored using absorption spectroscopy to measure reaction time. First, a series of molecules incorporating a biphenyl electron donor, linked to a rigid androstone bridge, linked to various acceptors was examined. By changing the electron affinities of the acceptors, a range of \(\Delta G\) values spanning 2.4 eV was tested. It was found that as \(\Delta G\) becomes more negative, \(k_{eT}\) first increases, then reaches a maximum value at a \(\Delta G\) of...
approximately -1.2 eV, then decreases as $\Delta G$ continues to become more negative (Figure 1-2a). This study represents excellent experimental evidence for the inverted region that was predicted by Marcus several years prior.

Next, a series of compounds incorporating a biphenyl donor and naphthalene acceptor joined by hydrocarbon spacers of varying size were used to examine the effect of donor-acceptor distance on the rate of electron transfer. The saturated hydrocarbon spacers were composed of 1-4 fused cyclohexane rings; as the number of cyclohexane rings increases, the distance between donor and acceptor increases (Figure 1-2b). It was found that as the number of $\sigma$ bonds separating the aromatic donor and acceptor increases, $k_{eT}$ mostly follows an exponential decrease (Figure 1-2c). Deviations from the exponential fit suggest that the number of $\sigma$ bonds separating donor and acceptor moieties is not the only variable effecting $k_{eT}$. Authors turned to stereochemistry to examine this discrepancy; the biphenyl donor and naphthalene acceptor can be linked to a cyclohexane ring in either an axial or equatorial position. It was assumed that the relative stereochemistry between donor and acceptor units effects electronic coupling (manifested in the pre-exponential factor, $A$), but $\Delta G$ is determined mainly by the donor-acceptor pair and should remain largely unaffected. Again, $k_{eT}$ as a function of separating $\sigma$ bonds is examined, although, only systems in which both the biphenyl donor and naphthalene acceptor are oriented equatorial to the cyclohexane rings are considered. As shown in Figure 1-2d, a nearly perfect linear relationship is found between increasing distance and exponential drop off of $k_{eT}$. This study clearly demonstrates the utility of covalently-linked donor-acceptor molecules for understanding mechanisms of electron transfer in organic materials.
Photoinduced electron transfer has also been studied using covalently-linked donor-acceptor dyads in solution. One interesting study examining photoinduced electron transfer utilized a carotenoid (C) linked to a porphyrin (P) linked to a quinone (Q). The reaction scheme proposed by the authors is presented in Figure 1-3. Using transient absorption spectroscopy, it was concluded that a 600 nm flash excitation generates excited states on the porphyrin (C-P-Q), followed by an initial electron transfer reaction to the quinone (C-P^+Q^-), step 1 in Figure 1-3b). Due to a dramatic decrease in the lifetime of the porphyrin excited states, it was concluded that this initial electron transfer reaction occurs with a quantum yield near unity. This reaction may then be followed by a
subsequent electron transfer from the carotenoid to the porphyrin, in other words, a hole transfer from the porphyrin to the carotenoid (C\(^{+}\)-P-Q\(^{-}\), step 2 in Figure 1-3b). This would yield what is referred to as a charge separated state. Either electron transfer reaction could also be followed by recombination to the ground state (steps 3 and 4 in Figure 1-3b). Authors suggest the key to obtaining charge separation over charge recombination is inclusion of the porphyrin ring between the relatively higher electron affinity quinone and relatively lower electron affinity carotenoid, but also note that selectivity between charge separation and recombination is strongly influenced by the surrounding environment.

Figure 1-3: An early example of photoinduced charge transfer in a covalently linked donor-acceptor molecule. (a) Chemical structure of the quinone-porphyrin-carotenoid (C-P-Q) molecule. (b) Proposed charge transfer mechanism. Reprinted with permission from ref.\(^{42}\) Copyright 1984 Springer Nature.

Another study examined photoinduced electron transfer using a similar system, although an aniline unit was used in place of the carotenoid.\(^{45}\) Transient absorption decay measurements suggest photoexcitation generates excited states on the porphyrin, followed by photoinduced electron transfer to the quinone. This step was followed by either: 1) subsequent electron transfer from aniline to porphyrin, measured to occur at a rate of \(\sim 10^{10}\) s\(^{-1}\) or 2) recombination to the ground
state, measured to occur at a rate of \( \sim 10^9 \text{ s}^{-1} \); electron transfer to form charge separated states occurs about an order of magnitude faster than recombination. Similarly, authors conclude that a mechanism including two electron transfer reactions is key to increasing selectivity of the charge separated state versus charge recombination.

Furthermore, another interesting study examined photoinduced electron transfer from a porphyrin donor to multiple different quinone acceptors. Different quinone moieties resulted in different \( \Delta G \) values for both electron transfer from the porphyrin to the quinone moiety and charge recombination to the ground state. Formation and decay of porphyrin-quinone radical pair was monitored following a 600 nm laser flash. As expected, the rate constant for electron transfer increased with increasing reaction exothermicity. Interestingly, as the reaction exothermicity for charge recombination increases, the rate constant decreases dramatically. This suggests that electron transfer falls within the “normal” region, while recombination falls within the Marcus inverted region. Using simple model systems, these studies begin to examine the complex relationship between charge separation and recombination in organic materials.

Studies of covalently linked donor-acceptor dyads represent invaluable contributions to electron transfer research. Because electron transfer is such a critical process in the functionality of many organic electronic devices, there are many lessons to be learned from these studies regarding structure-function relationships. Nevertheless, one material class not often considered in these fundamental studies is conjugated polymers. Many organic electronic devices, OPVs in particular, frequently employ conjugated polymers as the active material. It is known that increasing the conjugation length will alter optoelectronic properties of aromatic systems. Furthermore, many of the desirable properties of conjugated polymers are derived from their extended \( \pi \)-conjugated network. Thus, fundamental studies on electron transfer in covalently-linked conjugated polymers could also provide useful information.
1.3. A Brief Introduction to Organic Photovoltaics

Organic photovoltaics were briefly introduced in Section 1.1. This application is the main focus of this dissertation. Thus, a more in-depth discussion of the history, current understanding, and challenges of OPV is warranted.

In the 1970s, researchers realized the photovoltaic properties of organic dyes. These dyes were the first materials incorporated into organic solar cells; efficiencies of these initial OPV devices were well below 1%.\textsuperscript{48-50} In the 1980s, it was realized that layering an electron-rich “donor” and electron-deficient “acceptor” in the same cell would increase photovoltaic performance. Efficiencies of approximately 1% were achieved.\textsuperscript{51} Over the past 3 decades, numerous achievements have been made in this field. Today, the record power conversion efficiency of a laboratory-scale single-junction OPV device is over 13%.\textsuperscript{52-56} Nevertheless, commercially available inorganic solar modules operate at efficiencies closer to 20%, significantly higher than the record laboratory-scale OPV cell device.\textsuperscript{57}

There are inherent differences between inorganic and organic photovoltaic materials. Inorganic photovoltaic materials have relatively high dielectric constants (\(\varepsilon_0\)); photoexcitations generate free charge carriers. For instance, silicon has a \(\varepsilon_0\) of nearly 12. In contrast, organic photoactive materials have relatively low \(\varepsilon_0\) values. For example, the \(\varepsilon_0\) of poly(3-hexylthiophene-2,5-diyl) (P3HT), a well-known conjugated polymer, is approximately 3.3.\textsuperscript{58} In organic materials, photoexcitations generate tightly-bound electron-hole pairs known as excitons. As a consequence, two materials are required to facilitate exciton dissociation to free charge carriers: an electron donor material and an electron acceptor material. Exciton dissociation occurs at a donor-acceptor interface.

The electron donor is typically a conjugated polymer. Throughout the past two decades, soluble derivatives of fullerene, phenyl-C\textsubscript{60,61,70,71}-butyric acid methyl ester (PCBM), have been
most frequently employed as the electron acceptor of top-performing OPV devices; although, this is beginning to change. A typical device consists of a photoactive layer sandwiched between two electrodes. The active layer is usually made up of an electron donor and acceptor that have been physically blended together and cast into a thin film (on the order of 100 nm thick), yielding what is referred to as a bulk heterojunction morphology (Figure 1-4).

Solar cells are characterized by their power conversion efficiency ($\eta$), the ratio of power generated by the solar cell ($P_{OUT}$) to incident power ($P_{IN}$) (Equation 1-2). Output power is characterized using a current-voltage curve in which current flowing through the device is monitored as a function of applied voltage. There are three important terms used to calculate efficiency: 1) short-circuit current ($J_{SC}$), the current density when the applied voltage is 0; 2) open-circuit voltage ($V_{OC}$), the voltage when the current is 0; 3) fill factor (FF), the ratio of maximum power to the product of $J_{SC}$ and $V_{OC}$, effectively a measure of how “square” the current-voltage

Figure 1-4: (a) A cartoon representing a typical bulk heterojunction organic photovoltaic device. Red corresponds to donor-rich regions and blue corresponds to acceptor-rich regions. (b) A zoomed in cartoon of the photoactive layer illustrating a simplified description of the photocurrent generation mechanism: 1) exciton generation; 2) exciton dissociation to a charge transfer state at a donor-acceptor interface; 3) complete charge separation and transport through donor or acceptor domains to the electrodes.
curve appears. Two other important terms used to characterize photovoltaic performance are: 1) external quantum efficiency (EQE), the ratio of charges collected at the electrodes to incident photons and 2) internal quantum efficiency (IQE), the ratio of charges collected at the electrodes to photons absorbed in the active layer.

\[ \eta = \frac{P_{OUT}}{P_{IN}} = \frac{J_{SC} V_{OC} FF}{P_{IN}} \]  

As it stands, there is significant debate in the literature regarding the process of photocurrent generation in organic materials and a complete description of this mechanism remains elusive. For the most part, there is some consensus on the most basic processes leading to the generation of free charges. First, light is absorbed by the active layer, generating excitons. An electron is excited from the ground state to an excited state, leaving behind a positively charged hole. The electron and hole are both localized either on the electron donor or the electron acceptor and are Coulombically bound together. If the exciton is not already near to a donor-acceptor interface, it will diffuse randomly until reaching a donor-acceptor interface. At a heterojunction, the exciton dissociates into a charge transfer state. The hole is localized on the donor and the electron is localized on the acceptor, but significant Coulombic attraction between the charges remains. Next, the charges proceed to move away from each other, forming charge separated states; the charge carriers are no longer Coulombically bound to one another. The free electrons and holes then move through acceptor and donor domains, respectively, and are collected at the electrodes, creating photocurrent.
1.4. Material Design for High-Performance Organic Photovoltaics

With such extensive debate in the literature over the mechanisms and photophysics behind photocurrent generation (this will be discussed in detail in Section 1.5), it is challenging to extract a set of rules to guide logical design of new materials. As a result, material design in the field is mainly driven by empirical results, as opposed to a rational approach based on fundamental knowledge. A brief review of common materials used in high-performance organic photovoltaics is discussed. Chemical structures of the highlighted materials are presented in Figure 1-5.
Electron Donor Materials

The first organic solar cell to utilize both donor and acceptor materials incorporated a small molecule copper phthalocyanine electron donor. Today, the electron donor material is often a conjugated polymer. Poly(3-hexylthiophene-2,5-diyl) (P3HT) is perhaps the most well-known
conjugated polymer; it has frequently been employed as the electron donor material in devices. It is a “conjugated homopolymer”, meaning it consists of repeating electron-rich 3-hexylthiophene units. When P3HT is blended with phenyl-C61-butyric acid methyl ester (PC_{61}BM) in the active layer, conventional OPV devices achieve approximately 5% power conversion efficiency. Under the appropriate synthetic conditions, the molecular weight of P3HT can be precisely controlled; this will be discussed in detail in section 2.4. Thus, P3HT is frequently employed in model studies.

Poly[N-9’-heptadecanyl-2,7-carbazole-alt-5,5-(4’,7’-di-2-thienyl-2’,1’,3’-benzothiadiazole)] (PCDTBT) is another polymer frequently employed as the electron donor in the active layer of OPV devices. PCDTBT is an alternating “push-pull” copolymer, meaning it is made up of alternating electron-rich carbazole (C) and electron-deficient dithenyl benzothiadiazole (DTBT) units. Incorporating alternating electron-rich and electron-deficient units along the conjugated backbone is a common design technique used to produce low bandgap polymers. Electronic polarization along the backbone generates a low-energy internal charge transfer transition, yielding a smaller bandgap than either the “push” or “pull” moieties alone. When PCDTBT is blended with PC_{70}BM, additive-free devices with no post-processing treatment achieve an impressive 6% power conversion efficiency and nearly 100% IQE. Additionally, PCDTBT is known for having high thermal stability. Thus, PCDTBT is a robust material that is relatively straightforward to incorporate in efficient devices and also commonly used in model studies.

Poly[(4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]) (PTB7) and its derivative poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-2-carboxylate-2-6-diyl]) (PTB7-Th) are two push-pull polymers frequently incorporated as the electron donor in top-performing OPV devices. There are several reports of devices incorporating PTB7 or PTB7-Th as the electron donor that achieve very high
efficiencies, often over 10%. Many studies have attempted to elucidate fundamental material properties that yield such high performance in devices incorporating PTB7 and PTB7-Th.

**Electron Acceptor Materials**

The first donor-acceptor organic solar cell incorporated a perylene derivative electron acceptor. Buckminsterfullerene was introduced as an electron acceptor material later in the early 1990s. For the majority of the past two decades, fullerene acceptors have been employed almost exclusively as the electron acceptor in top-performing OPV devices. Fullerenes were unrivaled as an electron acceptor material due in part to their high electron mobility and high electron affinity. Measurements of organic field-effect transistors incorporating PC70BM indicate electron mobilities as high as $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The electron affinity of PC61BM films is estimated to be approximately 3.6-3.8 eV. Additionally, when incorporated into thin films at a high volume fraction, regions of aggregated fullerene form. Many studies have cited fullerene aggregation as a crucial factor for efficient charge separation.

Nevertheless, there are also disadvantages to the use of fullerene electron acceptors in OPV devices. Fullerene acceptors only weakly absorb visible and near-infrared radiation. For example, the absorption coefficient of PC61BM does not exceed $\sim 10^4 \text{ cm}^{-1}$ until approximately 400 nm at which point it increases substantially to approximately $\sim 10^5 \text{ cm}^{-1}$ at 300 nm. At 400 nm, the solar spectrum is already at approximately 50% of its maximum intensity and continues to fall to approximately 0 at 300 nm. Thus, if a fullerene electron acceptor is incorporated in the active layer at a high volume fraction (> 50%), often cited as being necessary for high photovoltaic performance, then > 50% of the active layer does not absorb sunlight efficiently. Therefore, fullerene acceptors place limits the potential EQE and $J_{SC}$ of an organic solar cell. Furthermore, the high electron affinity of fullerene acceptors places bounds on achievable $V_{OC}$ values.
OPV devices incorporating fullerene acceptors fail to leverage the key advantage of organic electronics: the ability to define functionality at the molecular level.

Very recently, there has been a resurgence of non-fullerene acceptors; these materials are rapidly being developed for use in high-performance OPV devices. In addition to electron donors, some n-type push-pull polymers are also promising materials for non-fullerene electron acceptors. These polymeric electron acceptors mostly incorporate alternating electron-rich thiophene and electron-deficient naphthalene diimide moieties, or various structurally similar derivatives. When paired with an appropriate electron donor polymer, devices incorporating poly([N,N-9-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis-(dicarboximide)-2,6-diyl]-alt-5,50-(2,20-bithiophene)) (PNDIT) as the electron donor have achieved power conversion efficiencies approaching 10%.86,95

Another rapidly developing class of non-fullerene acceptors is referred to as “small molecule” non-fullerene acceptors. The most common small molecule non-fullerene acceptors are 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(hexyl)-indaceno[1,2-b:5,6-b']dithiophene (IDIC) and 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (ITIC). There are several reports of devices using either IDIC or ITIC as the electron acceptor achieving over 11% power conversion efficiency.97-105 Furthermore, devices incorporating an alternating benzodithiophene-benzodithiophenedione electron donor and a fluorinated derivative of ITIC achieve an impressive 13.7% power conversion efficiency, the current record performance for single-junction organic solar cells.54 IDIC, ITIC, and their structurally-similar derivatives are composed of alternating electron-rich and electron-deficient aromatic cores, reminiscent of push-pull polymers. Furthermore, their molecular structures incorporate linear chains of approximately 10 aromatic rings. Thus, these small molecule non-fullerene acceptors can be considered “push-pull oligomers”; this will be considered further in Chapter 5.
Altogether, it can be concluded that material design in this field does not always follow a logical progression. Material design is frequently based on empirical results and focused on incrementally increasing device efficiency. Rational design of new materials for high-performance devices is severely impeded by the lack of a complete description for the mechanism of photocurrent generation in organic solar cells.

1.5. Elucidating the Mechanism of Photocurrent Generation in Organic Photovoltaics

The charge generation mechanism in OPVs is a fundamental, yet heavily debated issue. Significant efforts have been made in an attempt to elucidate this mechanism, particularly processes of charge transfer and charge separation at a donor-acceptor heterojunction. Many material and morphological processes have been proposed. The most important within the context of this dissertation are discussed.

**Energetic Offset**

It has been proposed that offset energy levels at the donor acceptor interface generate an electric field that drives exciton dissociation to a charge transfer state.\(^3,106-108\) This driving force is defined as the energy difference between the singlet exciton and charge transfer state (\(E_{S1} - E_{CT}\)). The Durrant group has developed an optical assay to quantify relative yields of long-lived polarons within organic films. Using transient absorption spectroscopy, the magnitude of transient polaron absorption is used to quantify charge separation which is measured across several systems as a function of the energetic offset. It was shown that the magnitude of transient polaron absorption measured in a donor-acceptor blend film correlates nicely with both \(J_{SC}\) and IQE of photovoltaic devices incorporating the material blend (Figure 1-6a).\(^{109}\) Using transient polaron absorption
measurements of multiple different classes of materials including thiophene, thiazolothiazole, and diketopyrrolopyrrole based polymer electron donors blended with PCBM and perylene diimide acceptors, authors demonstrated that increasing the driving force for charge separation increases the yield of long lived polarons (Figure 1-6b).\textsuperscript{110} In this study, the energetic driving charge separation ($-\Delta E_{CS}$) is used to characterize the driving force. $-\Delta E_{CS}$ is closely related to the driving force for charge transfer defined previously, $E_{SI} - E_{CT}$; although, $-\Delta E_{CS}$ does not account for Coulombic binding of the charge transfer state. Nevertheless, this work indicates that an energetic offset at the donor-acceptor interface can facilitate charge separation within organic films.

\textbf{Figure 1-6:} Previous reports indicate an energetic offset drives charge separation. (a) An optical assay measuring transient polaron absorption ($\Delta OD$) of polymer/fullerene films correlates with short-circuit current ($J_{SC}$) and internal quantum efficiency (IQE) of corresponding OPV devices. Reprinted with permission from ref.\textsuperscript{109} Copyright 2010 John Wiley and Sons. (b) For a series of diketopyrrolopyrrole, thiazolothiazole, and thiophene based polymers blended with PCBM, increasing the energy offset driving charge separation ($-\Delta E_{CS}$) increases the yield of dissociated charges. Reprinted with permission from ref.\textsuperscript{110} Copyright 2014 American Chemical Society.
Entropy

It has also been suggested that entropy gained as an electron and hole separate may drive charge separation.\textsuperscript{111-116} The entropic gain resulting from charge separation may be the result of a rise in available states as electron and hole separation distance increases. Simulations have also been used to suggest that disorder in a bulk heterojunction film can reduce the energetic barrier for charge separation such that thermal fluctuations provide sufficient activation energy.\textsuperscript{115} The role of entropy in facilitating charge generation can also be explained in terms of delocalization. Film morphologies with enhanced delocalization will increase volume sampled by free charges, thus, increasing entropy.

In a recent report, a combination of ultrafast transient absorption spectroscopy and a recently developed pump-push photocurrent spectroscopy was used to examine the effect of fullerene aggregation.\textsuperscript{111} A series of polymer films incorporating PCDTBT blended with various fullerene derivatives at either a 1:1 or 1:4 polymer:fullerene ratio were examined. A combination of small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) confirm larger fullerene aggregates form in the 1:4 blends relative to the 1:1 blends. In all samples measured, the rate of charge generation in the 1:4 blend films is greater than the 1:1 blend films. Authors conclude that increased fullerene aggregation increases the density of delocalized states on fullerene clusters, which in turn increases entropy and enhances charge generation. Thus, entropic gains resulting from increasing separation distance between electrons and holes may facilitate free charge generation.
**Thermally Excited Charge Transfer States**

There is evidence that charge carrier generation is facilitated by excess energy from thermally excited charge transfer states.\textsuperscript{117-120} According to this mechanism, ultrafast electron transfer occurs from the singlet excited state to a vibrationally excited, “hot”, charge transfer state. Hot charge transfer states have a high probability of dissociating into free charge carriers before thermal relaxation to the vibrationally relaxed CT state. It has been suggested that thermally relaxed charge transfer states do not have sufficient energy to overcome Coulombic binding of the electron and hole and thus, serve mainly as a recombination pathway.\textsuperscript{118}

This was studied using a combination of steady state photoluminescence quenching and transient absorption spectroscopy measurements of a series of films incorporating various polythiophene electron donors blended with a PC\textsubscript{60}BM electron acceptor.\textsuperscript{118} Small adjustments were made to the polythiophene backbone to tune the polymer donor ionization potential. When blended with PC\textsubscript{60}BM, different polymer ionization potentials yield different driving forces for charge transfer. Steady state photoluminescence quenching was quantified. All samples were measured to have high (70-90\%) quenching of polymer emission upon the addition of PC\textsubscript{60}BM, regardless of driving force. Interestingly, the yield of long-lived polarons measured by transient absorption spectroscopy varies by more than 2 orders of magnitude for the same samples. It was concluded that complete charge separation requires a larger driving force than formation of initial charge transfer states. This is consistent with a model where excess thermal energy of initially formed charge transfer states is required to overcome Coulombic attraction.

Another study using ultrafast vibrational spectroscopy demonstrated that the rate of charge carrier generation in poly(5-(2-(ethylhexyloxy)-2-methoxycyanovinylene-1,4-phenylene) (CN-MEH-PPV)/ PC\textsubscript{60}BM films is independent of temperature. Authors propose charge separation is a barrierless process and that excess vibrational energy remaining in initially formed charge transfer
states enables electrons and holes to escape the Coulomb potential. Thus, rather than simply undergoing fast thermal relaxation, hot charge transfer states with excess vibrational energy may facilitate charge generation in OPVs.

**Mixed Phases**

Significant arguments have also been made for the importance of molecularly mixed donor-acceptor phases. This has been mainly investigated in the context of solar cells incorporating polymer donor/fullerene acceptor bulk heterojunction active layers. Fullerene is partially miscible with many conjugated polymers. Thus, films incorporating high volume fractions of fullerene have multiple phases (Figure 1-7). The “mixed” phase is composed of molecularly mixed polymer/fullerene regions. A “pure” phase is composed of aggregated fullerene. If the polymer crystallizes, a second “pure” phase composed of crystalline polymer chains can also form. It has been proposed that an energetic cascade between mixed and pure phases provides a thermodynamically favorable pathway for electrons and holes to move away from each other following exciton dissociation.
For instance, this was examined using films of poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT) blended with PCBM at various compositions. X-ray diffraction demonstrates that PCBM will intercalate between the hexadecyl side chains of PBTTT, generating a well-defined co-crystal. Furthermore, films incorporating a high PCBM content (> 50%) are composed of 2 distinct phases: a molecularly mixed PBTTT/PCBM co-crystal phase and a crystalline PCBM phase. Cyclic voltammetry measurements of different blend compositions were used to characterize the relative electron affinities of PBTTT/PCBM co-crystal phases and pure PCBM phases. The composition corresponding to the onset of PCBM crystallization and thus, pure PCBM phases (> 44 wt % PCBM) was correlated with an increase in electron affinity of approximately 0.1-0.2 eV. Authors suggest the difference in electron affinity between mixed and pure phases acts as an energetic sink and driving force for the spatial separation of charge carriers. Very recently, it was suggested that in addition to mixed domains, high photovoltaic performance also requires highly pure donor/acceptor domains to achieve efficient charge extraction (high FF). By providing a thermodynamically favorable energetic pathway for electrons and holes to

**Figure 1-7:** A cartoon illustrating multiple phases of a polymer/fullerene blend film. Grey circles represent fullerene molecules and red lines represent polymer chains. Fullerene is partially miscible with amorphous regions of many conjugated polymers, yielding a “mixed phase” in which the polymer and fullerene are intimately mixed on a molecular scale. High fullerene volume fractions result in pure “aggregated fullerene” phases. If the polymer crystallizes, another pure phase composed of “crystalline polymer” can form.
separate, molecularly mixed donor-acceptor phases composed of amorphous polymer and fullerene moieties can facilitate charge generation.

**Delocalization**

Delocalization may also play a significant role in the generation of photocurrent.\(^{77,79,80,82,125,126}\) This has also been studied primarily in the context of photovoltaic devices incorporating a polymer/fullerene blend active layer. As discussed previously, when bulk heterojunction films are prepared with high fullerene volume fractions (typically > 50%), phases of aggregated fullerene emerge. The emergence of aggregated fullerene regions has been correlated with an increase in efficiency of corresponding photovoltaic devices. This trend can be rationalized by considering enhanced delocalization as fullerene aggregates form in the active layer.

It is suggested that enhanced delocalization increases the spatial extent of the charge transfer state and the sampling volume for an electron to move through following exciton dissociation.\(^ {127}\) This was examined using a model system consisting of a N,N’-bis(1-naphthyl)-N,’diphenyl-1,1’-biphenyl-4,4’-diamine (NPD) electron donor and C\(_ {60}\) electron acceptor. Efficiency and morphology of OPV devices with active layers incorporating various compositions of NPD and C\(_ {60}\) where characterized. Grazing incidence X-ray diffraction was used to quantify the size of C\(_ {60}\) crystallites within the active layer. A threshold C\(_ {60}\) crystallite size (4 nm) was correlated to a dramatic increase in photocurrent. Authors speculate that below this critical crystallite size, there is confinement of the charge transfer state wave function; the C\(_ {60}\) crystallite size is comparable to the natural spatial extent of the charge transfer state. Electroabsorption measurements indicate a significant increase in polarizability of the CT state when C\(_ {60}\) crystallites ≥ 4 nm form. Thus, authors conclude that efficient charge separation depends strongly on dissociation from a delocalized CT state.
High Local Charge Mobility

High local charge mobility immediately following exciton dissociation has also been proposed to facilitate charge separation.\textsuperscript{78,83,128,129} A recent study demonstrates that local charge carrier mobility in several different crystalline polymer/fullerene blend active layers correlates very nicely with power conversion efficiencies (after accounting for differences in $V_{OC}$ and active layer absorbance) of corresponding OPV devices.\textsuperscript{128} The local charge carrier mobilities in this study were measured by time-resolved microwave conductivity. This technique probes mobility on shorter length scales than space-charge-limited current or field-effect transistor measurements and is therefore more sensitive to local charge carrier mobilities.\textsuperscript{78} Thus, there is evidence that high local charge carrier mobility can facilitate charge separation.

Clearly, there is significant debate regarding the mechanism of photocurrent generation in organic materials. As a result, rational design of new materials for high-performance OPV devices is exceedingly challenging. Many excellent studies have revealed different factors that can influence charge generation (Figure 1-8). Nevertheless, most of this work was accomplished by studying bulk heterojunction films; an electron donor and acceptor are physically blended together and cast into a film with the expectation of forming a percolated network of nanoscale donor/acceptor domains. Solid state films incorporating a physical blend of electron donating and electron accepting materials are difficult to study experimentally due to complex and heterogeneous morphologies, intermolecular interactions, energetic landscapes, and molecular orientations at the donor-acceptor heterojunction. All of these factors significantly impact charge generation, but are challenging to characterize and control. Model systems that can be used to establish concrete structure-function relationships based on the electronic properties of the material, rather than film morphology, could have a strong impact in the field.
It has been proposed that donor-acceptor block copolymers can be used as the single active layer material in high-performance organic photovoltaic devices.\textsuperscript{130-148} Donor-acceptor block copolymers incorporate an electron donor block that is covalently linked to an electron acceptor block. Driven by chemical incompatibility between the blocks, block copolymers self-assemble into well-defined microstructures.\textsuperscript{149,150} Bulk heterojunction morphologies rely on the non-equilibrium, partial phase separation that occurs during film casting to form nanoscale domains.
Conversely, block copolymers can microphase separate into nanoscale equilibrium morphologies. It is thought that the use of donor-acceptor block copolymers in the active layer may enhance control over film morphology and interfacial structure. This could lead to improved performance of organic electronic devices. Block copolymers for photovoltaic applications may consist of one or more flexible blocks with electron donating or electron accepting materials appended to the backbone, one or more conjugated blocks joined by a saturated linking group, or two conjugated blocks that are directly linked to yield fully conjugated donor-acceptor block copolymers.

Our group has demonstrated use of the fully conjugated donor-acceptor block copolymer, poly(3-hexylthiophene)−block−poly((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3benzothiadiazole]-2′,2″-diyl) (P3HT-b-PFTBT) as the single active layer material in photovoltaic devices that perform at nearly 3% power conversion efficiency. Block copolymer device efficiency is nearly 3 times greater than that of the corresponding P3HT/PFTBT physical blend. The dramatic increase in performance is attributed to microphase separation of the block copolymer film into alternating donor-acceptor domains.

It has also been proposed that covalently linking a donor and acceptor, particularly in fully conjugated block copolymers, could be harmful to photovoltaic performance. Others have hypothesized that fully conjugated block copolymers may undergo very fast charge recombination due to high electronic coupling and overlap of donor/acceptor wave functions, enabled by the covalent linkage. In collaboration with our group, Asbury and coworkers have demonstrated that careful design of the aromatic moieties linking donor and acceptor blocks can avoid this fast charge recombination. In fact, using transient absorption spectroscopy, it was shown that charge recombination in P3HT-b-PFTBT block copolymer and P3HT/PFTBT physical blend films proceeds at the same rate.

Furthermore, it has been shown that a very small adjustment to the molecular structure of P3HT-b-PFTBT can induce this fast charge recombination that is detrimental to photovoltaic
device performance. It was shown that exchanging the fluorene (F) and dithenylbenzothiadiazole (TBT) moieties at the donor-acceptor interface, yielding P3HT-b-PTBTF, induces a drop in photovoltaic device efficiency from nearly 3% to 0.05%. Using model P3HT-FTBT and P3HT-TBTF materials, it was demonstrated that this striking drop in photovoltaic performance is due to a tightly bound charge transfer state that forms at the interface between P3HT and PTBTF. This charge transfer state serves as an efficient recombination pathway. Furthermore, it has been demonstrated that a small adjustment to the conjugated backbone of P3HT-b-PFTBT, replacing the quarternary carbon in the fluorene unit with a nitrogen to yield poly(3-hexylthiophene)-block-poly((9-(9-heptadecanyl)-9H-carbazole)-1,4-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) (P3HT-b-PCDTBT), also results in a significant decrease in device performance to 0.5% (Figure 1-9). Revealing the origin of this will be the topic of Chapter 3.

These results exemplify the key principle of organic electronics: defining functionality at the molecular level. There are only slight variations to the molecular structures of P3HT-b-PFTBT, P3HT-b-PTBTF, and P3HT-b-PCDTBT, yet photovoltaic performance varies by nearly two orders of magnitude. These studies begin to indicate that conjugated donor-acceptor block copolymers can be used as model systems to study photocurrent generation in organic materials. Although, it is challenging to determine whether differences in device performance between P3HT-b-PFTBT, P3HT-b-PTBTF, and P3HT-b-PCDTBT are due to differences in material electronic properties, or differences in film morphologies. By incorporating a donor-acceptor interface within the molecular structure, block copolymers enable studies of isolated polymer chains in solution, where electronic properties of the materials and donor-acceptor interface can be examined in the absence of solid state morphological properties. Throughout this work, we use donor-acceptor block copolymers to examine processes of charge and energy transfer within organic materials.
1.7. Dissertation Overview

This dissertation will establish conjugated block copolymers as effective model systems to examine fundamental photophysics of organic materials. Emphasis will be placed on elucidating mechanisms of photocurrent generation in donor-acceptor systems. In Chapter 1, we introduced relevant background content for this dissertation. Emphasis was placed on material design for high-performance organic photovoltaics and how this would be greatly aided by a more complete description of the mechanism for photocurrent generation.

Chapter 2 discusses the synthesis of conjugated polymers and block copolymers. After a discussion on techniques frequently employed to synthesize conjugated polymers, the focus will shift to synthesis of fully conjugated donor-acceptor block copolymers. Previous efforts will be reviewed. An optimized synthetic strategy developed by our group for fully conjugated donor-acceptor block copolymers with minimal homopolymer impurities will be discussed.

**Figure 1-9:** Using block copolymers to define functionality at the molecular level. (a) Chemical structures of P3HT-b-PFTBT, P3HT-b-PTBTF, and P3HT-b-PCDTBT. (b) Solar cell performance of the block copolymers. Data taken from the literature.\(^{132,144,148}\)
Chapter 3 establishes block copolymers as model systems. Using block copolymers dissolved in solution, we control electronic coupling and molecular orientation at the donor-acceptor interface. We introduce a procedure to quantify intramolecular charge transfer within isolated block copolymer chains. Block copolymer nanoparticles are synthesized. We demonstrate that while significant energy and charge transfer are observed in isolated block copolymer chains in solution, complete charge separation requires interchain coupling and aggregation of the electron donor.

In Chapter 4, we use block copolymers to examine the interplay between energetic and entropic contributions to the driving force for charge transfer. First, we quantify charge transfer occurring at the donor-acceptor interface between one donor and one acceptor. We show that, when entropy is reduced with respect to a solid state film, a significant energetic driving force is required for exciton dissociation. Block copolymers are also examined in the solid state, where entropy is increased with respect to isolated chains in solution. Charge transfer is significantly enhanced, suggesting the importance of entropy for efficient exciton dissociation.

Chapter 5 examines chain length effects on exciton dissociation. We introduce a series of block copolymers in which the synthetic scheme is adjusted to systematically tune the chain length of each block. By quantifying charge transfer as a function of chain length, we demonstrate that conjugated homopolymers require significant conjugation lengths to facilitate exciton dissociation. We also show that the polarized nature of excited states generated along push-pull polymers can facilitate efficient charge transfer, even when polymer chains are very short.

Finally, in Chapter 6 we briefly summarize main conclusions made throughout this dissertation. We conclude this work by proposing future experiments that could yield interesting and informative results.
Chapter 2

Conjugated Block Copolymer Synthesis

In theory, material design for organic electronics is limited only by the imagination of the researcher. In practice, material design is enabled through advances in synthetic chemistry. While development of synthetic methods for conjugated small molecules, including monomers that are incorporated in conjugated polymers, has been both nontrivial and instrumental in advancing the field of organic electronics, this section will focus on the synthesis of conjugated polymers.

In the 1970s and 80s, when conjugated polymers were first being developed, gas phase polymerization with a Ziegler-Natta catalyst, cationic polymerization, and electrochemical polymerization were used to synthesize conjugated polymers. Today, conjugated polymers are most commonly synthesized using either: 1) Suzuki polycondensation; 2) Stille polycondensation; 3) Kumada catalyst transfer polymerization (KCTP) (Scheme 2-1).

These transition metal catalyzed polycondensation reactions usually proceed by a step-growth mechanism. Nevertheless, under the right reaction conditions, these polycondensation reactions can follow a controlled chain-growth mechanism. For example, when the catalyst does not diffuse away from a growing chain, but rather “transfers” from monomer to monomer as the polymerization proceeds. In this chapter, we begin with an introduction to the inherent differences between step-growth and chain-growth polymerization mechanisms. We then introduce the reactions most frequently used to synthesize conjugated polymers: Suzuki polycondensation, Stille polycondensation, and Kumada catalyst transfer polymerization. We conclude this chapter with a more in-depth discussion on synthesis of fully conjugated donor-acceptor block copolymers.
**Scheme 2-1**: Common methods for conjugated polymer synthesis. (a) Suzuki coupling between boronic ester and halide (usually Br) functional groups. (b) Stille coupling between trialkyl tin and halide (usually Br) functional groups. (c) Kumada catalyst transfer polymerization. A dihalogenated monomer is functionalized in-situ with one equivalent of MgX (X = Cl or Br), yielding an asymmetric monomer that is polymerized with itself.

(a) \( n (RO)_{2}B-A-B(OR)_{2} + n X-B-X \xrightarrow{Suzuki} \left(\frac{A-B}{n}\right)_{n} + 2n X-B(OR)_{2} \)

(b) \( n R_{3}Sn-A-SnR_{3} + n X-B-X \xrightarrow{Stille} \left(\frac{A-B}{n}\right)_{n} + 2n X-SnR_{3} \)

(c) \( n X-A-MgX \xrightarrow{KCTP} \left(\frac{A}{n}\right)_{n} + n MgX_{2} \)

**2.1 Step-Growth vs. Chain-Growth Polymerization**

A polymerization can be classified into one of two categories based on the underlying reaction mechanism: step-growth or chain-growth. The defining features that distinguish step-growth and chain-growth polymerizations originate in the reaction kinetics. This section highlights key differences between the kinetics of step-growth and chain-growth reactions. Detailed derivations can be found elsewhere.\(^{159-163}\)

In step-growth reactions, polymer chains grow through reactions between any two molecular species. As illustrated in Figure 2-1a, two monomers can react, a monomer can react with a growing chain, or two growing chains can react. The overall polymerization rate is the sum of rates of all reactions between two molecular species. Assuming reactivity does not depend on size of the molecular species, number average degree of polymerization \((X_{n})\) and dispersity \((D)\) are expressed as:
In Equation 2-1 and Equation 2-2, $p$ is the extent of reaction, defined as the fraction of functional groups that have reacted at a given time. Defining features of a step-growth mechanism are that: monomers are consumed soon after the reaction begins, high molecular weight products are only formed as $p$ approaches 1, and $D$ approaches 2 as the reaction approaches completion ($p = 1$).

![Diagram](image)

**Figure 2-1**: Kinetics of step-growth vs controlled chain-growth polymerizations. (a) In a step-growth polymerization, any two molecular species can react. The degree of polymerization ($X_n$) grows according to $1/(1-p)$ where $p$ is the extent of reaction. (b) In a chain-growth polymerization, only one end of a growing chain reacts with monomers. When initiation is much faster than propagation, and termination reactions are negligible or nonexistent, $X_n$ grows linearly with $p$. 

\[ X_n = \frac{1}{1 - p} \]  \hspace{1cm} 2-1

\[ D = 1 + p \]  \hspace{1cm} 2-2
In chain-growth polymerizations, a chain grows only by reaction of a monomer with the active end of a growing chain. The kinetics of chain-growth polymerization are more complex than step-growth. A chain-growth mechanism consists of three individual reactions: initiation, propagation, and termination. The overall polymerization rate can be modeled as the net rate of the three competing reactions. The full rate expression depends on the nature of the individual reaction as well as relative rates of initiation, propagation, and termination. If termination takes place without combination of two chains, such as through disproportionation, then \( D \) follows Equation 2-2, as in step-growth polymerizations. If termination reactions require two chains ends to come together, such as through combination, then

\[
D = 1 + \frac{p}{2}
\]

and \( D \) approaches 1.5 at high \( p \). Some significant features that distinguish a chain-growth from step-growth mechanism are that monomers are consumed steadily throughout the reaction and high molecular weight polymers can form at low monomer conversions.

Living polymerization is a subset of chain-growth polymerizations. A living polymerization is defined as a chain-growth reaction in which no termination or chain transfer reactions occur during the polymerization (\( p < 1 \)). For optimal control over molecular weight with a narrow size distribution, there are additional criteria. First, the rate of initiation (\( r_i \)) must be much greater than the rate of propagation (\( r_p \)). If \( r_i \gg r_p \), initiation is effectively instantaneous and will be complete before propagation begins. In principle, this results in a constant number of polymer chains throughout the reaction. The second requirement is that all chains must be equally likely to react with a monomer throughout the polymerization; this ensures all chains grow at the same rate. When these conditions are satisfied, the resulting polymer molecular weight will follow a Poisson distribution. This mechanism is referred to as a “controlled chain-growth” polymerization.
2-1b). In a controlled chain-growth polymerization, all chains are initiated before propagation begins and grow at the same rate such that:

\[ X_n = \frac{M_0}{I} p \tag{2-4} \]

\[ D = 1 + \frac{IM_0p}{(I + M_0p)^2} \approx 1 + \frac{I}{M_0p} \tag{2-5} \]

\( M_0 \) and \( I \) represent the initial amounts of monomer and initiator, respectively.

Equation 2-4 leads to two important conclusions. First, assuming the reaction has gone to completion, the degree of polymerization can be calculated by the molar ratio of monomer to initiator. Second, the molecular weight increases linearly with extent of reaction. Furthermore, according to Equation 2-5, dispersity is \( \approx 1 \) for significant reaction conversion (approximately \( p \geq 0.2 \), but this depends on \( M_0 \) and \( I \)). Differences in reaction kinetics lead to different polymerization mechanisms that have important consequences in conjugated polymer synthesis.

### 2.2 Suzuki Polycondensation

Palladium catalyzed Suzuki cross-coupling was first developed for the synthesis of conjugated dienes in the late 1970s.\(^{164}\) It was later adapted for the synthesis of conjugated polymers.\(^{165,166}\) Suzuki polycondensation is frequently employed for the synthesis of conjugated polymers due to its chemical versatility, nontoxic reagents, and air-tolerance of condensation monomers. The reaction involves coupling between boronic acid or boronic ester and bromide, iodide, or triflate functional groups (Scheme 2-1a). Suzuki coupling proceeds by a typical cross-coupling catalytic cycle of oxidative addition, transmetalation, and reductive elimination steps.\(^{167}\) As with any step-growth polymerization, high purity of reactants and high conversions are necessary to achieve high
molecular weight products. Suzuki polycondensation has proved a very useful method to synthesize conjugated polymers with applications in high-performance organic electronic devices, notably poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT), which is known for its long-term stability.\textsuperscript{168,169} Nevertheless, there are drawbacks associated with Suzuki polycondensation. Within the context of conjugated polymers for organic photovoltaic applications, the most notable limitation of Suzuki coupling is that thiophene rings functionalized with boronic esters are prone to protodeborylation under typical reaction conditions.\textsuperscript{170} In principle, even a small amount of protodeborylation will have a detrimental effect on the product molecular weight. Thus, conjugated polymers that incorporate thiophene or thiophene-based units including benzdithiophene, thienothiophene, bithiophene, and cyclopentadiithiophene can typically not be synthesized using Suzuki coupling. Many conjugated polymers and non-fullerene acceptors used in the active layer of high-performance organic photovoltaics incorporate at least one thiophene-based molecular building block; Suzuki polycondensation has limited applicability for the synthesis of these materials. In addition, some functional groups may degrade under the required basic reaction conditions. Lastly, basic conditions normally result in a two-phase reaction system. Thus, using Suzuki polycondensation to synthesize polymers that abruptly decrease in solubility as molecular weight increases may result in low molecular weight product.\textsuperscript{171} In summary, although some materials are not amenable to Suzuki polycondensation, it remains an incredibly useful and frequently employed technique for conjugated polymer synthesis.

2.3 Stille Polycondensation

Stille coupling was also first introduced in the 1970s and later adapted for the synthesis of conjugated polymers in the late 1980s and early 1990s.\textsuperscript{172-174} The Stille reaction proceeds by
coupling between organostannanes and aryl halides to form sp\(^2\) hybridized C-C bonds (Scheme 2-1b). In many respects, Stille polycondensation is very similar to Suzuki polycondensation. The mechanism also proceeds by the typical cross-coupling catalytic cycle including oxidative addition, transmetalation, and reductive elimination steps.\(^{171,175}\) Advantages of Stille polycondensation include: high chemical versatility, high reaction yields, convenient preparation of organotin and organo halide monomers, and relatively low oxygen sensitivity of monomers.

Furthermore, Stille polycondensation overcomes many of the limitations associated with Suzuki coupling. Most notably, no added base is required. Therefore, Stille polycondensation is often used to synthesize conjugated polymers in which one or both condensation monomers incorporate thiophene or thiophene-based moieties. Stille polycondensation enables straightforward synthesis of many thiophene-based conjugated polymers, including polymers composed of alternating benzodithiophene and thienothiophene moieties that are frequently used as the electron donor material in top-performing organic solar cells.\(^{70,71}\)

One important drawback of Stille polycondensation is the high toxicity of organotin reagents. According to the National Institutes of Health, exposure to trimethyltin chloride causes severe and irreversible damage to the central nervous system in rats and marmosets.\(^{176}\) The probable lethal dose of trimethyltin chloride in hamsters, gerbils, and marmosets is approximately 3 mg kg\(^{-1}\); this is therefore assumed to be the lethal dose in humans as well.\(^{177}\) Thus, when performing Stille polycondensation, extreme caution must be exercised when handling hazardous organotin reagents as well as the crude reaction product. Generation of highly-toxic waste represents potential health and environmental hazards and represents a disadvantage of Stille polycondensation when compared to Suzuki polycondensation. Although toxic reagents necessitate the use of extreme safety precautions, Stille polycondensation is a versatile method often used to synthesize many conjugated polymers incorporated in high-performance organic electronic devices.
2.4 Kumada Catalyst Transfer Polymerization

In 1999, McCullough and coworkers reported the synthesis of regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) using Kumada-type coupling with a [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (Ni(dppp)Cl$_2$) catalyst. In a typical KCTP reaction, a dihalogenated aromatic moiety is functionalized in-situ with one equivalent of a Grignard reagent via a metal-halogen exchange, yielding an asymmetric polymerization monomer. Upon addition of a nickel catalyst, the asymmetric monomer is polymerized with itself in a condensation reaction (Scheme 2-1c). Polymerization proceeds according to a typical cross-coupling catalytic cycle of oxidative addition, transmetalation, and reductive elimination steps.

Nevertheless, five years after P3HT synthesis by a KCTP reaction was first established, it was independently reported by McCullough and Yokozawa that this method exhibits characteristics associated with a controlled chain-growth mechanism; molecular weight increases linearly with monomer conversion, molecular weight increases linearly with increasing $M_0/I$, and $D$ remains relatively low and steady throughout the reaction. It was proposed, for the first time, that upon reductive elimination the nickel catalyst forms a π-complex with the electron-donating thiophene monomer. This complex prevents the catalyst from diffusing away from the growing chain and leads to an intramolecular oxidative addition, facilitating a chain-growth mechanism. The success or failure of a chain-growth mechanism is strongly dependent on the stability and lifetime of this catalyst association. As it stands, the nickel π-complex has never been isolated from a successful reaction. Despite this, compelling evidence for the CTP mechanism has been established in the literature.

The mechanism for P3HT synthesis using KCTP is illustrated in Scheme 2-2. First, 2,5-dibromo-3-hexylthiophene is converted to the asymmetric polymerization monomer via a metal-halogen exchange reaction using one equivalent of a Grignard reagent (isopropyl magnesium
chloride, iPrMgCl, is frequently employed). Due to steric hindrance of the hexyl side chain, the bromine group in the 5 position will undergo metal-halogen exchange 3 times more often than the bromine in the 2 position. Nevertheless, the major product of the metal-halogen exchange, 2-bromo-5-magnesiumchloro-3-hexylthiophene, is selectively incorporated into the polymer, yielding regioregular P3HT. Upon addition of the nickel catalyst, an initial coupled dimer is formed, generating the “Br end” of P3HT chains. This is followed by a series of intramolecular oxidative addition, transmetalation, and reductive elimination reactions. The “living” end of the chain is protonated by acid during the termination step, generating the “H end” of P3HT chains. Thus, according to this mechanism, KCTP produces “H/Br P3HT”; one chain end is protonated and one chain end is functionalized with a Br group, enabling further reaction. This is very important for the synthesis of fully conjugated block copolymers, which is discussed in the next section.

**Scheme 2-2:** Synthesis of H/Br P3HT using KCTP. Adapted with permission from ref. 183 Copyright 2011 American Chemical Society.
Not long after the development of KCTP for P3HT, efforts turned to using this method for the controlled synthesis of other conjugated polymers. When poly(9,9-dioctylfluorene) (PFO) is synthesized by Kumada coupling using a Ni(dppp)Cl$_2$ catalyst, the polymerization proceeds by a chain-growth mechanism. The reaction does not proceed by a controlled chain-growth mechanism due to termination reactions, possibly caused by incomplete metal-halogen exchange of the Grignard reagent.$^{184,185}$ Similar results were obtained for PFO synthesis with [1,3-bis(diphenylphosphino)ethane]dichloronickel(II) (Ni(dppe)Cl$_2$), bis(triphenylphosphine)nickel(II) chloride (Ni(PPh$_3$)$_2$Cl$_2$), and [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene][3-chloropyridyl]palladium(II) (NHC ligated Pd), while [1,1′-bis(diphenylphosphino)ferrocene]nickel(II) chloride (Ni(dpff)Cl$_2$) does not yield significant polymer product under KCTP conditions.$^{184,186}$ When nickel(II) acetylacetonate/diphenylphosphinopropane (Ni(acac)$_2$/dppp) is used as the catalyst, polymerization of PFO proceeds by a controlled chain-growth mechanism, yielding polymers with $M_n$ ranging from 3 to 62 kg/mol. $M_n$ increases linearly with conversion and all $D$ values are about 1.2. When PFO octyl side chains are adjusted slightly to phenyl and triphenylamine groups, polymerizations with Ni(acac)$_2$/dppp result in dispersities ranging from ~ 1.3 – 1.4, suggesting decreased control.$^{187}$ If the Ni(acac)$_2$/dppp ligand is modified to Ni(acac)$_2$/dppp(m-Me), in which the dppp ligand has a methyl group on the meta position of the phenyl rings, this out-performs the Ni(acac)$_2$/dppp system. PFO can be synthesized in a controlled manner up to 91 kg/mol with $D$ ~ 1.2 – 1.3 throughout the polymerization. In contrast, Ni(acac)$_2$/dppp(o-Me), in which the methyl groups are incorporated on the ortho position of the phenyl rings, polymerizes PFO by a non-living chain-growth mechanism. $M_n$ increases rapidly and then plateaus around 30 kg/mol. When the Ni(acac)$_2$/dppp ligand is modified to Ni(acac)$_2$/dppp(p-Me), methyl groups are attached at the para position of the phenyl rings, results similar to the original Ni(acac)$_2$/dppp system are obtained.$^{188}$
Polyfluorene exemplifies a few very important aspects in the development of chain-growth syntheses for conjugated polymers. First, when developing a catalyst transfer polymerization of a new monomer, it is critical to distinguish the mechanism between step-growth, chain-growth, or controlled chain-growth through kinetic investigations. Second, the mechanism depends strongly on the interplay between the catalyst and monomer, resulting in system-specific catalyst-monomer interactions. For maximum control over end-groups and molecular weight, it is necessary to carefully match the catalyst/ligand to the monomer. This often requires extensive catalyst design and optimization.

In recent years, KCTP reactions that proceed by a controlled chain-growth mechanism have been demonstrated for other electron-rich monomers including furan\textsuperscript{189}, selenophene\textsuperscript{190-192}, tellurophene\textsuperscript{193}, pyrrole\textsuperscript{194}, thiazole\textsuperscript{195,196}, cyclopentadithiophene\textsuperscript{197}, and para-phenylene\textsuperscript{198}. Examples of electron-deficient monomers polymerized by a controlled chain-growth KCTP are very limited. Challenges associated with KCTP of electron-deficient monomers begin in the first step of the reaction; many electron-deficient monomers are incompatible with the metal-halogen exchange step required to form the organometallic monomer. Significant difficulties also arise in the polymerization step. Most electron-deficient monomers only have weak π-donation toward metal catalysts and do not form a stable associated complex\textsuperscript{199}.

A very interesting study may provide insight on how controlled chain-growth polymerizations can be developed for electron-deficient monomers. In an attempt to polymerize a benzotriazole monomer using KCTP, four nickel catalysts were designed. Various electron-donating ligands were used in an attempt to stabilize the associated π-complex and facilitate intramolecular oxidative addition\textsuperscript{200,201}. Energy of the associated π-complex was characterized using density-functional theory (DFT) calculations. Polymerization proceeds with all catalysts. A non-living chain-growth mechanism was observed for the two least electron-donating catalysts. The second-most electron-donating catalyst, acenaphthylene-(1,2-diylidene)bis(2-methoxyaniline
nickel(II) bromide (Ni(OMeAn)Br₂), exhibits evidence of an intermediate-type mechanism between chain-growth and controlled chain-growth. PBTz molecular weight increased linearly only until a conversion of approximately 40%. Dispersity remains relatively constant, but higher than expected for a controlled polymerization with values around 2 (Figure 2-2a). Strong evidence for a controlled chain-growth mechanism was observed for the most electron-donating catalyst, [N,N’-dimesityl-2–3-(1,8-naphthyl)-1,4-diazabutadiene] nickel(II) bromide (Ni(MesAn)Br₂) (Figure 2-2b). The molecular weight of the poly(benzotriazole) (PBTz) product increases linearly with monomer consumption and the dispersity remains relatively constant at about 1.5 (Figure 2-2c). Dispersity is higher than an ideal controlled chain-growth reaction; authors speculate this is the result of relatively slow initiation. This work exemplifies the requirement in catalyst transfer polymerizations for careful design and pairing of the catalyst and monomer; this is particularly critical when designing new catalysts for the polymerization of electron-deficient monomers.
In short, KCTP offers considerably less chemical versatility compared to Suzuki or Stille polymerization. Nevertheless, the controlled chain-growth mechanism enables precise control over molecular weight and dispersity, both of which can have substantial influence on solid state properties. The pseudo-living mechanism also provides a method for end-group functionalization of conjugated polymers. This enables further reaction and, importantly, synthesis of fully conjugated block copolymers.
2.5 Previous Reports of Conjugated Block Copolymer Synthesis

Fully conjugated donor-acceptor block copolymers are an exciting class of materials with potential applications as active layer components in organic electronic devices or as simple model systems to establish structure-function relationships. Nevertheless, synthesis of well-defined conjugated block copolymers is challenging. Under ideal circumstances, well-defined conjugated donor-acceptor block copolymers would be synthesized using a controlled chain-growth polymerization for each block. Block copolymers with controlled block lengths and end group functionalization could be synthesized by either sequential monomer addition or coupling together two mono-functional macroreagents. Perhaps the greatest obstacle in utilizing these methods is that electron acceptor polymers, as well as many electron donor polymers, incorporate electron-deficient aromatic moieties. As discussed in Section 2.4, there are very few examples of controlled chain-growth polymerization reactions for electron-deficient monomers. Examples that have been demonstrated required extensive monomer-catalyst optimization. In practice, synthesis of conjugated donor-acceptor block copolymers using controlled polymerization techniques is at best, very challenging.

Nevertheless, there are several examples of fully conjugated donor-acceptor block copolymers in the literature. These materials are most commonly synthesized using a two-step procedure. First, the electron donor block, usually P3HT, is synthesized using a KCTP reaction. As a result, one chain end is functionalized with a Br group, permitting further reaction. Second, the acceptor block is synthesized using a polycondensation reaction, usually Suzuki or Stille coupling. The block copolymer is formed during the second reaction. The first block is either used as a macroreagent, added at the beginning of the polycondensation reaction, or a chain-capping reagent, added at the end of the polycondensation reaction (Scheme 2-3). The advantage of this synthetic scheme is its incredible chemical versatility.
In principle, any conjugated polymer that can be synthesized using Suzuki or Stille coupling can be incorporated into a fully conjugated block copolymer with a P3HT block. The controlled nature of KCTP facilitates moderately clean reaction products with a reasonably high portion of diblock copolymer.

Scheme 2-3: Reaction scheme commonly used to synthesize fully conjugated donor-acceptor block copolymers. KCTP is used to synthesize the first block \((A)_n\). The block copolymer \((A)_n\)-b-(BC)_m is formed in the second reaction on using a Suzuki or Stille polycondensation. This representative scheme depicts a Suzuki coupling reaction. Using this procedure, diblock copolymer is typically formed as the major product. Although, side products including donor and acceptor block homopolymers and multiblock copolymers can also be produced.

\[
\begin{align*}
 n X-A-MgX & \rightarrow (A)_n + m(RO)_2B-B-B(OR)_2 + m X-C-X \rightarrow (A)_n(B-C)_m \\
 & + (A)_n \\
 & + (B-C)_m \\
 & + (A)_m(B-C)_m \\
 & + (A)_m(B-C)_m \\
 & + (A)_m(B-C)_m
\end{align*}
\]

Nevertheless, using this reaction scheme, significant side products can also form. The most probable side products are both donor and acceptor homopolymers as well as multiblock copolymers. Previous efforts to maximize diblock copolymer product and minimize homopolymer/multiblock copolymer impurities include: 1) purification by preparative gel permeation chromatography and 2) synthesis by sequential controlled chain-growth polymerization reactions.

Purification of a crude reaction product using preparative gel permeation chromatography (GPC) was demonstrated by Sommer and coworkers. Synthesis of poly(3-hexylthiophene)-block-poly-((9,9-dioctylfluorene)-2,7-diy1-alt-[4,7-bis(3-hexylthiophen-5-yl)-2,1,3-benzothiadiazole]-2’,2”-diyl) (P3HT-b-PFT6BT) was accomplished using monobrominated P3HT (H/Br P3HT) as an in-situ chain-capping reagent to terminate the Suzuki coupling reaction of
PFT6BT. In an effort to minimize PFT6BT homopolymer impurities, excess H/Br P3HT was added to the reaction. Two-dimensional gel permeation chromatography (GPC), which simultaneously monitors sample optical absorbance and elution time, indicates that approximately 50% of crude reaction product is P3HT homopolymer. Preparative GPC, where samples eluting from the separation column are collected in different fractions over time, is used to purify the crude reaction product. As shown in Figure 2-3, P3HT homopolymer was decreased from 50% in the crude reaction product to 10, 2, and < 1% in sequential preparative GPC fractions 1, 2, and 3, respectively. Due to excellent agreement of NMR signals corresponding to P3HT-F and P3HT-H bonds, authors assume significant quantities of both multiblock copolymer and PFT6BT homopolymer are not present in the purified product.

While this presents a useful method to produce well-defined diblock copolymers, preparative GPC is tedious and time-consuming. For example, if a sample requires 20 minutes to elute through a preparative GPC column, and 100 µL of a 1 mg mL⁻¹ solution is used for each injection, it would take 20,000 minutes (approximately 14 days) to purify 100 mg of reaction product.
Another approach to synthesize well-defined conjugated diblock copolymers is to synthesize both blocks using a controlled chain-growth polymerization reaction; the block copolymer is formed by sequential monomer additions. In Section 2.4, a study was described in which extensive catalyst design and synthesis, assisted by theoretical calculations, enabled successful controlled chain-growth polymerization of the electron-deficient benzotriazole moiety, yielding PBTz.\textsuperscript{200,201} The optimized catalyst, Ni(MesAn)Br\textsubscript{2}, was used to make P3HT-\textit{b}-PBTz, a fully conjugated donor-acceptor block copolymer. P3HT was polymerized first. After this reaction went to completion, the reactor was charged with benzotriazole monomer. Due to the pseudo-living nature of KCTP, P3HT chain ends were not terminated and P3HT-\textit{b}-PBTz formed (Figure 2-2d). Overlaying the GPC traces of the reaction product at the completion of P3HT monomer consumption and PBTz monomer consumption, a shift to lower elution times in P3HT-\textit{b}-PBTz

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2-3.png}
\caption{Two dimensional GPC chromatograms of synthesized P3HT-\textit{b}-PFT6BT. From top to bottom: crude (raw) reaction product, fractions 1, 2, 3, and P3HT-Br chain-capping reagent. P3HT-\textit{b}-PFT6BT is shifted to lower elution times and red shifted in absorbance wavelength relative to H/Br P3HT macroreagent. Fractions 1, 2, and 3 were collected at increasing elution times. Authors estimate 10, 2, and < 1 \% P3HT homopolymer in fractions 1, 2, and 3, respectively. Adapted with permission from ref.\textsuperscript{153} Copyright 2012 American Chemical Society.}
\end{figure}
indicates successful chain extension. This exciting result represents an ideal method to produce well-defined diblock copolymers with minimal impurities. Nevertheless, extensive catalyst design for each new material may not always be feasible.

2.6 Recent Studies on Conjugated Block Copolymer Synthesis

Our group has recently demonstrated an optimized approach for the synthesis of fully conjugated donor-acceptor block copolymers with minimal homopolymer impurities. Importantly, this procedure is straightforward to implement and does not require time-intensive purification steps or extensive catalyst design. Thus, as will be demonstrated throughout this dissertation, our generalized method can be successfully applied to synthesize a wide variety of conjugated donor-acceptor block copolymers that can be used for further applications.

In this study, we optimize the synthesis of poly(3-hexylthiophene-2,5-diyl)-block-poly((9,9-bis-(2-octyl)fuorene-2,7-diyl)-alt(4,7-di(thiophene-2-yl)-2,1,3-benzothiadiazole)-5',5''-diyl) (P3HTb-PFTBT) to confirm our approach is effective. Importantly, this procedure can easily be generalized for the synthesis of many different block copolymers. P3HT-b-PFTBT was selected because of its relevance to the field of OPVs. Prior to this study, our group demonstrated photovoltaic devices that perform moderately well using P3HT-b-PFTBT as the single active layer material, described in Section 1.6. Our synthetic method utilizes a common approach for synthesis of fully conjugated donor-acceptor block copolymers described in Scheme 2-4. First P3HT with a high degree of Br chain end functionality (H/Br P3HT) is synthesized using a KCTP reaction. Second, a Suzuki polycondensation chain extension reaction is used to synthesize the PFTBT block. Our results identify two key parameters that result in minimal homopolymer impurities: 1) precise quantification of commercial Grignard reagent concentration in the first
reaction to maximize end-group control of P3HT; 2) use of an asymmetric monomer feed ratio in
the second reaction to control the relative number of P3HT/PFTBT chains.

**Scheme 2-4:** Synthetic method used to synthesize P3HT-\(b\)-PFTBT. In practice, P3HT synthesis
results in imperfect end group functionalization; H/Br, H/H, and Br/Br P3HT are present in the
reaction product. The uncontrolled step-growth nature of Suzuki polycondensation used for PFTBT
can result in a mixture of diblock copolymer, P3HT homopolymer, PFTBT homopolymer, and
multiblock copolymer.

H/Br P3HT end group functionalization is crucial for the synthesis of well-defined diblock
copolymers. H/H P3HT is not able to participate in the chain-extension reaction, resulting in
homopolymer impurities. While Br/Br P3HT chains can lead to diblock copolymers, two
functionalized ends mean there are two routes to form triblock copolymers (compared to only one
route for H/Br P3HT chains).

In principle, the population of P3HT chains produced from a well-controlled KCTP
reaction should each contain one brominated end and one protonated end (H/Br P3HT). The Br end
group originates from the first coupled dimer that is formed upon initiation and the “living end” of
the chain is protonated when the polymerization is quenched with acid, as described in Section 2.4.
Nevertheless, unreacted Grignard reagent present during the polymerization, possibly the result of
adding a molar excess, can react with the Br end of a growing chain by a metal–halogen exchange.
As a consequence, both chain ends will be protonated upon addition of acid, resulting in H/H P3HT chains. Br/Br P3HT occurs when both chain ends are brominated as a result of chain transfer or homocoupling reactions. In practice, P3HT synthesized by CTP will contain a mixture of H/Br, H/H, and Br/Br end-groups.

In order to maximize the H/Br content, it is necessary to optimize reaction conditions, in particular, the molar equivalent of Grignard reagent used. In order to add a precise stoichiometric ratio, it is essential to accurately quantify the concentration of a commercially available Grignard reagent using a strong acid-weak base titration. Isopropylmagnesium chloride lithium chloride complex (iPrMgCl, ~ 1.3 M in tetrahydrofuran, THF) was purchased from Sigma-Aldrich. Accurate concentration of the Grignard reagent was determined using an acid-base titration. The iPrMgCl was first diluted in THF and then quenched with excess water, yielding Mg(OH)Cl and isopropane. Dilute hydrochloric acid was carefully titrated into the solution and the concentration of the iPrMgCl solution was back-calculated from the equivalence point. Final concentration of the Grignard reagent was determined by averaging at least three trials.

Once the concentration of a commercial Grignard reagent was accurately quantified, three P3HT samples were prepared with either excess (1.25 eq., P3HT(1.25)), equimolar (1.0 eq., P3HT(1.0)), or deficient (0.75 eq., P3HT(0.75)) equivalents of iPrMgCl relative to the 2,5-dibromo-3-hexylthiophene (3HT) starting material. Matrix assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF MS) was used to characterize end-group composition of synthesized P3HT (Figure 2-4). The percent yields and end group composition of the different P3HT batches are presented in Table 2-1. Of the samples studied, P3HT synthesized with excess iPrMgCl contains the lowest portion of H/Br chain ends and the highest portion of H/H chain ends, 73% and 11%, respectively. P3HT batches synthesized with both equimolar and deficient equivalents of iPrMgCl had > 90% H/Br and ≤ 2% H/H chain ends. Nevertheless, the reaction yield of P3HT(0.75) was only 16%, likely due to low conversion of 2,5-dibromo-3-
hexylthiophene to the active monomer used in the polymerization. Thus, we propose a precise 1:1 stoichiometry of iPrMgCl:2,5-dibromo-3-hexylthiophene, enabled by titration of an easily attainable commercial Grignard reagent, will facilitate synthesis of P3HT with a high portion of H/Br P3HT chain ends.

Figure 2-4: MALDI-TOF spectra of (a) P3HT(1.25), (b) P3HT(1.0), and (c) P3HT(0.75). The inset of each spectra is a zoomed-in view illustrating the distribution of H/H, H/Br, and Br/Br of P3HT chains with $n = 13$. 
The chemical versatility allowed for by Suzuki polycondensation makes it an invaluable tool in conjugated polymer synthesis. Nevertheless, under conditions employed here, it proceeds by an uncontrolled step-growth mechanism. Therefore, it is very challenging to control the molecular weight and number of chains of the product. Alternatively, Carothers equation (Equation 2-6) predicts that an asymmetric monomer ratio \( r \) will limit the maximum attainable degree of polymerization \( X_n \) of a step-growth polycondensation.

\[
X_n = \frac{1 + r}{1 - r}
\]  

Thus, in an otherwise uncontrolled step-growth reaction, some control can be exerted over the molar mass distribution and total number of polymer chains by carefully tuning \( r \). We use this concept to synthesize P3HT-\( b \)-PFTBT. In principle, perfect formation of diblock copolymer with no homopolymer impurities necessitates exactly a 1:1 ratio of P3HT:PFTBT polymer chains. Thus, balancing the relative number of P3HT chains added to the reaction and PFTBT chains synthesized during the reaction should minimize homopolymer impurities.

Three batches of P3HT-\( b \)-PFTBT were synthesized using different molar ratios of the condensation monomers. Block copolymers are named P3HT-\( b \)-PFTBT(\( x \)) where \( x \) corresponds to mol fraction fluorene (F) monomer (relative to dithienyl benzothiadiazole (TBT) monomer) added

<table>
<thead>
<tr>
<th>Feed ratio of iPrMgCl:3HT</th>
<th>Yield (%)</th>
<th>H/Br (^a)</th>
<th>H/H (^a)</th>
<th>Br/Br (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT(1.25) 1.25</td>
<td>43</td>
<td>0.73</td>
<td>0.11</td>
<td>0.16</td>
</tr>
<tr>
<td>P3HT(1.0)  1.0</td>
<td>36</td>
<td>0.92</td>
<td>0.02</td>
<td>0.06</td>
</tr>
<tr>
<td>P3HT(0.75) 0.75</td>
<td>16</td>
<td>0.93</td>
<td>0.01</td>
<td>0.06</td>
</tr>
</tbody>
</table>

\(^a\) MALDI-TOF MS

Table 2-1: End group characterization of synthesized P3HT.
to the condensation reaction, either 0.48, 0.50, or 0.55. All block copolymers were synthesized using P3HT(1.0) as the macroreagent. One dimensional GPC refractive index traces were deconvoluted to quantify the amount of homopolymer impurities remaining in the purified products (Figure 2-5a). As the mol fraction of F increases, the fraction of homopolymer impurities decreases from approximately 60% to 50% to 20%. In principle, when an excess of TBT is used (P3HT-\textit{b}-PFTBT(0.48)), PFTBT molecular weight will be limited and number of chains balanced with the P3HT macroreagent. Nevertheless, chains will likely be capped with TBT-Br groups which cannot couple to P3HT-Br, and thus are likely to yield homopolymer impurities.

![Figure 2-5: GPC characterization of P3HT-\textit{b}-PFTBT synthesized with varying monomer feed ratios. (a) GPC refractive index traces of P3HT-\textit{b}-PFTBT synthesized with different molar ratios of F (0.48, 0.50, or 0.52) overlaid with the corresponding P3HT macroreagent (P3HT(1.0)). (b) 2D GPC traces simultaneously monitoring absorbance as a function of wavelength and retention time of P3HT(1.0) and P3HT-\textit{b}-PFTBT(0.55). (c) GPC absorbance traces monitored at 420 nm, where P3HT absorbance is maximized, of P3HT(1.0) and P3HT-\textit{b}-PFTBT(0.55).](image-url)

Two-dimensional GPC traces obtained from a multi-wavelength detector were also used to confirm chain extension and demonstrate that including a molar excess of F (P3HT-\textit{b}-
PFTBT(0.55)) produces P3HT-\textit{b}-PFTBT with minimal homopolymer impurities (Figure 2-5b). Compared to the P3HT macroreagent, 2D GPC traces of the block copolymer (P3HT-\textit{b}-
PFTBT(0.55)) clearly exhibit a shift to lower retention time and a red-shift in absorbance. This indicates: 1) an increase in molecular weight; and 2) incorporation of PFTBT (PFTBT absorbs at higher wavelengths than P3HT in solution), suggesting successful chain-extension. Although unlikely, a blend of high molecular weight PFTBT homopolymer and P3HT macroreagent cannot be ruled out at this point. Further analysis was performed using 1D traces from the multi-wavelength detector to monitor absorbance at 420 nm, where P3HT absorbance is maximized and PFTBT absorbance is minimized. If the product was a mixture of high molecular weight PFTBT homopolymer and P3HT macroreagent, then the low retention time signal, presumably due to PFTBT homopolymer, should be significantly reduced relative to the signal at high retention time, presumably due to P3HT macroreagent. This trend is not observed; peak absorbance of the low retention time signal at 420 nm is greater than peak absorbance of the high retention time signal at 420 nm (Figure 2-5c). Furthermore, the GPC trace monitoring absorbance at 420 nm, is qualitatively similar to the refractive index trace. Altogether, these results confirm the presence of P3HT at low retention times and successful chain extension.

In summary, our group has established an optimized reaction protocol to synthesize fully conjugated donor-acceptor block copolymers with minimal homopolymer impurities. Importantly, this protocol is easily generalized and readily applied to the synthesis of virtually any donor-acceptor block copolymer containing an electron donor block synthesized by a KCTP reaction and acceptor block synthesized by a Suzuki or Stille polycondensation reaction.
Chapter 3

Conjugated Block Copolymers as Model Systems to Examine Mechanisms of Charge Generation in Donor-Acceptor Materials

Fully conjugated donor-acceptor block copolymers are established as model systems to elucidate fundamental mechanisms of photocurrent generation in organic photovoltaics. Using analysis of steady-state photoluminescence quenching, exciton dissociation to a charge transfer state within individual block copolymer chains is quantified. By making a small adjustment to the conjugated backbone, the electronic properties are altered enough to disrupt charge transfer almost entirely. Strong intermolecular coupling of the electron donor is introduced by synthesizing block copolymer nanoparticles. Transient absorption spectroscopy is used to monitor charge generation in block copolymer isolated chains and nanoparticles. While efficient charge transfer is observed in isolated chains, there is no indication of complete charge separation. In the nanoparticles, long-lived polarons are observed as early as ~ 15 ns. Thus, aggregation of electron donors can facilitate efficient charge generation.

3.1 Introduction

The working mechanisms for organic light-emitting diodes, solar fuels, and organic photovoltaics (OPVs) all rely on charge and energy transfer. Thus, understanding the fundamental photophysics of these processes within organic materials is instrumental in designing new high-performance organic electronic devices. As a consequence, significant work has been dedicated to elucidating mechanisms of photophysical processes in organic molecules, particularly in the context of charge photogeneration in OPVs.\textsuperscript{79,125,231-237} Despite several noteworthy studies, there
remains significant debate in the literature and a complete description of charge generation mechanisms remains elusive.

Substantial evidence indicates that in polymer donor/fullerene acceptor systems, aggregation of fullerene into pure domains plays a critical role in charge generation.\textsuperscript{77-81,83,238} It has been shown that fullerene is partially miscible with many amorphous polymers.\textsuperscript{121,122} Thus, mixing samples with large volume fractions of fullerene leads to multiple co-existing phases. One phase is composed of intimately mixed polymer/fullerene regions, another is composed of pure aggregated fullerene regions, and a third pure polymer phase can form if the polymer crystallizes. Because of these complex morphologies, it is challenging to independently tune polymer donor aggregation without affecting fullerene aggregation as well.

Nanoparticles of conjugated polymer/fullerene blends have been used previously as model systems to provide insight into the relationship between morphology and photophysical processes.\textsuperscript{239-241} A recent study examined the relationship between nanocomposites of regioregular and regiorandom poly(3-hexylthiophene-2,5-diyl) (P3HT) blended with [6,6]-phenyl-C61 butyric acid methyl ester (PCBM).\textsuperscript{240} It was found that regioregular P3HT forms a highly ordered, $\pi$-stacked structure in the nanoparticles. Regiorandom P3HT forms much less ordered domains. Photoluminescence quenching was more efficient in nanoparticles incorporating regiorandom P3HT, suggesting a more homogeneous PCBM distribution, and therefore, more interfacial area or donor-acceptor contacts. Transient absorption spectroscopy measurements of regioregular P3HT/PCBM nanoparticles show that increasing PCBM concentration leads to a stronger signature of polarons that is attributed to an increase in interfacial area. Perturbing the solid state packing of P3HT, as it relates to the number of donor-acceptor intermolecular contacts that are lost with crystallization of the donor and gained with high concentrations of the acceptor, clearly impacts charge photogeneration.
Another study attempted to tune intermolecular interactions by adjusting the alkyl side chains of benzodithiophene-thienothiophene alternating copolymers. Relative to linear side chains, branched side chains disrupt π-stacking of aromatic rings. The authors conclude that high polymer crystallinity can hinder charge separation. Large, pure polymer domains decrease the probability that excitons reach a donor-acceptor interface to undergo charge separation. Thus, perturbing intermolecular interactions in thin films and nanoparticles does not reveal any effects on the mechanism of charge photogeneration beyond the role of the nanoscale morphology.

It has been speculated that in a manner analogous to fullerene aggregation, polymer aggregation may also facilitate charge separation. Previous work suggests that polymer donor aggregation could be more beneficial than acceptor aggregation by promoting extremely fast charge transport along the conjugated backbone. It has also recently been suggested that strong phase separation within amorphous polymer/acceptor domains is necessary to achieve high fill factors in OPV devices. Nevertheless, the effect of polymer aggregation is challenging to probe in films. Even if intermolecular interactions could be completely removed, this would also severely disrupt charge extraction and preclude characterization of electronic devices based on these hypothetical materials.

In this work, we use block copolymers as model systems to examine fundamental mechanisms of charge generation in organic materials. By covalently linking the electron donor and acceptor, a donor-acceptor interface is incorporated within the molecular structure. This enables model studies of charge and energy transfer within isolated block copolymer chains in solution where intermolecular interactions are completely removed. Small chemical modifications of the conjugated backbone can be used to tune electronic properties of the material, enabling the development of structure-property relationships without the influence of film morphology. Previous studies on conjugated donor-acceptor block copolymers have focused on block copolymers in solution, aggregates, and films to examine energy transfer, exciplex formation,
and charge transfer while relying on a poorly-defined interface between a donor polymer and a random copolymer where the direct linkage of the donor and acceptor blocks is not controlled.219

Covalently linked donor-acceptor dyads have been studied for many years.244 These materials have been used as model systems to experimentally confirm the governing physics behind electron transfer reactions, Marcus theory. Conclusions drawn from these simple model systems have greatly aided in understanding solar energy conversion, photosynthesis, corrosion, and electrochemical reactions in batteries. Our aim here is to use conjugated block copolymers as model systems to examine the photophysics behind solar energy conversion within organic thin films. Unlike covalently linked small molecules that are often separated by a saturated hydrocarbon linking group, block copolymers facilitate studies of covalently linked donor-acceptor materials with extended conjugated networks of delocalized π-electrons. These materials are typically most relevant to OPV devices that often incorporate conjugated polymers. To this end, the same materials that are used for model studies can also be incorporated as the single active material in OPV devices.144 Conclusions drawn in this chapter can deepen our understanding of the charge and energy transfer processes that govern photovoltaic performance in OPVs as well as other organic electronics applications.

To demonstrate the value of block copolymers as model systems, we examine charge generation in a block copolymer with a well-defined donor-acceptor interface, the junction point between two specific moieties. This enables the use of block copolymers to examine effects of: 1) small perturbations to the chemical structure; and 2) polymer donor interactions on charge generation. A P3HT electron donor is covalently linked to a push-pull polymer electron acceptor. First, block copolymers are studied as isolated chains in solution where intermolecular interactions are completely removed. The efficiency of exciton dissociation to a charge transfer state is dramatically affected by substitutions to the “push” moiety in the acceptor block. In the isolated chains, charge transfer is observed, but charge separation is not, even for systems that perform well.
in organic photovoltaic devices. Next, block copolymer nanoparticles are synthesized to introduce aggregation of P3HT donor chains. Long-lived charge separated states are observed, suggesting charge generation is facilitated by intermolecular coupling within aggregated domains of the polymer electron donor.

3.2 Experimental Section

Polymer Synthesis

P3HT was synthesized using Kumada catalyst transfer polymerization. A 3-neck 100 mL round bottom flask containing a magnetic stir bar was charged with 2,5-dibromo-3-hexylthiophene (9 mmol, 3 g) and then capped with septa. The flask was put under vacuum for \(~2\) minutes and then refilled with argon. Tetrahydrofuran (THF, 5 mL) was added through one of the septa. The reactor was purged for \(~15\) minutes and cooled to \(0^\circ\text{C}\) at which time isopropyl magnesium chloride lithium chloride complex (8.1 mmol, 1.4 M, 5.8 mL) was added dropwise. The reaction was allowed to proceed at room temperature for \(~3\) hours. After 3 hours, the reactor was purged with argon for \(~15\) minutes and diluted with an additional 35 mL of THF. Polymerization was initiated through the addition of \([1,3\text{-Bis(diphenylphosphino)propane}]\text{dichloronickel(II)}\) \((\text{Ni(dppp)Cl}_2)\) catalyst (0.18 mmol, 98 mg) by opening one of the septa and pouring the catalyst into the reaction mixture. The polymerization proceeded for 20 minutes and then was quenched by the addition of 5 mL of 6M hydrochloric acid. The reaction mixture was precipitated into methanol, filtered, and purified by sequential soxhlet washes of methanol and acetone. The chloroform fraction was collected and dried under vacuum for 24 hours.

P3HT-\(b\)-PCT6BT and P3HT-\(b\)-PFT6BT block copolymers were synthesized using P3HT as a macrorreagent. The second block was added on using a Suzuki polycondensation chain
extension reaction. A 100 mL Schlenk flask was charged with P3HT (~ 0.02 mmol, 100 mg), either 9-(9-heptadecanyl)-9H-carbazole-2,7-diboronic acid bis(pinacol) ester (C, 0.2 mmol, 132 mg) or 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (F, 0.2 mmol, 111 mg), 4,7-Bis(5-bromo-4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (T6BT, 0.14 mmol, 88 mg), and toluene (15 mL). The reactor was purged with argon for ~ 20 minutes. The septum was opened and tetraethylammonium hydroxide (20% in water, 3.5 mL), Aliquat 336 (2 drops), and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh3)4, 0.0225 mmol, 26 mg) were added. Oxygen was removed from the reaction solution by 3 freeze-pump-thaw cycles, and at the end the reactor was then back-filled with argon to preserve an inert atmosphere. Polymerization was initiated by heating the reactor to 80°C and allowed to proceed for ~ 48 hours. The reaction was terminated by adding bromobenzene (4 mL) as an end-capper. The aqueous phase was separated and discarded and the product was precipitated into methanol. The product was purified by sequential Soxhlet extractions using methanol, acetone, and hexane. The isolated, purified polymer then was dried under vacuum for 24 hours. PCT6BT and PFT6BT homopolymers were synthesized using an identical procedure as the corresponding block copolymer, omitting the addition of P3HT to the reactor.

P3HT: Yield: ~ 700 mg, ~ 50%. 1H NMR (850 MHz, CDCl3, δ): 6.96 (1H), 2.78 (2H), 1.69 (2H), 1.42 (2H), 1.33 (4H), 0.90 ppm

P3HT-b-PCT6BT: Yield = 100 mg, 41%. 1HNMR (850 MHz, CDCl3, δ): 8.2-8.1, 7.92, 7.72, 7.49-7.4, 6.96, 2.86, 2.78, 2.34, 1.97, 1.77, 1.68, 1.41, 1.32, 1.14, 0.90-0.80 ppm

P3HT-b-PFT6BT: Yield = 190 mg, 48%. 1HNMR (360 MHz, CDCl3, δ): 8.06, 7.90, 7.77, 7.49, 6.96, 2.78, 2.01, 1.66, 1.33, 1.08, 0.88, 0.77 ppm

PCT6BT: Yield = 110 mg, 36%. 1HNMR (360 MHz, CDCl3, δ): 8.31-8.07 (4H), 7.92 (2H), 7.72 (2H), 7.29 (2H), 4.62 (1H), 2.86 (4H), 2.50-1.65 (12H), 1.50-1.00 (30H), 0.95-0.59 (15H) ppm
PFT6BT: Yield = 104 mg, 67%. $^1$HNMR (360 MHz, CDCl$_3$, δ): 8.06 (2H), 7.90 (2H), 7.77 (2H), 7.49 (4H), 7.79 (4H), 2.03 (4H), 1.73 (4H), 1.54 (4H), 1.28 (14H), 1.08 (15H), 0.78 (15H) ppm

**Polymer Characterization**

Chain extension in the block copolymers and molar mass distribution of all synthesized polymers were determined using an Agilent Technologies gel permeation chromatograph (GPC) (ResiPore 300 x 7.5 mm column, Agilent 1260) equipped with refractive index, multiwavelength, light scattering, and viscometer detectors. Chlorobenzene was used as the mobile phase at 40°C with a flow rate of 0.5 mL min$^{-1}$. Molar mass distributions were determined relative to polystyrene standards. GPC refractive index traces of the block copolymers (colored) overlaid with the P3HT macroreagent (black). A shift of the block copolymer trace to lower elution times, corresponding to higher molecular weight, confirms successful chain extension and block copolymer synthesis.

![Figure 3-1: GPC refractive index (RI) traces of block copolymers (colored) overlaid with P3HT macroreagent (black). All traces are normalized for clarity.](image)

The molecular weight of P3HT and composition of the block copolymers was determined by $^1$H NMR analysis on a Bruker 850 MHz instrument (Avance-III-850 MHz) using deuterated chloroform as the solvent. Together, these were used to determine the number-averaged molecular
weight ($M_n$) of the block copolymers. Weight-averaged molecular weights ($M_w$) were determined using the dispersity ($D$) obtained from GPC. NMR spectra are presented in Figure 3-2.

**Figure 3-2:** NMR spectra of all synthesized polymers measured in deuterated chloroform on a Bruker 850 MHz instrument (Avance-III-850 MHz).

**Constrained Density Functional Theory (CDFT)**

Density functional theory (DFT) calculations were used to study block copolymer CT states. First, the geometries of the molecules were optimized using the NWChem software package. To reduce computational costs, polymer structures were simplified to a 10-mer of P3HT and a 2-mer of the acceptors. Additionally, all alkyl side chains were replaced with methyl groups.
Geometries were optimized in a chloroform environment using the conductor-like screening model (COSMO); the dielectric cavity is constructed using optimized atom-centered spheres with radii ~20% larger than the Van der Waal radius of each atom.\textsuperscript{246,247} These calculations are performed at the B3LYP/6-31G** level of theory, which incorporates a fraction (20%) of nonlocal exact exchange energy.\textsuperscript{248,249} CT state energies were then obtained by constraining a beta electron to the acceptor of the neutral molecules self-consistently using the constrained density functional theory (CDFT) formalism.\textsuperscript{250} In this approach, both charge and spin can self-consistently be constrained to a specific area of the system, defined by a list of atoms and population scheme. The Löwdin scheme was used for this study.\textsuperscript{251,252}

**Nanoparticle Synthesis**

Nanoparticle dispersions of P3HT-\textit{b}-PFT6BT in water were prepared using the good-solvent evaporation method,\textsuperscript{253} which was adapted from the flash reprecipitation method.\textsuperscript{240} P3HT-\textit{b}-PFT6BT was dissolved at 0.1 mg mL\textsuperscript{-1} in THF to a total volume of ~ 10 mL and stirred for 1 hour at ~ 50°C. The solution was then removed from heat and ~ 10 mL of water was added dropwise while stirring to induce formation of the nanoparticle dispersion. The majority of THF was removed by passing a flow of compressed air over the liquid until the total volume was reduced by about half. The sample was diluted with water to a final concentration of ~ 0.007 mg/mL for all measurements.

**Dynamic Light Scattering**

Isolated chain solutions were prepared at ~ 0.1 mg mL\textsuperscript{-1} in chloroform, stirred overnight, and filtered through a 0.2 µm filter three times into a glass vial used for measurements. The
nanoparticle dispersion was measured without filtration. Multiangle DLS measurements were performed on a Brookhaven Instruments BI-200 SM static/dynamic light scattering system equipped with a 35 mW diode laser ($\lambda=637$ nm). Particle size distributions are calculated using the CONTIN algorithm.\textsuperscript{254} For each sample, scattering was measured from at least 5 different angles (15-120°). At least 3 different measurements were recorded and averaged at each angle. Scattering was recorded for approximately 10-30 minutes for each measurement of the isolated chains samples. Scattering was recorded for approximately 2 minutes for each measurement of the nanoparticle dispersion.

The mean decay rate ($\Gamma$) of the autocorrelation function was calculated using the CONTIN algorithm.\textsuperscript{254} Diffusion coefficients of the particles in the different solutions were obtained by plotting $\Gamma$ versus the scattering vector ($q$) squared. Using Stokes-Einstein equation, the hydrodynamic radius ($R_h$) was calculated from the diffusion coefficient. This is an apparent $R_h$ by virtue of being determined at finite concentration. To achieve sufficient scattered intensity for reasonable light intensity autocorrelation functions, block copolymer isolated chain DLS solutions were ~ 100 times more concentrated than those used for absorbance and fluorescence measurements.

**Figure 3-3:** Particle size distributions of block copolymer isolated chains and nanoparticle dispersion.
In-situ Liquid Scanning Transmission Electron Microscopy

In-situ scanning transmission electron microscopy (STEM) was performed using a Protochips Poseidon 510 holder in the FEI Talos 200FX S/TEM at an accelerating voltage of 200 kV and a beam current of approximately 0.25 nA. HAADF-STEM (high angle annular dark field) was chosen over TEM in order to provide enhanced mass contrast as well as superior resolution for the relatively thick liquid cell configuration, which results in strong electron beam scattering. One microliter of the nanoparticle dispersion was encapsulated between two plasma-cleaned e-chips, each with a 50 nm thick electron beam transparent window, and separated by a spacer height of 150nm. Using this configuration, the liquid sample is at least 150 nm thick; nevertheless, bowing of the chips due to the pressure differential in the column leads to a greater effective thickness in the center of the windows.

Spectroscopic Characterization

Solutions of isolated polymer chains were prepared by dissolving the polymers at ~ 1 mg mL$^{-1}$ in chloroform and stirring overnight in a nitrogen-filled glovebox. Solutions were then diluted to ~ 1 µg mL$^{-1}$, loaded into 1 cm quartz cuvettes, sealed, and removed from the glovebox for testing. Absorbance spectra were measured on an Agilent Technologies Cary 60 UV-vis. Fluorescence emission spectra were measured at several different excitation wavelengths (410, 430, 450, and 470 nm) on a Photon Technology International QuantaMaster 300 fluorimeter equipped with a Xe Arc lamp and 914 photomultiplier detection system. Given the dilute concentrations used in these experiments (optical densities of approximately 0.05), photoluminescence emission is expected to be isotropic. Therefore, quantum yields ($\Phi$) of homopolymers and block copolymers were
measured by comparing absorbance and fluorescence spectra to a dye of known quantum yield, 4-
(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (Φ = 0.44 in ethanol). Transient absorption spectroscopy was performed using a homebuilt laser flash photolysis system described previously. A frequency-doubled (532 nm) Nd:YAG laser (Surelite, Continuum; San Jose, CA) with a repetition rate of 30 Hz and a pulse duration of ~10 ns was used as the excitation pulse. The excitation energy density absorbed by each sample was adjusted to ~35 μJ cm⁻². The probe source was a tungsten halogen lamp (ASBN-W, Spectral Products; Putnam, CT) filtered using a 720 nm longpass optical filter before transmitting the samples. The transmitted beam was then dispersed using a monochromator (DK240, Spectral Products; Putnam CT) and detected using a 5 ns rise-time InGaAs photodiode (DET10N, Thorlabs; Newton, NJ). The detected signal was amplified using a 200 MHz preamplifier (HVA-200M-40-B, Femto; Berlin, Germany) and digitized using a 200 MHz PC oscilloscope (Pico-500, Pico Technology; Cambridgeshire, United Kingdom). All samples were measured in a 1 cm quartz cuvette.

**Estimating Rate Constants of P3HT Exciton Decay**

The rate of exciton quenching due to Förster resonance energy transfer (FRET), \( k_{FRET} \), from a donor to an acceptor, is described by Equation 3.1. In our system, P3HT is the donor and PCT6BT or PFT6BT is the acceptor.

\[
k_{FRET} = \frac{1}{\tau} \left( \frac{R_0}{r} \right)^6
\]

Where \( \tau \) is the lifetime of the donor in the absence of the acceptor (estimated to be approximately 600 ps for P3HT in solution\(^{257,258}\)), \( R_0 \) is the Förster distance, and \( r \) is the distance from the donor-
acceptor interface. \( R_0 \) is defined as the donor-acceptor distance at which FRET efficiency drops to 50% and is given by\(^{255}\):

\[
R_0 = \frac{9(\ln 10) \kappa^2 \Phi_{P3HT}}{128 \pi^5 N n^4 j}
\]

\( \kappa^2 \) describes the relative orientation of the donor-acceptor transition dipoles, assumed to be 2/3, \( \Phi_{P3HT} \) is the quantum efficiency of P3HT (~ 0.25), \( N \) is Avogadro’s number, \( n \) is the refractive index of the solvent \( (n_{CHCl_3} = 1.445) \), and \( J \) is the overlap integral. The overlap integral describes the degree of spectral overlap between donor emission and acceptor absorbance as shown in Equation 3-3.

\[
J = \int_0^\infty F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda
\]

\( F_D(\lambda) \) is the corrected fluorescence emission of the donor with total area under the curve normalized to one and \( \varepsilon_A(\lambda) \) is the extinction coefficient of the acceptor. We calculate \( J \) values of 3.5 \( \times \) 10\(^{14} \) and 2.5 \( \times \) 10\(^{14} \) M\(^{-1} \) cm\(^{-1} \) nm\(^4 \) for energy transfer from P3HT to PCT6BT and PFT6BT, respectively. This leads to \( R_0 \) values of 3.25 and 3.07 nm for energy transfer from P3HT to PCT6BT and PFT6BT, respectively.

The rate of radiative decay \( k_{rad} \) is given by:

\[
k_{rad} = \frac{\Phi_{P3HT}}{\tau}
\]

Values for \( k_{FRET} \) and \( k_{rad} \) are plotted as a function of \( r \) in Figure 3-4. The contour length of the P3HT block is estimated to be 9.4 nm. Thus, along the length of the P3HT chain, FRET is expected to compete very efficiently with radiative decay.
When dispersed in solution, conjugated polymers can adopt many different conformations that limit the effective conjugation length. A smaller conjugation length localizes and increases the energy of excited states. When cast in a film, both P3HT and PFT6BT/PFT7BT chains become increasingly ordered and their conjugations lengths increase, as evidenced by a reduction in the optical bandgap. Additionally, in P3HT films vibronic peaks at low energies develop, signifying the formation of π-stacked aggregates. The nanoparticle spectrum is described nicely by a summation of the P3HT film spectrum and a combination of the PFT6BT solution, PFT6BT film, and PFT7BT film spectra. This indicates that, within the nanoparticles, P3HT domains are significantly more ordered than PFT6BT domains.

We assume that PFT6BT/PFT7BT have nearly identical electronic properties and the additional hexyl sidechains in PFT6BT serve mainly to enhance solubility. This is evident from absorption spectra presented in Figure 3-9. When PFT6BT is nicely dissolved in solution, it can
adopt many different conformations. This limits the conjugation length and results in a relatively large optical bandgap, $E_{S1} = 2.12$ eV. When PFTBT is cast to a film, chains adopts significantly more planar conformations. This increases the conjugation length and decreases the optical bandgap, $E_{S1} = 1.89$ eV. When PFT6BT is cast into a film, the conjugation length is increased relative to the solution ($E_{S1} = 2.02$ eV), but the hexyl side chains perturb solid state packing and prevent the same conjugation length as in PFTBT film. When PFTBT is dissolved in solution, the lack of solubilizing side chains prevent complete dispersion of the polymer. The optical bandgap is the same as PFT6BT film, $E_{S1} = 2.02$ eV. Thus, we propose that the additional side chains in PFT6BT minimally alter the electronic core of PFTBT and that differences in absorption spectra can be explained by polymer chains adopting different conformations in different environments.
Transient Absorption Spectroscopy Control Experiments

Transient absorption of P3HT and PFT6BT homopolymers dissolved in carbon tetrachloride was monitored at 992 nm (Figure 3-6). Significant quenching of aerated samples relative to nitrogen-saturated samples confirms the presence of triplet states.

**Figure 3-5:** Steady state absorbance spectra comparing spectroscopic features of polymer solutions and films. (a) P3HT solution (gray) and film (red) spectra. (b) PFT6BT solution (gray) and film (light blue) spectra as well as PFTBT solution (dark blue) and film (dark gray) spectra. (c) Nanoparticle absorbance spectra (gray). The nanoparticle spectra is described well by a linear combination (green) of the P3HT film (red) and combination of PFT6BT (blue) spectra. (d) The component of the nanoparticle spectra that originates from P3HT is described by the ordered P3HT film only, with no need to introduce spectra from P3HT solutions. The PFT6BT component of the nanoparticle spectra is described by a combination of the PFT6BT solution, PFT6BT film, and PFTBT solution spectra.
Transient absorption of block copolymer isolated chains (dissolved in THF) and nanoparticles (dissolved in water) was also monitored at 992 nm. In the block copolymer isolated chains, the first decay component at approximately 10 ns is assigned to singlet absorption. Decay profiles of block copolymer fluorescence and the first decay component of transient absorption at 992 nm match nicely (Figure 3-7). Additionally, this signal is insensitive to the presence of oxygen, supporting the assignment of this decay component to singlet excitons in the P3HT-\(b\)-PFT6BT isolated chains (Figure 3-8). The second decay component (~ 100-1000 ns) of the isolated chain signal is significantly quenched in the presence of oxygen, confirming the formation of triplet states. The nanoparticle signal is not influenced by the presence of oxygen, confirming the detection of long-lived polarons.

Figure 3-6: Transient absorption kinetics traces of (a) P3HT and (b) PFT6BT (blue) homopolymers in carbon tetrachloride in the presence (aerated) and absence (\(N_2\) saturated) of oxygen.
Figure 3-7: Decay profiles of P3HT-b-PFT6BT isolated chain fluorescence and transient absorption at 992 nm.

Figure 3-8: Transient absorption kinetics traces of P3HT-b-PFT6BT isolated chains in the presence (green) and absence (gray) of oxygen as well as nanoparticle dispersion in the presence (orange) and absence (blue) of oxygen.
3.3 Results and Discussion

Block Copolymer Design and Size Characterization

Two fully conjugated donor-acceptor block copolymers were designed based on two block copolymers yielding the highest efficiencies when used as the single photoactive material in solar cell devices, poly(3-hexylthiophene)-block-poly-((9-(9-heptadecanyl)-9H-carbazole)-1,4-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2’,2”-diyl) (P3HT-b-PCDTBT)\textsuperscript{132} and poly(3-hexylthiophene)-block-poly-((9,9 dioctylfluorene)-2,7-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2’,2”-diyl) (P3HT-b-PFTBT)\textsuperscript{144}. Both block copolymers consist of a P3HT electron donor covalently linked to a push-pull polymer electron acceptor. The acceptors incorporate a dithienyl-benzothiadiazole electron-deficient “pull” unit and either a fluorene (PFTBT) or carbazole (PCDTBT) electron-rich “push” unit. Despite the similarity in chemical structure between the two block copolymers, when used as the single active material in photovoltaic devices, P3HT-b-PCDTBT leads to power conversion efficiencies of less than 1%, while P3HT-b-PFTBT leads to efficiencies as high as 3.1% (Table 3-1).\textsuperscript{132,144} OPV device performance is characterized by short-circuit current ($J_{SC}$), open-circuit voltage ($V_{OC}$), and fill factor (FF). In going from P3HT-b-PCDTBT to P3HT-b-PFTBT devices, $J_{SC}$ increases by nearly a factor of four, while $V_{OC}$ and FF change much less drastically. Thus, in the first part of our study, we use block copolymers as model systems to elucidate how such a small difference in the molecular structure appears to result in a very significant change in photovoltaic efficiency, predominately represented by an increase in $J_{SC}$. In doing so, we will prove that block copolymers can be used as model systems to understand more about the physics behind photocurrent generation in organic solar cells.
In this study, we designed and synthesized two block copolymers with identical conjugated backbones to P3HT-b-PCDTBT and P3HT-b-PFTBT. Additional hexyl side chains were added to the thiophene units flanking the benzothiadiazole moiety in the acceptor block to enhance solubility and ensure isolated chains in solution, yielding poly(3-hexylthiophene)-block-poly-(9-(9-heptadecanyl)-9H-carbazole)-1,4-diyl-alt-[4,7-bis(3-hexylthiophen-5-yl)-2,1,3-benzothiadiazole]-2′,2″-diyl) (P3HT-b-PCT6BT) and poly(3-hexylthiophene)-block-poly-((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(3-hexylthiophen-5-yl)-2,1,3-benzothiadiazole]-2′,2″-diyl) (P3HT-b-PFT6BT) (Figure 3-9a). Although alkyl side chains minimally alter the electronic properties of the block copolymers, as evidenced by the similar absorption spectra, they are likely to influence the morphology when incorporated in a bulk film (Figure 3-5).\textsuperscript{132} This could be why devices incorporating “TBT” block copolymers perform significantly better than devices incorporating “T6BT” block copolymers, despite identical conjugated backbones.

<table>
<thead>
<tr>
<th></th>
<th>$\eta$ (%)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>Fill factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT-b-PCT6BT</td>
<td>0.003 ± 0.002</td>
<td>0.07 ± 0.05</td>
<td>0.14 ± 0.03</td>
<td>0.28 ± 0.09</td>
</tr>
<tr>
<td>P3HT-b-PFT6BT</td>
<td>0.80 ± 0.1</td>
<td>2.9 ± 0.2</td>
<td>0.93 ± 0.07</td>
<td>0.29 ± 0.01</td>
</tr>
<tr>
<td>P3HT-b-PCDTBT</td>
<td>0.55 ± 0.2</td>
<td>1.3 ± 0.3</td>
<td>1.12 ± 0.08</td>
<td>0.37 ± 0.03</td>
</tr>
<tr>
<td>P3HT-b-PFTBT</td>
<td>2.7 ± 0.4</td>
<td>5.0 ± 0.3</td>
<td>1.14 ± 0.08</td>
<td>0.45 ± 0.02</td>
</tr>
</tbody>
</table>

Table 3-1: Device characterization of solar cells incorporating P3HT-b-PCT6BT, P3HT-b-PFT6BT, P3HT-b-PCDTBT, and P3HT-b-PFTBT as photoactive material. Results are either taken from the literature (as indicated) or were measured from devices fabricated in-house ($n \geq 6$ devices).
P3HT-b-PCT6BT and P3HT-b-PFT6BT were synthesized using a method reported previously. Briefly, the block copolymers were synthesized in two steps. First, P3HT that is functionalized on one end with a Br group was synthesized using a Kumada catalyst transfer polymerization reaction. P3HT was then used as a macoreagent, and the acceptor block, either PFT6BT or PCT6BT, was added on using a Suzuki polycondensation reaction. For consistency, the same P3HT macoreagent was used to synthesize both P3HT-b-PCT6BT and P3HT-b-PFT6BT.
PCT6BT. Under conditions employed here, Suzuki polycondensation follows an uncontrolled step growth polymerization mechanism, making control over the acceptor block molecular weight exceedingly challenging. Nonetheless, we utilized an asymmetric monomer feed ratio to limit the maximum attainable molecular weight of the acceptor block. While we do not expect charge transfer to depend on the molecular weight or composition of the block copolymer (see Chapter 5), synthesized P3HT-b-PCT6BT and P3HT-b-PFT6BT have similar donor-acceptor composition, identical P3HT block molecular weights, and similar acceptor block molecular weights (Table 3-2).

Table 3-2: Molecular characteristics of block copolymers.

<table>
<thead>
<tr>
<th></th>
<th>P3HT-b-PCT6BT</th>
<th>P3HT-b-PFT6BT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_n$ (g mol$^{-1}$)$^a$</td>
<td>6900</td>
<td>6500</td>
</tr>
<tr>
<td>$D$$^b$</td>
<td>1.3</td>
<td>1.4</td>
</tr>
<tr>
<td>P3HT weight fraction</td>
<td>0.56</td>
<td>0.60</td>
</tr>
<tr>
<td>Acceptor weight fraction</td>
<td>0.44</td>
<td>0.40</td>
</tr>
<tr>
<td>Theoretical $R_h$ (nm)$^c$</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Measured $R_h$ (nm)</td>
<td>3</td>
<td>6</td>
</tr>
</tbody>
</table>

$^a$H NMR; $^b$GPC; and $^c$freely-rotating worm-like chain model

We have demonstrated that the dielectric environment can impact efficiency of exciton dissociation to a charge transfer state (Chapter 4). In an attempt to create an environment similar to the active layer of an OPV device, block copolymers are dissolved in chloroform which has a similar static dielectric constant (4.81) to that of conjugated polymers (~ 3.3 for regioregular P3HT).\footnote{58}

Multiangle dynamic light scattering was used to confirm the block copolymers can be completely dispersed in solution as isolated chains. We calculate apparent hydrodynamic radii ($R_h$) of 3 and 6 nm for P3HT-b-PCT6BT and P3HT-b-PFT6BT, respectively (Figure 3-9b). Assuming persistence lengths of ~ 3 nm for P3HT and ~ 4 nm for PCT6BT and PFT6BT, we expect chain dimensions on the order of 10 nm for isolated block copolymer chains in solution according to the
freely-rotating worm-like chain model. Molecular weight and size data are presented in Table 3-2. At the modest molecular weights used in this study, the contour length of each block is approximately 2 to 3 times the persistence length. The stiff backbone prevents the chain from folding back onto itself and creating additional donor-acceptor contacts, other than at the covalent linkage between the blocks. Thus, P3HT-b-PCT6BT and P3HT-b-PFT6BT in solution serve as model donor-acceptor systems in which the donor-acceptor “interface” is set by the block copolymer junction and the local environment is established by the solvent.

**Charge Transfer within Isolated Block Copolymer Chains**

Exciton dissociation to a charge transfer state within individual block copolymer chains was examined in the absence of intermolecular interactions using photoluminescence quenching measurements. Dilute solutions were prepared such that the maximum absorbance is ~ 0.05, ensuring no aggregation of polymer chains or significant reabsorption of emitted photons. Absorbance and emission spectra of P3HT-b-PCT6BT and P3HT-b-PFT6BT are presented in Figure 3-9c, with absorbance presented as the extinction coefficient. Photoluminescence intensity is normalized by the fraction of light absorbed at the excitation wavelength (spectra presented in Figure 3-9c were excited at 470 nm).

For both absorbance and emission, summation of constituent homopolymer spectra nicely describe the block copolymer spectra. Block copolymer absorbance spectra were deconvoluted to determine the absorbance fraction of each block as a function of wavelength. Block copolymer emission spectra were deconvoluted to determine the contribution of each block to the total block copolymer emission and ascertain the degree of photoluminescence quenching in each block. The fraction of quenched P3HT excited states \( f_Q \) was calculated by comparing the emission contribution of the P3HT block in the block copolymer to the emission of the P3HT homopolymer
In both P3HT-b-PCT6BT and P3HT-b-PFT6BT, there is significant quenching of excited states generated on the P3HT block, $f_Q \sim 0.5$.

![Figure 3-10](image)

**Figure 3-10**: Photoluminescence quenching analysis of isolated block copolymer chains. (a) P3HT quench fraction ($f_Q$) and (b) acceptor block quantum yield, ($Q_{E_A}$) for P3HT-b-PFT6BT and P3HT-b-PCT6BT at several excitation energies. (c) Overall quenching of excited states generated by each block copolymer. Overall quenching is attributed to intramolecular charge transfer and is therefore proportional to the charge transfer (CT) state yield. (d) A simple kinetic scheme depicting the competing pathways of donor and acceptor absorbance ($k_{absD}$, $k_{absA}$), donor and acceptor emission ($k_{emD}$, $k_{emA}$), energy transfer from P3HT to the acceptor ($k_{ET}$), and nonradiative decay which is interpreted as charge transfer ($k_{CT}$).

In chloroform solutions, both PCT6BT and PFT6BT have the same optical bandgap (2.12 eV), which is significantly smaller than the bandgap of P3HT (2.31 eV). Thus, energy transfer from P3HT to the acceptor blocks results in significant quenching of P3HT emission. Energy transfer is detected by measuring the quantum yield of the acceptor block, $\Phi_A$. This was calculated by comparing the emission contribution of the acceptor block in the block copolymer to the emission of the acceptor homopolymer (Figure 3-10b). A $\Phi_A$ greater than 1 indicates that the quantum yield of the acceptor is enhanced when it is linked to the P3HT donor block, signifying energy transfer.
In both P3HT-\textit{b-}PCT6BT and P3HT-\textit{b-}PFT6BT, \(\Phi_A\) values much greater than 1 are measured, revealing a substantial amount of energy transfer in isolated block copolymer chains.

We believe that energy transfer from P3HT to PCT6BT and PFT6BT occurs through dipole-dipole coupling according to the Förster resonance energy transfer (FRET) mechanism. Upon close inspection of acceptor absorbance and donor emission spectra, it may appear that spectral overlap is insufficient to cause such a large amount of quenching (approximately 50\% of P3HT emission). Nevertheless, we estimate FRET rate constants ranging from \(10^8\) – \(10^{12}\) s\(^{-1}\) along the contour length of P3HT; the rate of FRET will increase substantially as distance from the donor-acceptor interface decreases. These values are certainly high enough to compete with radiative emission, where we estimate a rate constant of roughly \(10^9\) s\(^{-1}\). As will be discussed in detail below, we do not expect charge transfer from P3HT to the acceptors to be efficient in either system. Thus, dependence of the FRET rate constant on distance and short contour lengths of the block copolymers justify the high yields of energy transfer calculated.

Overall quenching of block copolymer excited states was quantified by calculating an expected block copolymer quantum yield assuming all quenched P3HT excited states have undergone an energy transfer to the acceptor, followed by radiative decay in the acceptor block. By comparing the expected block copolymer quantum yield to the measured block copolymer quantum yield, overall quenching of block copolymer excited states was calculated (Figure 3-10c). Any significant overall quenching is indicative of a non-radiative decay pathway in the block copolymer that is not present in the homopolymers. This is interpreted as intramolecular charge transfer and is therefore proportional to the charge transfer (CT) state yield. Our data suggests there is no significant charge transfer occurring via electron transfer from P3HT to the acceptors, and thus, any observed charge transfer is the result of hole transfer from the acceptor to P3HT; this will be discussed in detail below. A simple kinetic scheme is presented in Figure 3-10d. The expected block copolymer quantum yield is calculated considering emission (\(k_{\text{emA}}\)) as the relevant decay
pathway for singlet excited states on the acceptor. The measured block copolymer quantum yield is the result of competing rates for emission and non-radiative decay (present in the block copolymer and not observed in the homopolymer), which is interpreted as charge transfer ($k_{CT}$). Steady-state fluorescence cannot reveal whether CT states recombine or further dissociate into charge separated states; to address this, time resolved measurements probing CT state dissociation are discussed below.

Photoluminescence quenching analysis demonstrates significant intramolecular charge transfer in P3HT-$b$-PFT6BT ($9 \pm 2\%$ of excitons are quenched) and almost no intramolecular charge transfer in P3HT-$b$-PCT6BT ($1 \pm 2\%$ of excitons are quenched). This trend is consistent with power conversion efficiencies of OPV devices fabricated from P3HT-$b$-PFTBT and P3HT-$b$-PCDTBT.\textsuperscript{132,144} Again, there is only a subtle difference in the conjugated backbones of P3HT-$b$-PFT6BT/P3HT-$b$-PFTBT and P3HT-$b$-PCT6BT/P3HT-$b$-PCDTBT. The donor blocks are identical; in the acceptor blocks, the quaternary carbon of the fluorene in PFT6BT/PFTBT is replaced with a nitrogen, yielding PCT6BT/PCDTBT. It is surprising that such a small difference in the chemical structure results in such a large difference in intramolecular charge transfer within isolated block copolymer chains. This suggests the large difference in power conversion efficiencies of devices cannot be attributed solely to differences in morphology and must be due, at least in part, to different electronic properties of the materials. PCT6BT/PCDTBT and PFT6BT/PFTBT are identical except for the addition of a single nitrogen atom in the former, which leads to decreased acceptor character of the entire block. Nevertheless, despite the different “push” moieties, PCT6BT and PFT6BT have the same optical bandgap in dilute chloroform solution, 2.12 eV. The significant difference in exciton quenching despite mostly identical molecular structures warrants examination of the electronic properties of P3HT-$b$-PCT6BT and P3HT-$b$-PFT6BT.

Constrained density-functional theory (CDFT) was used to characterize CT state energies of the isolated block copolymer chains. In general, accurate characterization of large systems
necessitates the use of linear response time-dependent DFT (LR-TDDFT) with long-range corrected functionals that accurately describe the excited state and non-local interactions. CDFT was chosen here for its ability to construct charge-localized diabatic states for electron transfer reactions. Compared to the more conventional LR-TDDFT approach, CDFT has been proven an effective method for calculating CT state energies, even with hybrid functionals without range separation, such as B3LYP. Given the well-defined molecular orientation at the donor-acceptor interface, the CT state energy of block copolymers can be accurately calculated. In polymer/fullerene systems, it has been demonstrated that different molecular orientations at the donor-acceptor interface have different electrostatic and electronic interactions that dramatically influence the CT state energy; energy distributions of up to 0.6 eV have been calculated for different molecular configurations. In a thin film, it is not always possible to characterize molecular orientation at the donor-acceptor interface. As discussed previously, due to the modest molecular weights and backbone stiffness of P3HT-\textit{b}-PCT6BT and P3HT-\textit{b}-PFT6BT, chains will be mostly extended such that charge transfer occurs through the block copolymer junction. Thus, these block copolymers are ideal model systems to compare experiments to charge transfer state energy ($E_{CT}$) calculations.

One source of uncertainty in our CDFT calculations of CT state energies is chain torsion, particularly at the donor-acceptor junction. Based on the dihedral potential calculated for the thiophene/fluorene bond, we expect that block copolymers are able to explore many different dihedral angles in solution. Stereochemistry and torsion along the backbone are expected to affect the rate of charge transfer, manifested in the electronic coupling matrix element. According to electron transfer theory, the electronic coupling matrix element will influence the rate, but energies of the initial and final states should remain nearly the same. Additionally, the block copolymers were intentionally designed such that electronic coupling between donor and acceptor blocks of P3HT-\textit{b}-PCT6BT and P3HT-\textit{b}-PFT6BT is relatively weak in solution. This was
accomplished by linking the electron-rich unit of the acceptor block directly to the P3HT donor block, preventing strong electronic coupling between P3HT and the highly electron-withdrawing benzothiadiazole. Absorption spectra of the block copolymers can be described nearly perfectly by a summation of the homopolymer spectra, indicating no significant changes to the ground state electronics when the donor and acceptor blocks are covalently linked. We assume electronic coupling is sufficiently weak that, to a first order approximation, it does not significantly alter the character of the CT state, which is primarily dependent on the distance between the electron and hole and the dielectric constant of the environment. We rely on the confined geometries of donor-acceptor block copolymers to obtain $E_{CT}$ values in chloroform solutions for P3HT-$b$-PCT6BT (1.87 eV) and P3HT-$b$-PFT6BT (1.83 eV).

In non-fullerene photovoltaic devices where the electron acceptor efficiently absorbs sunlight, there are two pathways for exciton dissociation to a charge transfer state: 1) excited state electron transfer from donor to acceptor and 2) hole transfer from acceptor to donor. The driving force for electron transfer is defined as the energetic offset between the singlet excited state of the electron donor and the charge transfer state ($E_{S1D} - E_{CT}$). Likewise, the driving force for hole transfer is defined as the energetic offset between the singlet excited state of the electron acceptor and the charge transfer state ($E_{S1A} - E_{CT}$). $E_S$ values are the optical bandgaps measured by the absorption onset of the homopolymers in chloroform solution and $E_{CT}$ values are calculated by CDFT. In P3HT-$b$-PCT6BT, we calculate a modest driving force for hole transfer of 0.25 eV and a much higher driving force for electron transfer of 0.44 eV. In P3HT-$b$-PFT6BT, we calculate a larger driving force for hole transfer of 0.29 eV and a driving force for electron transfer of 0.48 eV.

It is surprising that the quantum efficiencies of exciton dissociation to a CT state in P3HT-$b$-PCT6BT and P3HT-$b$-PFT6BT are not higher. Despite modest driving forces for hole transfer, both P3HT-$b$-PCT6BT and P3HT-$b$-PFT6BT have relatively high driving forces for electron transfer (> 0.4 eV). Both block copolymers consist of a P3HT electron donor covalently linked to
a push-pull polymer electron acceptor. They are designed such that the electron-rich unit of the acceptor is linked directly to the P3HT donor, generating a well-defined donor-acceptor junction. It has been demonstrated that the direct linkage of P3HT and the highly electron-withdrawing benzothiadiazole unit results in the formation of a tightly-bound charge transfer state that serves as an efficient recombination pathway and is detrimental to photovoltaic performance.\textsuperscript{148,152} Our results indicate that inserting the electron-rich unit of the acceptor between the strong P3HT donor and benzothiadiazole acceptor disrupts electronic coupling between the two moieties. Furthermore, not only does the electron-rich unit of the acceptor block disrupt electronic coupling enough to prevent the tightly-bound CT state, but the negligible CT state yield measured for P3HT-\textit{b}-PCT6BT suggests that it disrupts electronic coupling enough to prevent excited state electron transfer from P3HT to the acceptor almost entirely.

Our results begin to indicate that a driving force for hole transfer close to 0.3 eV is necessary to achieve efficient charge transfer within isolated block copolymer chains. Although, given the small sample size, a more in-depth investigation is warranted to closely examine the influence of the driving force for hole transfer on exciton dissociation within individual block copolymer chains; this is the topic of Chapter 4. In short, small adjustments of the block copolymer donor-acceptor junction can have a profound impact on electronic coupling at the donor-acceptor interface and hole transfer from the acceptor to P3HT. Unlike a physical blend of donor and acceptor materials, the block copolymer structure facilitates excellent control over electronic properties of materials and electronic coupling between them.

**Charge Separation in Block Copolymer Nanoparticles**

Next, we investigated the influence of strong intermolecular coupling and aggregation of the electron donor on charge generation. To systematically introduce intermolecular interactions in
P3HT-\(b\)-PFT6BT, we dissolve the block copolymers in a poor solvent, inducing aggregation and the formation of dispersed nanoparticles (Figure 3-11). Nanoparticle size was characterized using multiangle DLS and in-situ liquid STEM. According to DLS, the nanoparticles have an apparent \(R_h\) of 103 nm (Figure 3-11b). STEM micrographs complement DLS data and confirm roughly spherical nanoparticles with a radius of \(\sim\) 100 nm (Figure 3-11c). Thus, while in isolated chain studies charge transfer is examined in the absence of any intermolecular interactions, with nanoparticles we introduce intermolecular interactions without the complex heterogeneity of a bulk film.

**Figure 3-11:** P3HT-\(b\)-PFT6BT nanoparticles selectively tune P3HT aggregation. (a) A cartoon of P3HT-\(b\)-PFT6BT isolated chains and nanoparticles. The isolated chains in solution are on the order of 10 nm, compared to the nanoparticles that have a diameter on the order of 100 nm. (b) Mean decay rate \((\Gamma)\) as a function of the scattering vector \((q)\) squared from multiangle dynamic light scattering of the nanoparticle dispersion in water. The apparent \(R_h\) of the particles is \(\sim\) 103 nm. (c) In-situ liquid scanning transmission electron micrograph of block copolymer nanoparticles.

Optical properties of polymer chains within the nanoparticles were examined using steady-state UV-vis absorbance spectroscopy. This information is used to characterize planarity and
aggregation of polymer chains within the nanoparticles, morphological properties that can influence charge generation. Relative to the isolated chains absorption spectrum, in the nanoparticle absorption spectrum a redshift of ~ 50 nm and vibronic structure at longer wavelengths are observed (Figure 3-12). These features are due to increased planarity of P3HT chains, π-stacking of thiophene rings, and thus, an increase in the effective conjugation length.\textsuperscript{258,264,265} The P3HT component of the nanoparticle absorbance is effectively identical to that of a pristine P3HT film (Figure 3-5). Thus, within the nanoparticles, molecular orientation and intermolecular coupling of P3HT chains are similar to a highly-ordered semicrystalline P3HT film. In contrast, PFT6BT chains within the nanoparticles are not well organized. The spectroscopic signature of PFT6BT in the nanoparticles is between that of PFT6BT isolated chains in solution and a bulk film, indicating that the chains are largely disordered. Because P3HT is significantly more ordered than PFT6BT, we attribute changes in charge generation characteristics between the isolated chains and nanoparticles to strong intermolecular coupling and aggregation of the P3HT donor block.
Near-infrared transient absorption spectroscopy was employed to determine the fate of initially photogenerated singlet excitons in the P3HT-\textit{b}-PFT6BT isolated chains and nanoparticle dispersion (Figure 3-12b). Samples were excited at 532 nm, generating singlet excited states in both P3HT and PFT6BT domains for the nanoparticle dispersion, and predominately in PFT6BT for the isolated chains. Transient absorption was monitored at 992 nm (1.25 eV) for both samples, the location of the peak maximum of the localized polaron band in P3HT. Both singlet and triplet

\[ \Delta mO.D. \]

\[ \text{Time (ns)} \]

\[ \text{Wavelength (nm)} \]

Figure 3-12: Steady state and transient absorption spectroscopy reveal significantly different photophysics between isolated chains and nanoparticles. (a) Steady state absorbance spectra of P3HT-\textit{b}-PFT6BT isolated chains (gray) and nanoparticle dispersion (blue). (b) Transient absorption kinetics traces of P3HT-\textit{b}-PFT6BT isolated chains (gray markers) and nanoparticle dispersion (blue markers). The isolated chain spectrum was fit with a biexponential function (solid gray line) and the nanoparticle spectrum was fit with a power law (solid blue line). Transient absorption is presented as difference in milli-optical density (\( \Delta mO.D. \)). The inset shows the transient absorption spectrum of the nanoparticles averaged from 25 – 10,000 ns. The red arrow indicates 992 nm, the wavelength used to monitor excited state kinetics.
absorption in the isolated block copolymer chains are also detectable at 992 nm (Figure 3-6, Figure 3-7, Figure 3-8). Decay kinetics measured for isolated chains are well-described using a sum of two exponentials, consistent with the expectation for both unimolecular singlet decay and unimolecular triplet decay. The first decay signal at approximately 10 ns is assigned to singlet absorbance. This signal has the same decay profile as fluorescence from isolated block copolymer chains, and is not quenched by oxygen, supporting the assignment of singlet absorbance. The second decay component around 100-1000 ns is assigned to triplet absorption. This signal is significantly quenched in the presence of oxygen, confirming the formation of triplet states.

In contrast, decay kinetics measured for the dispersed nanoparticles are well-described using a power law function and cannot be described adequately using a sum of exponential decays. Power law functions are characteristic of bimolecular decay processes and appear with unique linear forms when plotted on a logarithmic plot as in Figure 3-12b. This linear form is quite distinct from the shape of multiexponential decay functions that are plotted in the same way. This indicates that polarons, which characteristically decay bimolecularly on the nano- to microsecond timescale, were preferentially formed over triplet states in the nanoparticle dispersion. The transient absorption spectrum of the nanoparticles (inset in Figure 3-12) qualitatively matches previous spectra used to characterize polaron formation in P3HT and P3HT-b-PFTBT films, further validating this assignment. The data reveal that polaron absorption is observed as early as 15 ns. The presence of oxygen does not influence the intensity or decay kinetics of the nanoparticle dispersion, further indicating that the signal cannot be attributed to triplet decay (Figure 3-8). Thus, charge separation is possible within the nanoparticles, while within isolated chains all charge transfer states recombine through either radiative or non-radiative processes.

Transient absorption spectroscopy of the block copolymer nanoparticles demonstrates that aggregation and strong intermolecular coupling of the electron donor can facilitate charge separation in donor-acceptor systems. When intermolecular interactions are introduced through the
use of block copolymer nanoparticles, P3HT chains $\pi$-stack and become planar. Previous work on polymer/fullerene blend systems has demonstrated that fullerene aggregation and crystallization can enhance charge separation.\textsuperscript{34,40-47} We assume that polymer donor aggregation facilitates charge generation in an analogous manner. Therefore, we consider three likely processes that may promote charge generation due to aggregation of the donor: 1) enhanced delocalization or increased density of states; 2) perturbed energetics; 3) high local charge mobility.

Delocalization within P3HT domains may enable charge separation. As P3HT chains aggregate, the thiophene rings $\pi$-stack and the polymer chains planarize. This increases the effective conjugation length and greatly enhances delocalization.\textsuperscript{267-270} Charge carriers become more spatially delocalized along planar polymer chains due to increased overlap of $\pi$ orbitals along the backbone. This increases the volume sampled by charges and in turn, facilitates charge separation.\textsuperscript{77,79,80,125} Furthermore, intermolecular interactions and delocalization will increase the density of states available to dissociated charges.\textsuperscript{111,114} This provides an entropic driving force for charge dissociation. Enhanced delocalization as P3HT chains $\pi$-stack may facilitate charge separation in the block copolymer nanoparticles, but will also perturb the energetics of the system.

Energetics more favorable for charge transfer may also contribute to enhanced charge separation within aggregated P3HT domains. When P3HT chains go from a disordered solution to a more ordered film, the bandgap decreases by almost 0.4 eV (Figure 3-5). There is evidence that the bandgap reduction is primarily caused by a shift in the highest occupied molecular orbital (HOMO) level.\textsuperscript{271-273} This increases the “hole affinity” of P3HT, creating a more favorable energetic offset driving charge transfer and thereby enhancing charge separation. Furthermore, an energy cascade favorable for charge separation could be created if amorphous P3HT chains are concentrated near the donor-acceptor interface and aggregated chains are concentrated further away. Thus, the different energetics of aggregated P3HT chains with respect to amorphous P3HT chains could enhance charge separation.
Lastly, high local charge mobility could also contribute to charge separation observed in the aggregated chains but not the isolated chains.\textsuperscript{83,128} In a conjugated polymer film, charges can either move intramolecularly along the polymer backbone, or intermolecularly, hopping from chain to chain. Intramolecular charge transport along the backbone is much faster than intermolecular hopping.\textsuperscript{274-276} It has been demonstrated that molecular packing and planarity of P3HT can greatly affect charge mobility.\textsuperscript{277} In the nanoparticles, planar P3HT chains could provide a pathway for fast hole transport along a polymer backbone immediately following exciton dissociation to a charge transfer state. Additionally, the increased availability of intrachain delocalization discussed previously could also enable high charge mobility along a polymer chain. High local charge mobility would not be available in a polymer solution due to considerable dihedral disorder, but could explain the charge separation observed in the block copolymer nanoparticles.\textsuperscript{278,279}

Our results are summarized in Figure 3-13. In the block copolymer isolated chains, efficient energy transfer from donor to acceptor is observed in both P3HT-\textit{b}-PCT6BT and P3HT-\textit{b}-PFT6BT. In P3HT-\textit{b}-PCT6BT, no significant exciton dissociation is measured, likely due to an insufficient driving force for hole transfer. When the driving force for hole transfer is increased slightly in P3HT-\textit{b}-PFT6BT, charge transfer is observed in isolated block copolymer chains, but complete charge separation is not. When P3HT chains aggregate and π-stack in the block copolymer nanoparticles, signatures of charge separation are observed. Plausible explanations for this are illustrated in Figure 3-13c. Altogether, our results suggest a mechanism for photocurrent generation in OPVs could be energy transfer from donor to acceptor followed by hole transfer from acceptor to donor.
In isolated block copolymer chains, photoluminescence quenching results suggest a pathway for charge generation that could become increasingly important as non-fullerene acceptors continue to be developed: energy transfer from donor to acceptor, followed by hole transfer from acceptor to donor (Figure 3-13a). Figure 3-10a demonstrates significant quenching of P3HT in both P3HT-b-PCT6BT and P3HT-b-PFT6BT. Additionally, Figure 3-10b demonstrates quantum yield enhancement of the acceptor block when linked to P3HT in both P3HT-b-PCT6BT and P3HT-b-PFT6BT. Together, these results demonstrate significant energy transfer from P3HT to the acceptor. Furthermore, no quenching of block copolymer emission is observed in P3HT-b-PCT6BT. This indicates that charge transfer, a non-radiative quenching mechanism, does not occur despite a significant driving force for electron transfer from P3HT to PCT6BT (> 0.4 eV). This is
consistent with low electronic coupling between the donor block and strong benzothiadiazole acceptor, resulting from the electron-rich moiety between them. Altogether, these results suggest that quenching of P3HT excitons must be the result of energy transfer to the acceptor in both systems rather than excited state electron transfer. Thus, any measured exciton dissociation must be the result of hole transfer from the acceptor to P3HT. Provided the energetics in the solid state are appropriately aligned, a pathway for photocurrent generation in organic solar cells could be energy transfer from the donor to the acceptor followed by hole transfer from the acceptor to the donor.

### 3.4 Conclusion

In this chapter, we demonstrate that conjugated block copolymers are useful model systems to help answer important questions regarding fundamental photophysics of organic donor-acceptor materials. Our study reveals that small changes to the chemical structure can yield significant differences in the efficiency of exciton dissociation to a charge transfer state. By simply changing the fluorene moiety in P3HT-b-PFT6BT to a carbazole in P3HT-b-PCT6BT, the efficiency of intramolecular charge transfer within individual block copolymer chains decreases dramatically from 9% to 1%. Our results suggest that the modest driving force for hole transfer in P3HT-b-PCT6BT prevents efficient exciton dissociation, but further studies of why such a small change in chemical structure leads to such a striking difference in functionality are warranted. Furthermore, block copolymer nanoparticles reveal that, analogous to fullerene aggregation in polymer/fullerene blend systems, ordering of polymer donor chains can facilitate efficient charge generation. The possibility that aggregation may turn on charge transfer or charge separation in low driving force systems is examined in Chapter 4. These results have important implications to the design of new donor/acceptor pairs, and in particular the importance of pure or aggregated domains.
Our work demonstrates the potential of conjugated block copolymers as useful model systems for fundamental studies of the charge generation mechanism in OPVs. The covalent linkage enables studies of model donor-acceptor interfaces at length scales ranging from isolated chains in solution, where there are no added variables due to solid state morphology, to nanoparticles, which offer control over intermolecular interactions, to bulk films with model morphologies. Small perturbations of the chemical structure reveal consequences to charge and energy transfer in donor-acceptor systems. As the versatility of organic synthesis methods to control the assembly of conjugated moieties into sophisticated architectures continues to provide nearly infinite possibilities of materials for light emitting diodes, solar fuels, and organic solar cells, we propose that carefully designed donor-acceptor molecules can reveal fundamental photophysical processes and aid in the design of new materials.

This chapter is adapted from:
Chapter 4

Revealing the Importance of Energetic and Entropic Contributions to the Driving Force for Charge Photogeneration

Despite recent progress in organic photovoltaics, much about the mechanism for charge photogeneration remains unknown. Here, we use conjugated block copolymers as model systems to examine the effects of energetic and entropic driving forces in organic donor-acceptor materials. The block copolymers are designed such that an electron donor block and an electron acceptor block are covalently linked, embedding a donor-acceptor interface within the molecular structure. This enables model studies in solution where processes occurring between one donor and one acceptor are examined. First, energy levels that make up the driving force for charge transfer are systematically tuned and charge transfer within individual block copolymer chains is quantified. Results indicate that in isolated chains a significant driving force of ~ 0.3 eV is necessary to facilitate significant exciton dissociation. Next, block copolymers are cast into films, allowing for intermolecular interactions and charge delocalization over multiple chains. In the solid state, charge transfer is significantly enhanced relative to isolated block copolymer chains. Results indicate changes in the energetic driving force alone cannot explain the increased efficiency of exciton dissociation in the solid state. This implies that increasing the number of accessible states for charge transfer introduces an entropic driving force that can play an important role in the charge generation mechanism of organic materials.
4.1 Introduction

Over the past two decades, significant efforts have attempted to elucidate the mechanism of photocurrent generation in organic photovoltaics. Several studies have suggested an energetic offset is required to dissociate excited states and should be ≥ 0.3 eV for high photovoltaic efficiency. This energetic offset is defined as the energy difference between the singlet exciton and charge transfer (CT) state, $E_{S1} - E_{CT}$. It is important to minimize $E_{S1} - E_{CT}$ without decreasing the quantum yield of CT states, as this gap introduces an energy loss that reduces photovoltage. Recently, multiple studies have reported high quantum efficiencies with driving forces significantly below the empirical value of 0.3 eV, suggesting a pathway to push device efficiencies beyond 15%. Very low energy losses ($E_{loss}$) between the singlet exciton and open circuit voltage ($V_{OC}$), $E_{loss} = E_{S1} - qV_{OC}$, of 0.52 eV support a small energetic offset. While $E_{S1}$ is easily measured from absorbance spectra, authors are unable to accurately quantify $E_{CT}$ using spectroscopic methods commonly used to characterize CT states, including photothermal deflection spectroscopy and sensitive EQE measurements. A shoulder present in both the photoluminescence and electroluminescence spectra is assigned to CT state emission. This value is used to quantify the energetic offset as $\leq 0.05$ eV. In addition to rigorous characterization of the CT state in low $E_{loss}$ systems, crucial material properties needed to achieve high performance with a low driving force remain unclear.
Although often neglected, the role of entropic gains during the charge generation process has been examined in a few recent studies.\textsuperscript{111-116,300} For example, the role of entropy was investigated using temperature dependent $V_{OC}$ measurements of devices incorporating a poly(3-hexylthiophene-2,5-diyl) (P3HT) electron donor blended with PC\textsubscript{60}BM.\textsuperscript{113} It is predicted that $V_{OC}$ should increase linearly with decreasing temperature.\textsuperscript{301} Unexpectedly, when the devices were examined at temperatures below 100 K, it was found that $V_{OC}$ decreases as temperature decreases. The authors rule out nonselective contacts, disorder in the film, and a decrease in the effective bandgap as plausible explanations for this trend. They conclude that the decrease in $V_{OC}$ must be due to decreased charge carrier density. This is interpreted as a decrease in charge separation efficiency. With no evidence for a temperature dependence on energetic (enthalpic) driving forces, the authors assume the observed temperature dependence of $V_{OC}$ must be due to the temperature dependence of the entropic contribution to the free energy (\textit{i.e.}, $\Delta G = \Delta H - T\Delta S$).

The influence of entropy has also been examined by adjusting the active layer morphology of different polymer/fullerene blend systems.\textsuperscript{111} Mixing two different electron donor polymers with various fullerene acceptors led to enthalpic driving forces (defined by the authors as the difference between LUMO energies of donor and acceptor) ranging from 0.7-1.3 eV. First, samples were made using a 1:1 polymer:fullerene blend ratio. Despite different material systems, a consistent trend is observed; as driving energy increases, the rate of charge generation increases roughly linearly. The size of fullerene aggregates in the polymer/fullerene blend films was increased by incorporating high fullerene volume fractions (1:4 polymer:fullerene blend ratio). This in turn increases the density of delocalized states on fullerene, and potential entropic gain during the exciton dissociation process. Any changes to the enthalpic driving force as fullerene aggregate size increases are neglected and thus, differences in charge generation are attributed to increased density of delocalized states (entropy). In all of the 1:4 polymer:fullerene blend samples, charge generation is enhanced, but the rate at which charge generation increases with enthalpic driving force is
dependent on the donor polymer. Thus, although both energetic and entropic driving forces are likely important for charge photogeneration, the relative contributions are not obvious.

The energetic landscape in an organic film is complex, particularly near interfaces. As a consequence, it is challenging to decouple the roles of energetic and entropic driving forces. Furthermore, it may not be possible to accurately characterize the driving force for charge transfer in a film. It has been demonstrated that molecular orientation at the donor-acceptor interface can have a profound effect on $E_{CT}$, leading to energy distributions of up to 0.6 eV.\textsuperscript{261,262} Given the complex, non-equilibrium morphologies present in a bulk heterojunction film, there is likely to be a broad distribution of molecular orientations at the donor-acceptor interface. Furthermore, to provide insight on the mechanism for photocurrent generation in systems with a small energetic offset, it is desirable to examine entropic effects in systems that do not already have a significant energetic driving force ($E_{SI} - E_{CT} < 0.7$ eV). Studies on simple model systems could provide additional insight into the roles of the energetic offset and entropy.

In this chapter, we present a fundamental study using conjugated donor-acceptor block copolymers as model systems to investigate both the energetic offset and entropic driving force. The block copolymers consist of a P3HT electron donor block covalently linked to a push-pull polymer electron acceptor. When the block copolymers are dissolved as isolated chains in solution, entropic effects are reduced compared to a polymer film and molecular orientation at the donor-acceptor interface is established by the covalent linkage. Exciton dissociation is quantified at the donor-acceptor interface between a single donor and a single acceptor. The energetic driving force is adjusted by selectively tuning the constituent energy levels, $E_{SI}$ and $E_{CT}$. Charge transfer is examined in systems with a wide range of energetic driving forces including values similar to those observed in “low-loss” systems, $E_{SI} - E_{CT} \approx 0$ eV, as well as values previously suggested to be necessary for efficient charge generation, $E_{SI} - E_{CT} \approx 0.3$ eV. The entropic driving force is increased by casting the block copolymers into thin films. This introduces intermolecular interactions which
increase the number of accessible states and enhance delocalization. We find that both energetic and entropic driving forces are important for exciton dissociation.

4.2 Experimental Section

Polymer Synthesis

Poly(3-hexylthiophene)-block-2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopentadithiophene)-alt-[4,7-bis(3-dodecylthiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) (P3HT-b-PCPDT12BT), poly(3-hexylthiophene)-block-poly-((9-(9-heptadecanyl)-9H-carbazole)-1,4-diyl-alt-[4,7-bis(3-hexylthiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) (P3HT-b-PCT6BT), poly(3-hexylthiophene)-block-poly-((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(3-hexylthiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) (P3HT-b-PFT6BT), poly(3-hexylthiophene)-block-poly-((2,5-dihexylphenylene)-1,4-diyl-alt-[4,7-bis(3-hexylthiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) (P3HT-b-PPT6BT), poly(3-hexylthiophene)-block-2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopentadithiophene)-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) (P3HT-b-PCPDTBT), poly(3-hexylthiophene)-block-poly-((9-(9-heptadecanyl)-9H-carbazole)-1,4-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) (P3HT-b-PCDTBT), poly(3-hexylthiophene)-block-poly-((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) (P3HT-b-PFTBT), poly(3-hexylthiophene)-block-poly-((2,5-dihexylphenylene)-1,4-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) (P3HT-b-PPDTBT), and the corresponding homopolymers were synthesized using procedures described in Chapters 2 and 3.
Nuclear Magnetic Resonance (NMR) Spectroscopy

Solutions were prepared at ~ 10 mg mL in deuterated chloroform. \(^1\)H NMR analysis was carried out on Bruker Avance-III-850 MHz, Bruker AVIII-HD-500 MHz, or Bruker AV-360 instruments. The number average molecular weight (\(M_n\)) of P3HT was determined by end-group analysis. The weight composition of the block copolymers was determined by comparing the relative intensities of signals known to correspond to P3HT and the acceptor block. Together, these values were used to determine \(M_n\) of the block copolymers.
Figure 4-1: NMR spectra of block copolymers in deuterated chloroform.
Gel Permeation Chromatography (GPC)

Chain extension in the block copolymers and molecular weight distributions were characterized using GPC. Samples were prepared in HPLC-grade chlorobenzene at 1 mg mL\(^{-1}\), dissolved overnight, and filtered through 0.2 µm filters before injection. Data was obtained on an Agilent Technologies gel permeation chromatograph (ResiPore 300 x 7.5 mm column, Agilent 1260) equipped with refractive index, multiwavelength, light scattering, and viscometer detectors. Chlorobenzene was used as the mobile phase at 40°C with a flow rate of 0.5 mL min\(^{-1}\). Molar mass distributions were determined relative to polystyrene standards.

By overlaying normalized gel permeation chromatography (GPC) traces of the block copolymers with the corresponding P3HT macromeragent, successful chain extension is confirmed (Figure 4-2). All traces are measured using the refractive index detector with the exception of P3HT-\(b\)-PCPDTBT, which was measured using the viscometer detector. All traces are normalized to 1 for clarity.
**Constrained Density-Functional Theory (CDFT)**

$E_{\text{CT}}$ values were calculated in 1,2,4-trichlorobenzene ($\varepsilon_0 = 2.24$), chloroform ($\varepsilon_0 = 4.81$), and 1,2-dichlorobenzene ($\varepsilon_0 = 9.93$) using CDFT as described in Chapter 3.

**Dynamic Light Scattering (DLS)**

Isolated chain solutions were prepared at ~ 0.1-0.5 mg mL$^{-1}$, stirred overnight, filtered through a 0.1 µm filter at least three times, and loaded into a 10 mL test tube for measurements. DLS measurements were performed on a Brookhaven Instruments BI-200 SM static/dynamic light
scattering system equipped with a 35 mW diode laser ($\lambda = 637$ nm) and 90 mW near infrared laser ($\lambda = 781$ nm). The mean decay rate ($\Gamma$) of the autocorrelation function was calculated using the CONTIN algorithm.\textsuperscript{254} Diffusion coefficients of the particles in the different solutions were estimated by plotting $\Gamma$ versus the scattering vector ($q$) squared. The apparent hydrodynamic radius ($R_h$) was calculated from the diffusion coefficient according to the Stokes-Einstein relationship. To achieve sufficient scattering signal, block copolymer isolated chain DLS solutions were approximately 100-500 times more concentrated than those used for absorbance and fluorescence measurements.

**Absorbance and Fluorescence Spectroscopy**

Solutions of isolated polymer chains were prepared by dissolving samples at $\sim 1$ mg mL\textsuperscript{-1} in solution and stirring overnight in a nitrogen-filled glovebox. Solutions were then diluted to $\sim 1$ mg L\textsuperscript{-1}, loaded into 1 cm quartz cuvettes, sealed, and removed from the glovebox for testing. Polymer films were prepared by dissolving polymers at 10 mg mL\textsuperscript{-1} in chloroform, stirring overnight at 80°C, filtering through a 0.2 µm PVDF filter, and spincoating onto 1 cm\textsuperscript{2} quartz substrates. Films were thermally annealed at 165°C for 10 minutes.

Absorbance spectra were measured on an Agilent Technologies Cary 60 UV-vis. Fluorescence emission spectra of polymer solutions were measured at several different excitation wavelengths (410, 430, 450, and 470 nm) on a Photon Technology International QuantaMaster 300 fluorometer equipped with a Xe Arc lamp and 914 photomultiplier detection system. Quantum yields ($\Phi$) of homopolymers and block copolymers in solution were measured by comparing absorbance and fluorescence spectra to a dye of known quantum efficiency, 4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran ($\Phi = 0.44$ in ethanol).\textsuperscript{255,256} Fluorescence spectra of polymer films were excited at 550 nm using the same setup.
For low-temperature photoluminescence measurements of the polymer films, samples were mounted in an optically accessible Janis ST-100 liquid-nitrogen cryostat. Temperature was monitored with a LakeShore 335 Cryogenic Temperature Controller. Films were excited with a 10 mW continuous wave laser (\( \lambda = 532 \) nm), and emission was collected with a Horiba fibre-coupled spectrometer and cooled Si CCD array. Spectra were calibrated with an Ocean Optics tungsten-halogen calibration lamp.

### 4.3 Model for CT state yield in isolated block copolymer chains

We assume radiative decay and charge transfer are the dominant decay pathways for exciton decay. Thus, the CT state yield is described by Equation 4-1.

\[
CT = \frac{k_{CT}}{k_{CT} + k_R}
\]

Equation 4-1

The rate of emission \((k_R)\) depends on the measured lifetime of the excited state \((\tau)\) as well as its fluorescence quantum yield \((\Phi)\) according to Equation 4-2.\(^{255}\) We assume all acceptors have a quantum yield of approximately 0.5 and an excited state lifetime of around 500 ps.\(^{257}\)

\[
k_R = \frac{\Phi}{\tau}
\]

Equation 4-2

Marcus theory is appropriate to describe electron transfer in covalently-linked donor-acceptor systems in solution where the donor and acceptor are weakly coupled.\(^{34,244}\) The rate constant for electron transfer according to Marcus theory is presented in Equation 4-3.

\[
k_{CT} = \frac{2\pi}{h} \frac{1}{\sqrt{4\pi k_B T}} |W|^2 \exp\left(-\frac{(\Delta G + \lambda)^2}{4\lambda k_B T}\right) = k_0 \exp\left(-\frac{(\Delta G + \lambda)^2}{4\lambda k_B T}\right)
\]

Equation 4-3
Where $k_{CT}$ is the rate of electron transfer, $\lambda$ is the reorganization energy, $k_B T$ is thermal energy (about 30 meV at room temperature), $V$ is the electronic coupling matrix element, and $\Delta G$ is driving force (change in free energy). All of the pre-exponential terms can be described by a single constant, $k_0$.

$\lambda$ is the sum of solvent ($\lambda_S$) and internal ($\lambda_i$) reorganization energies (Equation 4-4). $\lambda_S$ is described by Equation 4-5.

$$\lambda = \lambda_S + \lambda_i$$  \hspace{1cm} 4-4

$$\lambda_S = (\Delta e)^2 \left( \frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{R} \right) \left( \frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_0} \right)$$  \hspace{1cm} 4-5

Where $\Delta e$ is the amount of charge transferred, $r_D$ is the radius of the donor, $r_A$ is the radius of the acceptor, $R$ is the center to center distance between donor and acceptor, $\varepsilon_{\infty}$ is the high frequency dielectric constant, and $\varepsilon_0$ is the low frequency dielectric constant. We assume donor and acceptor radii of 3 nm based on the end to end distance of P3HT and acceptor blocks of moderate molecular weight ($\sim 3500$ g mol$^{-1}$) according to the freely-rotating worm-like chain model.

The pre-exponential term, $k_0$, can be further broken up to account for terms we expect will depend on the solvent; terms we expect to be independent of solvent are described by a single constant, $A$.

$$k_0 = \frac{A}{\sqrt{\lambda_S}}$$  \hspace{1cm} 4-6

Thus, we fit $R$, $A$, and $\lambda_i$ to Equation 4-1, Equation 4-3, Equation 4-4, Equation 4-5, and Equation 4-6. We fit the data to a 95% confidence interval to obtain the following results:
Standard errors encompass some results that are not physically meaningful; specifically negative $A$ values (corresponding to a negative rate of electron transfer) and $R$ values less than 3 nm (corresponding to an overlapping donor and acceptor), yielding an inverted parabola centered about ~ 0 eV. An $R$ value of 3.4 nm corresponds physically to charge transfer occurring within ~ 2 nm of the donor-acceptor interface which we believe is quite reasonable. 2 nm is similar to the exciton diffusion length of P3HT in chloroform solution (see Chapter 5) as well as the repeat unit size of the acceptor blocks. Fixing $R$ to 3.4 nm and fitting $A$ and $\lambda_i$, returns approximately the same values, but with significantly reduced standard error; $A = 4.1 \pm 3 \times 10^8 \text{ eV}^{1/2} \text{ s}^{-1}$ and $\lambda_i = 0.5 \pm 0.1 \text{ eV}$.

Allowing the fit parameters to vary within the standard error of the fit, we expect maximum CT state yields ranging from 48 to 62% while still nicely describing the data and yielding values of $R$, $A$, and $\lambda_i$ that are physically meaningful.

**Table 4-1:** Parameters used to model CT state yield within a 95% confidence interval

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$ (nm)</td>
<td>3.4 ± 0.6</td>
</tr>
<tr>
<td>$A \times 10^8$ eV$^{1/2}$ s$^{-1}$</td>
<td>4.2 ± 6</td>
</tr>
<tr>
<td>$\lambda_i$ (eV)</td>
<td>0.5 ± 0.2</td>
</tr>
</tbody>
</table>
4.4 Results and Discussion


In Chapter 3, we demonstrated that small differences in molecular structure can have a profound impact on the efficiency of exciton dissociation within individual block copolymer chains. Here, we make further perturbations to the molecular structure in order to adjust the energetic offset and examine exciton dissociation in isolated block copolymer chains.

The block copolymers consist of a P3HT electron donor covalently linked to various push-pull polymer electron acceptors. Materials were synthesized using previously established procedures. Briefly, the P3HT donor block was synthesized using a Kumada catalyst transfer polymerization, yielding P3HT that is functionalized on one end with a bromine group. Using P3HT as a macroreagent, the acceptor block was added on in a chain-extension reaction using Suzuki or Stille polycondensation, yielding the series of block copolymers that are denoted in Figure 4-3. The corresponding acceptor homopolymers were also synthesized using standard Suzuki or Stille reaction conditions. Molecular weight characterization is presented in Table 4-2. Most block copolymers and acceptor homopolymers were synthesized using Suzuki coupling. To prevent protodeboronation of boronic ester functional groups on cyclopentadithiophene monomers, Stille polycondensation was used for the chain extension reaction of P3HT-\textit{b}-PCPDT12BT and P3HT-\textit{b}-PCPDTBHT block copolymers and polymerization of PCPDT12BT and PCPDTBHT homopolymers. The dithienyl benzothiadiazole moieties were designed with different R groups to enhance either solubility or solid-state packing. To enhance solubility, either hexyl or dodecyl alkyl chains were appended to the thienyl units flanking the benzothiadiazole (R = C\textsubscript{6}H\textsubscript{13}, T6BT or C\textsubscript{12}H\textsubscript{25}, T12BT). To enhance solid state packing, these additional alkyl side chains were removed (R = H, TBT). Thus, “T6BT” and “T12BT” derivatives were used for isolated chain solution
experiments and “TBT” derivatives were used for solid-state film experiments. We assume that side chains do not significantly alter electronics of the conjugated backbone but will have a profound effect on solubility and solid state packing.\textsuperscript{302,303}

Figure 4-3: Chemical structures of block copolymers. All block copolymers consist of a P3HT electron donor covalently linked to a push-pull polymer electron acceptor. In the conjugated backbone, the electron-rich unit of the acceptor block (colored aromatic moieties) is adjusted to tune the bandgap. R groups are also adjusted to enhance solubility or solid-state packing without altering the electronics of the conjugated backbone.

Table 4-2: Molecular weight characterization of the block copolymers

<table>
<thead>
<tr>
<th>Block Copolymer</th>
<th>P3HT $M_n$ (g/mol)</th>
<th>Acceptor $M_n$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT-b-PCPDT12BT</td>
<td>5100</td>
<td>3500</td>
</tr>
<tr>
<td>P3HT-b-PCPDTBT</td>
<td>4800</td>
<td>1700</td>
</tr>
<tr>
<td>P3HT-b-PCT6BT</td>
<td>3900</td>
<td>4300</td>
</tr>
<tr>
<td>P3HT-b-PCDTBT</td>
<td>3900</td>
<td>2000</td>
</tr>
<tr>
<td>P3HT-b-PFT6BT</td>
<td>3900</td>
<td>3000</td>
</tr>
<tr>
<td>P3HT-b-PFTBT</td>
<td>6000</td>
<td>2100</td>
</tr>
<tr>
<td>P3HT-b-PPT6BT</td>
<td>3900</td>
<td>6900</td>
</tr>
<tr>
<td>P3HT-b-PPDTBT</td>
<td>3500</td>
<td>2700</td>
</tr>
</tbody>
</table>
Block copolymers were designed such that in solution, there is only one dominant pathway available for efficient charge transfer. In principle, when both the electron donor and acceptor efficiently absorb light, there are two pathways for charge transfer: electron transfer from donor to acceptor and hole transfer from the acceptor to the donor. As demonstrated in Chapter 3, linking the P3HT electron donor directly to the “push” unit of the push-pull polymer acceptor disrupts electronic coupling between P3HT and the highly electron withdrawing benzothiadiazole, which suppresses excited state electron transfer. Thus, we assume that in solution charge transfer predominantly occurs via hole transfer from acceptor to donor; this is discussed in more detail below. The energetic driving force for exciton dissociation to a charge transfer state is therefore defined as the energy difference between the singlet excited state of the acceptor block and the charge transfer state \((E_{S1A} - E_{CT})\). Values of \(E_{S1A}\) and \(E_{CT}\) are selectively tuned by altering the electronics of the acceptor block and the dielectric polarization of the surrounding environment, enabling a systematic investigation on the role of the energetic driving force on exciton dissociation to a charge transfer state.

\(E_{S1A}\) is tuned by altering the chemical structure of the acceptor block. To precisely tune \(E_{S1A}\), all acceptor blocks incorporate the same electron-deficient unit, a dithienyl benzothiadiazole, but different electron-rich units. Throughout the series, the electron donating ability of the electron-rich unit in the acceptor is systematically decreased by incorporating cycopentadithiophene (P3HT-\(b\)-PCPDT12BT), carbazole (P3HT-\(b\)-PCT6BT), fluorene (P3HT-\(b\)-PFT6BT), and phenyl (P3HT-\(b\)-PPT6BT) moieties, respectively. This in turn, systematically increases \(E_{S1A}\), as measured by the absorbance onset of the acceptor homopolymers in dilute solution. Polymers were dissolved in either 1,2,4-trichlorobenzene \((\varepsilon_0 = 2.24)\), chloroform \((\varepsilon_0 = 4.81)\), or 1,2-dichlorobenzene \((\varepsilon_0 = 9.93)\). \(E_{S1A}\) values vary minimally with solvent, < 0.1 eV. As the molecular structure of the acceptor block is synthetically tuned, the \(E_{S1A}\) values range from ~ 1.6 to 2.2 eV.
$E_{CT}$ is tuned by altering the static dielectric constant ($\varepsilon_0$) of the surrounding environment, the solvent. $E_{CT}$ is calculated using constrained density-functional theory (CDFT), which is able to accurately characterize the CT state in these donor-acceptor systems (see Chapter 3 for more details). Theoretical calculations demonstrate that as the static dielectric constant of the surrounding environment increases from \( \sim 2 \) – 10, the intramolecular charge transfer state is stabilized by roughly 0.5 eV. Across P3HT-$b$-PCT6BT, P3HT-$b$-PFT6BT, and P3HT-$b$-PPT6BT, $E_{CT}$ values are roughly constant, but vary significantly with $\varepsilon_0$ of the solvent. $E_{CT}$ of P3HT-$b$-PCPDT12BT is consistently \( \sim 0.2 \) eV less than the other block copolymers due to small $E_{S1}$ of the PCPDT12BT acceptor block (\( \sim 1.7 \) eV). In addition to using chemistry to tune $E_{S1A}$, $E_{CT}$ is selectively tuned by altering the dielectric polarization of the surrounding environment. Thus, we selectively tune both $E_{S1A}$ and $E_{CT}$, the energy levels that make up the driving force for charge transfer (Figure 4-4).

![Figure 4-4](image-url)

**Figure 4-4:** Energy level characterization of the block copolymers in solution. Optical bandgaps of the acceptor blocks ($E_{S1A}$) are measured from the absorption onset. Charge transfer state energies ($E_{CT}$) are calculated using constrained density-functional theory (CDFT). The driving force for hole transfer is defined as the difference between these two energies, $E_{S1A} - E_{CT}$. All values are plotted in eV as a function of the static dielectric constant of the solvent ($\varepsilon_0$).
Photoluminescence Quenching of Isolated Block Copolymer Chains

We quantify intramolecular exciton dissociation to a charge transfer state within isolated block copolymer chains in solution. Multiangle dynamic light scattering confirms that block copolymer solutions are indeed isolated chains in solution. The decay rate of the autocorrelation function ($I$) is plotted as a function of the scattering vector ($q$) squared (Figure 4-5). Fitting this to a linear regression, the diffusion coefficient (slope) is extracted and used to calculate the hydrodynamic radius ($R_h$). Expected $R_h$ values are calculated using the freely rotating wormlike chain model assuming persistence lengths of approximately 3 nm for P3HT and 4 nm for the acceptor polymers (Table 4-3). All measured $R_h$ values are consistent with isolated semiflexible chains in solution. Furthermore, at the relatively low molecular weights used in this study, the contour length of the chains are approximately 2-3 times the persistence length. The chain stiffness prevents the backbone from folding back onto itself, and prevents the formation of additional donor-acceptor contacts other than the covalent linkage between the blocks. Thus, any exciton dissociation observed occurs at the donor-acceptor interface embedded in the conjugated backbone.
Figure 4-5: Multiangle dynamic light scattering of isolated block copolymer chains. (a) Representative particle size distributions in chloroform solution. The diffusion coefficient is measured by plotting the mean decay rate ($\Gamma$) of the autocorrelation function as a function of the scattering vector ($q$) squared in (b) 1,2-trichlorobenzene, (c) chloroform, and (d) 1,2-dichlorobenzene. Stokes-Einstein relationship is then used to estimate the apparent hydrodynamic radius.
Steady state absorbance and photoluminescence spectra of the block copolymers and constituent homopolymers are measured in the different solvents (Figure 4-6). In solution, linear combinations of the homopolymer absorbance and emission spectra describe the block copolymer absorbance and emission spectra. The block copolymer spectra are deconvoluted to measure the individual contributions of each block to both absorbance and emission. Exciton dissociation to a CT state at the donor-acceptor interface, the CT state yield, is quantified by examining quenching of block copolymer photoluminescence, as previously discussed in Chapter 3.

### Table 4-3: Characterization of block copolymer chain size in dilute solution

<table>
<thead>
<tr>
<th></th>
<th>Expected $R_h$ (nm)$^a$</th>
<th>1,2,4-Trichlorobenzene $R_h$ (nm)</th>
<th>Chloroform $R_h$ (nm)</th>
<th>1,2-Dichlorobenzene $R_h$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT-$b$-PCPD12BT</td>
<td>3</td>
<td>4</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>P3HT-$b$-PC6BT</td>
<td>3</td>
<td>5</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>P3HT-$b$-PFT6BT</td>
<td>4</td>
<td>6</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>P3HT-$b$-PPT6BT</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>3</td>
</tr>
</tbody>
</table>

$^a$ Freely rotating wormlike chain model
The CT state yield is measured for all 4 block copolymers in 3 different solvents (i.e., under 12 different driving forces). We plot the CT state yield as a function of the driving force in Figure 4-7. The data is fit assuming charge transfer ($k_{CT}$) and radiative decay to the ground state ($k_R$) are the dominant decay mechanisms for excited states along the acceptor block. The rate of charge transfer is estimated using Marcus theory and the rate of radiative decay is estimated using standard models for fluorescence emission. The fit parameters used include the center-to-center distance between donor and acceptor, $R$, a pre-exponential factor, $A$, which is predominately
determined by electronic coupling between the donor and acceptor, and the internal reorganization energy, $\lambda_i$. We fit the data to an $R$ value of $3.4 \pm 0.6$ nm, an $A$ value of $4.2 \pm 6 \times 10^8$ eV$^{1/2}$ s$^{-1}$, and a $\lambda_i$ value of $0.5 \pm 0.2$ eV; upper and lower bounds were calculated from standard error of the fit (see Section 4.3 for details). An $R$ value of 3.4 nm corresponds physically to charge transfer occurring within ~2 nm of the donor-acceptor interface which we believe is quite reasonable. 2 nm is similar to the exciton diffusion length of P3HT in chloroform solution (see Chapter 5) as well as the repeat unit size of the acceptor blocks. Furthermore, a $\lambda_i$ value of ~0.5 eV is reasonable considering previous reports of $\lambda$ for solid state OPV systems. Results for block copolymers dissolved in 1,2,4-trichlorobenzene are not fit as significant charge transfer is not observed in this solvent. Based on our model, we predict a maximum CT state yield ranging from 48-62% based on uncertainty in the fitting parameters.
In the isolated chains in dilute solutions, the entropic driving force is reduced relative to a film; there is likely a lower number of accessible states for dissociation to a CT state. Quantifying the CT state yield as a function of driving force reveals that within isolated chains, where exciton dissociation occurs between one donor and one acceptor, a driving energy of ~ 0.3 eV is necessary for significant exciton dissociation.

While the driving force for hole transfer is systematically varied by adjusting the molecular structure of the block copolymers, the driving force for electron transfer ($E_{S1A} - E_{CT}$) is designed to remain mostly fixed (with the exception of P3HT-b-PCPDT12BT) (Figure 4-8). Due to stabilization of the CT state, as the dielectric constant of the surrounding environment increases, the driving force for electron transfer will also increase. Previous work (Chapter 3) suggests that

**Figure 4-7:** CT state yield ($Y_{CT}$) as a function of driving force, $E_{S1A} - E_{CT}$. Each block copolymer (colored markers) has a driving force dependent on solvent, yielding 3 different driving forces for each block copolymer and a total of 12 different data points. Squares represent samples measured in 1,2,4-trichlorobenzene, circles represent chloroform (CF), and triangles represent 1,2-dichlorobenzene (DCB). The CT state yield is modeled assuming charge transfer ($k_{CT}$) and radiative decay to the ground state ($k_R$) are the dominant mechanisms for exciton decay. Due to differences in solvent reorganization energy, CT state yield will have a slightly different function in each solvent. The model for chloroform is shown in grey and 1,2-dichlorobenzene is shown in black. Data for 1,2,4-trichlorobenzene is not modeled.
when the block copolymers are dissolved as isolated chains, the electron-rich unit of the acceptor block disrupts electronic coupling between the P3HT electron donor and highly electron withdrawing benzothiadiazole enough to prevent significant excited state electron transfer. P3HT-\textit{b}-PCPDT12BT was judiciously designed to further verify this conclusion. P3HT-\textit{b}-PCPDT12BT maintains a significantly greater driving force for electron transfer, ranging from 0.3 to 0.7 eV, and a significantly smaller driving force for hole transfer, ranging from -0.2 to 0.2 eV, compared to the other block copolymers (Figure 4-4 and Figure 4-8). No appreciable charge transfer is observed in this system across all solvents. Results established in this chapter indicate that a driving force $\geq 0.3$ eV should facilitate efficient exciton dissociation. Altogether, this demonstrates that within the block copolymer isolated chains, electron transfer is effectively shut-off and therefore, any charge transfer observed must be the result of hole transfer from the acceptor to the donor.

\textbf{Figure 4-8}: Characterization of the driving force for electron transfer, $E_{\text{SIPHT} - E_{\text{CT}}}$, as a function of dielectric constant ($\varepsilon_0$) of the surrounding environment. $E_{\text{SIPHT}}$ is measured from the absorbance onset in solution and $E_{\text{CT}}$ is calculated using CDFT.
Photoluminescence Quenching of Block Copolymer Films

In block copolymer thin films, intermolecular interactions increase the number of states available for exciton dissociation to a CT state. Furthermore, in the solid state, polymer chains adopt longer effective conjugation lengths, as evidenced by a reduction in the optical bandgap of ~0.1 – 0.3 eV, which enhances delocalization. The block copolymers used in solid-state measurements were the “TBT” derivatives (P3HT-b-PCPDTBT, P3HT-b-PCDTBT, P3HT-b-PFTBT, and P3HT-b-PPDTBT) where the solubilizing alkyl side chains on the TBT unit are removed to enhance solid state packing and promote planarization. Previous work has shown that photovoltaic performance of devices incorporating polymers with TBT moieties are significantly enhanced relative to the more soluble analogues with additional alkyl side chains. This is attributed to morphological differences within the active layer. Block copolymers were cast onto quartz substrates and steady state absorbance and photoluminescence spectra were measured.

In the solid state, a linear superposition of the homopolymer absorbance and emission (550 nm excitation) spectra is able to mostly describe the block copolymer spectra (Figure 4-9). Differences in molecular orientation and intermolecular coupling of chains in the block copolymer films, compared to the pristine homopolymer films, will alter the energetics and therefore the optical spectra. Imperfections in solid state linear superpositions are attributed to variations in solid state packing of the block copolymer films relative to the homopolymer films. Exciton dissociation to a charge transfer state is quantified using an analogous method as the block copolymer solutions. In the block copolymer films, due to the imperfect superposition of the homopolymer spectra and complex energetic landscapes, we expect there to be a certain amount of error in our calculations. We estimate this error will be no more than 20%. As shown in Figure 4-10, charge transfer state yields are significantly enhanced in the solid state relative to the isolated chains in solution for all of the block copolymers, demonstrating a more favorable free energy for CT state formation.
Figure 4-9: Steady state absorbance as absorption coefficient (circles) and photoluminescence (squares) normalized by absorbance at 550 nm spectra of polymer films. Filled-in colored markers are the block copolymers, unfilled black markers are P3HT homopolymer, and unfilled gray markers are the different acceptor homopolymers. A linear superposition of the homopolymer spectra (solid black lines) mostly fits the block copolymer spectra. The homopolymer spectra are scaled by their contribution to the block copolymer spectra.
Unfortunately, in going from isolated block copolymer chains to a polymer film, we lose much of the simplicity of our model system. To this end, it may not be possible to accurately characterize the energetic driving force for charge transfer in the block copolymer films. Through careful material design, the driving force for hole transfer is the main pathway available for exciton dissociation in our isolated block copolymer chains. Moreover, molecular orientation at the donor-acceptor interface is established by the covalent linkage between the blocks. These properties do not hold true in block copolymer films. From the data available, it is not possible to determine which pathways are leading to charge transfer and what the associated energy levels are.

Nevertheless, CT state yields in the film are significantly enhanced relative to isolated chains in solution in all materials tested. In some materials, the difference in CT state yield going from isolated chains to a film is larger than the variation over the entire energy range of polymers in solution (-0.2 – 0.5 eV) and CT state yields over 75% are measured. While the energetics will

<table>
<thead>
<tr>
<th>Block Copolymer</th>
<th>Solution, ( \epsilon_0 )</th>
<th>Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT-b-PCPDT12BT/PCPDTBT</td>
<td>2.24</td>
<td></td>
</tr>
<tr>
<td>P3HT-b-PCT6BT/PCDTPBT</td>
<td>4.81</td>
<td></td>
</tr>
<tr>
<td>P3HT-b-PFT6BT/PFTBT</td>
<td>9.93</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 4-10:** CT state yield of the block copolymers in solution (grey bars) and film (black bars). Solution measurements are performed on block copolymers with additional side chains on the TBT unit (R = C\(_6\)H\(_{13}\) or C\(_{12}\)H\(_{25}\)), designed to enhance solubility. Film measurements are performed on block copolymers without additional side chains on the TBT unit (R = H), designed to enhance solid state packing. Charge transfer is significantly enhanced in the block copolymer films.
certainly change in going from isolated chains in solution to films, our results from the isolated chains indicate such a large enhancement in CT state yield would necessitate an enthalpic driving force significantly greater than 0.5 eV, which is unexpected. Furthermore, our model in Figure 4-7 suggests the CT state yield is unlikely to exceed ~ 62% for any enthalpic driving force. Altogether, these results imply that energetics alone cannot fully explain the high CT state yields observed in block copolymer films.

We propose the increase in CT state yield in the block copolymer thin films is at least in part the result of an enhanced entropic driving force. Indeed, this is confirmed using temperature dependent photoluminescence quenching measurements. To confirm a low enthalpic barrier relative to entropic barrier in block copolymer films, temperature-dependent photoluminescence quenching experiments were carried out. We measure photoluminescence emission of P3HT-PPDTBT films, the block copolymer where we observe the greatest CT state yield, as well as the corresponding P3HT and PPDTBT homopolymer films at temperatures ranging from 90 – 294 K. As expected, the normalized photoluminescence emission intensity increases as temperature decreases, due to diminishing vibrational motion at low temperature (Figure 4-11). Photoluminescence quenching in P3HT-PPDTBT films is quantified by first calculating the expected block copolymer integrated emission assuming no interaction between donor and acceptor blocks. To calculate quenching, which is assumed to be proportional to the CT state yield, the expected block copolymer emission is compared to the measured block copolymer emission. (Figure 4-11d).
Again, we assume the CT state yield can be calculated according to Equation 4-1 and that the rate of radiative decay can be modeled using Equation 4-2. We assume a fluorescence quantum yield ($\Phi$) on the order of 0.05 and an excited state lifetime ($\tau$) at 294 K of approximately 500 ps. $\Phi$ should increase with temperature according to the increase in integrated emission and we assume $\tau$ is proportional to $T^{1/2}$. Estimated $k_R$ values are used to calculate $k_{CT}$ as a function of temperature according to Equation 4-1. The Eyring equation is then used to calculate the contributions of enthalpy ($\Delta H^\ddagger$) and entropy ($\Delta S^\ddagger$) to the barrier for charge transfer (Figure 4-12).

Figure 4-11: Temperature dependent photoluminescence of P3HT-b-PPDTBT films. Temperature dependent photoluminescence emission spectra of (a) P3HT, (b) PPDTBT, and (c) P3HT-b-PPDTBT films. (d) CT state yield is calculated at the different temperatures. Spectra were measured at 294, 255, 210, 165, and 90 K. All samples were excited at 550 nm.
Results suggest a minimal enthalpic barrier, $\Delta H^\ddagger = -0.02$ eV, and more significant entropic barrier, $T\Delta S^\ddagger = 0.27$ eV at 294 K.

Figure 4-12: The Eyring equation is used to quantify relative contributions of enthalpy and entropy to the barrier for charge transfer. We plot $\ln(k_{CT}/T \times (\hbar/k_B))$ as a function of $1/T$ to obtain $\Delta H^\ddagger = -0.02$ eV and $T\Delta S^\ddagger = 0.27$ eV at 294 K.

We suspect this is due to an increase in the number of accessible sites for exciton dissociation or enhanced delocalization. In polymer films, intermolecular interactions introduce pathways for intermolecular charge transfer, increasing the number of accessible states. Furthermore, the increase in effective conjugation length observed as polymers pack in a solid state film will enhance delocalization. Although, recent work on the mechanism of polaron formation in P3HT suggests significant intermolecular delocalization may not be necessary; even in a two-dimensional lattice, polarons are about the width of two thiophene rings and tend to localize on single chains.\textsuperscript{307} Thus, we conclude that an increased entropic driving force in the solid state can enhance exciton dissociation, likely due to the greater number of accessible states. Furthermore, it is possible that the enhanced entropic driving force in films, compared to isolated block copolymer
chains, may be able to compensate for low energetic driving forces and facilitate efficient charge transfer in systems with a low energetic offset.

4.5 Conclusion

Our study makes use of conjugated block copolymers as ideal model materials to systematically investigate energetic and entropic contributions to the driving force for charge transfer. We examine intramolecular charge transfer in isolated block copolymer chains where the number of states available for charge transfer is reduced with respect to a polymer film. The energetic driving force can be precisely tuned using different molecular structures and dielectric environments. Hole transfer from acceptor to donor within individual block copolymer chains was quantified as the energetics of the singlet exciton and charge transfer state were selectively tuned. In a model system, where exciton dissociation occurs via hole transfer from one donor to one acceptor, a significant energetic offset of ~ 0.3 eV is critical for significant charge transfer.

Entropic effects were investigated by examining the block copolymers in solid state films, introducing intermolecular interactions and increasing the number of states available for exciton dissociation. While it is not straightforward to precisely characterize the relevant energetic driving forces for charge transfer, in all cases exciton dissociation is more efficient than in isolated chains. According to our model for exciton dissociation within isolated block copolymer chains, altered energetics alone cannot account for the dramatic increase in exciton dissociation in block copolymer films versus isolated chains. We utilize temperature-dependent measurements to demonstrate a minimal enthalpic barrier and significant entropic barrier for exciton dissociation in the solid state. Altogether, our results suggest that both an energetic driving force and an entropic driving force are important to facilitate efficient photocurrent generation. This entropic driving force could be important to facilitate efficient photocurrent generation in systems with a low
energetic offset that are warranted to simultaneously maximize photocurrent and photovoltage in organic solar cell devices.

This chapter is adapted from:

Chapter 5

Push-Pull Architecture Eliminates Chain Length Effects on Exciton Dissociation

Recently, “small molecule” non-fullerene acceptors have been rapidly developed and are now being incorporated in the top-performing organic photovoltaic devices. These non-fullerene acceptors typically consist of ~ 10 aromatic rings arranged in an alternating electron-rich/ electron-deficient architecture reminiscent of push-pull polymers, making them “push-pull oligomers”. Without the extended conjugation length of a polymer, it is perhaps surprising that devices incorporating these oligomeric non-fullerene acceptors perform so well. To investigate exciton dissociation as a function of chain length, a series of donor-acceptor block copolymers consisting of a conjugated homopolymer electron donor, poly(3-hexylthiophene-2,5-diyl) (P3HT), covalently linked to a push-pull polymer electron acceptor, poly-((2,5-dihexylphenylene)-1,4-diyl-alt-[4,7-bis(3-hexylthiophen-5-yl)-2,1,3-benzothiadiazole]-2’,2”-diyl) (PPT6BT), was synthesized. By adjusting synthetic parameters, the chain length of each block is selectively tuned. The block copolymers are dissolved as isolated chains in dilute solutions and intramolecular charge transfer is quantified. When the P3HT block is very short (< 3 nm), charge transfer is inhibited. Nevertheless, efficient charge transfer is observed for PPT6BT block lengths ranging from ~ 3 – 16 nm. This indicates that the polarized nature and charge transfer character of excited states generated along push-pull polymers facilitates exciton dissociation.
5.1 Introduction

Performance of organic photovoltaic (OPV) devices is increasing rapidly with the top power conversion efficiencies of single-junction cells now exceeding 13%. For the past several years, the active layer of top-performing OPV devices has been composed of a push-pull polymer electron donor, made up of alternating electron-rich (push) and electron-deficient (pull) moieties, blended with a solubilized fullerene derivative electron acceptor. While push-pull polymers remain unrivaled as electron donors, recently, non-fullerene acceptors have rapidly emerged as champion materials; efficiencies of devices incorporating non-fullerene acceptors now surpass efficiencies of polymer/fullerene devices.

In addition to electron donors, n-type push-pull polymers are also promising materials for non-fullerene electron acceptors. Non-fullerene OPV devices incorporating an alternating naphthalene diimide-bithiophene polymer as the electron acceptor have achieved efficiencies that approach 10%. Nevertheless, the top-performing non-fullerene OPVs incorporate “small molecule” non-fullerene acceptors. The chemical structures of these acceptors typically include linear chains of aromatic moieties (~ 10 aromatic rings) arranged in an alternating electron-rich/electron-deficient pattern reminiscent of push-pull polymers. It is surprising that OPV devices incorporating these “push-pull oligomer” non-fullerene acceptors perform well despite the electron acceptor not having the extended conjugation length of a polymer.

When blended with another material, polymer chain length will influence morphological properties including crystallinity, crystal packing, and domain spacing. As a result, chain length can have a profound effect on exciton diffusion, charge transport, and thus, overall photovoltaic device performance. For example, using fluorescence quenching experiments to measure vertical exciton diffusion (normal to the substrate) within P3HT films, the exciton diffusion coefficient was found to be an order of magnitude greater within high molecular weight P3HT (76...
kg mol$^{-1}$) than within lower molecular weight P3HT (14 kg mol$^{-1}$), $\sim10^{-3}$ cm$^2$ s$^{-1}$ versus $\sim10^{-4}$ cm$^2$ s$^{-1}$. This was attributed to greater disorder in crystal texturing within the high molecular weight film, such that more polymer chains were oriented face-on with respect to the substrate. Thus, vertical exciton diffusion is potentially enhanced due to more out-of-plane tight chain packing. Alternatively, increasing molecular weight could enhance exciton diffusion as intramolecular charge transport is known to be much faster than intermolecular charge transport. Thus, it is unclear whether the difference in exciton diffusion is due to different polymer chain lengths or if it is purely due to differences in film morphology.

Chain length can also influence the optoelectronic properties of a conjugated polymer. For example, oligothiophenes do not have the same optical bandgap as high molecular weight P3HT, indicating that P3HT oligomers have a shorter effective conjugation length than the polymer. This result holds when the materials are dissolved in solution and cast into a film. P3HT is a conjugated homopolymer, consisting of repeating electron-rich thiophene units. OPV devices incorporating a monodisperse P3HT oligomer (number of repeat units, $n = 16$) electron donor blended with [6,6]-phenyl-C61 butyric acid methyl ester (PC$_{61}$BM) fullerene electron acceptor perform significantly worse than devices incorporating high molecular weight P3HT blended with PC$_{61}$BM (efficiencies $< 1\%$ vs $5\%)$. Interestingly, OPV devices incorporating an oligothiophene ($n = 7$) blended with PC$_{61}$BM can achieve efficiencies of $5.1\%$ when the oligothiophene is functionalized with electron withdrawing cyanoacrylate groups. Functionalizing the oligothiophene with electron-deficient groups introduces the push-pull motif common in the polymer donors and non-fullerene acceptors often used in top-performing OPV devices.

Here, we use conjugated block copolymers to examine the effect of chain length on exciton dissociation in both conjugated homopolymers and push-pull alternating copolymers. The block copolymers are studied as isolated chains in dilute solutions, decoupling exciton dissociation from
the morphological effects present in a polymer film. In the past, covalently linked donor-acceptor
dyads have been used extensively to examine intramolecular electron transfer processes. These
materials are typically composed of small molecule electron donors and acceptors joined by a
saturated hydrocarbon linking group that limits intramolecular electronic coupling. Using block
copolymers composed of conjugated donors and acceptors gives us the unique ability to examine
intramolecular charge transfer as a function of donor and acceptor conjugation length.

The block copolymers studied consist of a P3HT conjugated homopolymer electron donor
covalently linked to a push-pull polymer electron acceptor, poly-((2,5-dihexylphenylene)-1,4-diy-
al-t-[4,7-bis(3-hexylthiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) (PPT6BT), yielding P3HT-
b-PPT6BT. By adjusting the synthetic procedure for the block copolymers, the chain length of each
block is systematically tuned. The block copolymers are designed to decouple energy transfer and
charge transfer occurring within individual block copolymer chains, allowing us to monitor each
process individually. Intramolecular charge transfer is quantified and chain length effects on
exciton dissociation are examined in conjugated homopolymers and push-pull polymers. Results
suggest a push-pull architecture decreases the requirement of an extended conjugation length for
efficient exciton dissociation to a charge transfer state.

5.2 Experimental Section

Polymer Synthesis

P3HT was synthesized using typical Kumada catalyst transfer polymerization reaction
conditions according to a previously reported procedure. The molar ratio of monomer/catalyst
was adjusted to tune P3HT molecular weight. Block copolymers were synthesized using the end-
functionalized P3HT as a macroreagent; the PPT6BT block was added on using a Suzuki
polycondensation according to a previously reported procedure (See Chapter 3). PPT6BT homopolymer was synthesized using the same procedure as the block copolymers, omitting P3HT from the reaction.

P3HT(7), P3HT(29), P3HT(23), P3HT(31): Yields: ~ 700 mg, ~ 50%. \(^1\)H NMR (850 MHz, CDCl\(_3\), \(\delta\)): 6.96 (1H), 2.78 (2H), 1.69 (2H), 1.42 (2H), 1.33 (4H), 0.90 (3H)

PPT6BT: Yield: 238 mg, 89%. \(^1\)H NMR (850 MHz, CDCl\(_3\), \(\delta\)): 8.08 (2H), 7.88 (2H), 7.25 (2H), 2.60 (4H), 2.49 (4H), 1.64 (4H), 1.53 (4H), 1.24 (24H), 0.87 (6H), 0.80 (6H).

P3HT(7)-b-PPT6BT(8), P3HT(7)-b-PPT6BT(10), P3HT(23)-b-PPT6BT(5), P3HT(29)-b-PPT6BT(2), P3HT(29)-b-PPT6BT(10), P3HT(31)-b-PPT6BT(6): Yields: ~ 100-200 mg, ~ 60-80%. \(^1\)H NMR (360 or 500 MHz, CDCl\(_3\), \(\delta\)): 8.08, 7.88, 7.25, 6.96, 2.78, 2.60, 2.49, 1.69, 1.42, 133-1.22, 0.90, 0.80

**Gel Permeation Chromatography (GPC)**

Chain extension and molar mass distributions were determined using an Agilent Technologies gel permeation chromatograph (ResiPore 300 x 7.5 mm column, Agilent 1260) equipped with multiwavelength (MWD) and refractive index (RID) detectors. Chlorobenzene was used as the mobile phase at 40°C and a flow rate of 0.5 mL min\(^{-1}\). Molar mass distributions were determined relative to polystyrene standards.

\(^1\)H NMR

Number average molecular weight (\(M_n\)) and contour length (\(L\)) of each block were characterized using \(^1\)H NMR analysis. NMR was performed on a Bruker 850 MHz instrument (Bruker Avance-III-850 MHz); all samples were prepared in deuterated chloroform (Figure 5-1 and
$M_n$ of P3HT was calculated by end-group analysis using the signals at 2.78, 2.60, and 2.55 ppm, corresponding to the protons on the $\alpha$-CH$_2$ of the thiophene rings within the chain, on the protonated chain end, and on the brominated chain end, respectively. $M_n$ of the PPT6BT block was calculated using the peak ratios corresponding to P3HT ($\delta = 2.78, 6.96$ ppm) and PPT6BT ($\delta = 2.59, 2.49, 7.94, 8.14, 7.31$ ppm) to obtain the relative weight fractions. The $M_n$ of PPT6BT was then calculated using the weight fraction and $M_n$ of P3HT. The contour length of each block is calculated as the product of monomer width (P3HT $\sim 0.4$ nm$^{259}$, PPT6BT $\sim 1.6$ nm) and the number average degree of polymerization, $X_n$.

**Figure 5-1:** NMR spectra of all synthesized P3HT macroragents measured in deuterated chloroform on a Bruker 850 MHz instrument (Avance-III-850 MHz).
Dynamic light scattering (DLS)

DLS measurements were performed on P3HT-\textit{b}-PPT6BT in chloroform (dissolved at ~ 0.1 – 0.25 mg mL$^{-1}$ in chloroform) at room temperature using a Brookhaven Instruments BI-200 SM static/dynamic light scattering system equipped with a 30 mW diode laser ($\lambda=637$ nm). Particle size distributions were determined at various scattering angles ranging from 30 to 150°. The CONTIN$^{254}$ algorithm was used to calculate the mean decay rate ($\Gamma$) of the autocorrelation function. Diffusion coefficients of the particles in chloroform were obtained by plotting $\Gamma$ versus the scattering vector.

Figure 5-2: NMR spectra of all synthesized P3HT-\textit{b}-PPT6BT block copolymers measured in deuterated chloroform on a Bruker 850 MHz instrument (360 or 500 MHz).
(q) squared. Stokes-Einstein equation was used to calculate the apparent hydrodynamic radius from the diffusion coefficient.

**Absorbance and Fluorescence Spectroscopy**

Polymer solutions were prepared at 1 mg mL\(^{-1}\) in chloroform and stirred overnight in an inert atmosphere to ensure full dissolution. Solutions were diluted to 1 µg mL\(^{-1}\), loaded into 1 cm path length quartz cuvettes, sealed and removed from the glovebox for testing. Absorbance spectra were measured on an Agilent Technologies Cary 60 UV-vis. Fluorescence emission spectra were measured on a Photon Technology International QuantaMaster 300 fluorometer. Quantum yield measurements were made by comparing absorbance and fluorescence spectra to a dye of known quantum efficiency, 4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (Φ = 0.44 in ethanol). 255,256

**5.3 Measuring Spectral Overlap for Resonance Energy Transfer**

The overlap integral (J) describes the degree of spectral overlap between donor emission and acceptor absorbance (Equation 5-1). 255

\[
J = \int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda
\]

\[\text{Equation 5-1}\]

\(F_D(\lambda)\) is the corrected fluorescence emission of the donor with total area under the curve normalized to one and \(\varepsilon_A(\lambda)\) is the extinction coefficient of the acceptor. We calculate an overlap integral for energy transfer from P3HT to PPT6BT, \(J = 5.9 \times 10^{13} \text{ M}^{-1} \text{ cm}^{-1} \lambda^4\) and the overlap integral for energy transfer from PPT6BT to P3HT, \(J = 5.9 \times 10^{11} \text{ M}^{-1} \text{ cm}^{-1} \lambda^4\) (Figure 5-3).
5.4 Model to Calculate Exciton Diffusion Length Along P3HT Chains in Chloroform Solution

The exciton density profile along P3HT chains was modeled using an equation for one dimensional diffusion. We assume energy transfer to PPT6BT is the only source of P3HT exciton quenching in the block copolymer not present in the P3HT homopolymer. The exciton density profile along the P3HT homopolymer is modeled as:

\[
D \frac{d^2y(x)}{dx^2} - \frac{y(x)}{\tau} + k_{gen}c = 0
\]
Where $D$ is the diffusion coefficient, $y(x)$ is the exciton density as a function of distance along the chain ($x$), $\tau$ is the exciton lifetime in the absence of the PPT6BT (assumed to be $\sim 600$ ps for P3HT$^{257,258}$), and $k_{gen}$ is the rate of exciton formation. This differential equation can be solved analytically assuming a constant density profile along the chain. The boundary conditions used were:

$$\frac{dy(0)}{dx} = \frac{dy(L)}{dx} = 0$$  \hspace{1cm} 5-3

Where the contour length of the chain extends from 0 to $L$.

The exciton density profile along the P3HT block of P3HT-$b$-PPT6BT is modeled as:

$$D \frac{d^2 y(x)}{dx^2} - \frac{y(x)}{\tau} + k_{gen} - k_{FRET}(x)y(x) = 0$$  \hspace{1cm} 5-4

Where $k_{FRET}$ is the quenching rate due to Förster resonance energy transfer (FRET)$^{255}$. The rate constant for energy transfer is calculated according to Equation 5-5.

$$k_{FRET} = \frac{1}{\tau} \left( \frac{R_0}{L - x} \right)$$  \hspace{1cm} 5-5

Where $R_0$ is the Förster distance, defined as the donor-acceptor distance at which FRET efficiency drops to 50%.$^{255}$ The PPT6BT block is linked at $L$ and therefore $L - x$ is the distance from the P3HT-PPT6BT donor-acceptor interface. $R_0$ is calculated using Equation 5-6.

$$R_0^6 = \frac{9(ln10)k^2\Phi_{P3HT}}{128\pi^6 N n^4} \int_{0}^{\infty} F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda$$  \hspace{1cm} 5-6

$k^2$ describes the relative orientation of the transition dipoles of the donor and acceptor, assumed to be 2/3, $\Phi_{P3HT}$ is the quantum yield of P3HT ($\sim 0.25$), $N$ is Avogadro’s number, and $n$ is the refractive index of the solvent ($n_{CHCL3} = 1.45$). We calculate an $R_0$ value of approximately 2.4 nm.
The exciton density profile along the block copolymer must be solved numerically using boundary conditions:

\[ \frac{dy(0)}{dx} = 0; \quad y(L-c) = 0 \]

Mathematically, assuming the exciton density goes to 0 at \( L \) would result in a singularity; the donor and acceptor are directly linked. Therefore, we assume that the distance \( c \) from \( L \) at which the FRET rate constant becomes approximately 2 orders of magnitude greater than the rate constant for radiative emission \( (k_{\text{rad}} = \Phi_{\text{P3HT}}/\tau \sim 4 \times 10^8 \text{ s}^{-1}) \), the exciton density is effectively 0. At a \( c \) value of 1.5 nm away from the donor-acceptor interface \( k_{\text{FRET}} \) is \( \sim 3 \times 10^{10} \text{ s}^{-1} \) and thus, the exciton density is assumed to go to 0 at this point.

\( f_Q \) is modeled by comparing the integrated exciton density along the length of the P3HT homopolymer and block copolymer. The data was fit using a diffusion coefficient, \( D = 1.0 \text{ nm}^2 \text{ s}^{-1} \). Solving \( L_D = \sqrt{D\tau} \) for the exciton diffusion length, \( L_D \), we obtain \( L_D = 2.5 \text{ nm} \).

### 5.5 Model to Estimate Number of Monofunctional P3HT-PT6BT Chains in Each Sample

Due to the statistical nature of polymers and step-growth mechanism used to synthesize the PPT6BT block, we expect there to be a relatively broad distribution of chain lengths in all synthesized samples of P3HT-\( b \)-PPT6BT. We can calculate the expected fraction of \( i \)-mers \( (i \) is the number of repeat units) based on the dispersity \( (D) \) and number average molecular weight \( (M_n) \) using the Shulz-Zimm distribution (Equation 5-8).\(^{163}\)

\[
P(M_i) = \frac{Z^{i+1}}{\Gamma(z + 1)} \frac{M_i^{z-1}}{M_n^z} e^{-zM_i/M_n} \]
\[ z = \frac{1}{D - 1} \]

\( P(M_i) \) is the probability of a polymer chain with \( i \) repeat units, \( z \) describes the dispersity according to Equation 5-9, and \( \Gamma \) is the gamma function. For relatively broad molecular weight distributions, \( D \sim 2 \), the mol fraction of \( i \)-mers decreases monotonically with \( i \). Therefore, chains functionalized with a single PPT6BT repeat unit, referred to as P3HT-PT6BT, have the highest probability of forming relative to any other \( i \)-mer. We estimate a \( D \) of 2 in P3HT(29)-b-PPT6BT(2), consistent with expectations for a step-growth polymerization mechanism.\(^{163}\) Using Equation 5-8, we calculate that \( \sim 40\% \) of P3HT chains within the P3HT(29)-b-PPT6BT(2) sample are likely to be functionalized with only one PT6BT repeat unit (P3HT-PT6BT).

### 5.6 Results and Discussion

#### Material Design

The block copolymers studied in this work consist of a conjugated homopolymer (P3HT) covalently linked to a push-pull polymer (PPT6BT). Molecular structures are shown in Figure 5-4. Using two similar block copolymers, poly(3-hexylthiophene)-\( block \)-poly-((9-(9-heptadecanyl)-9H-carbazole)-1,4-diyl-alt-[4,7-bis(3-hexylthiophen-5-yl)-2,1,3-benzothiadiazole]-2’,2”-diyl) (P3HT-\( b \)-PCT6BT) and poly(3-hexylthiophene)-\( block \)-poly-((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(3-hexylthiophen-5-yl)-2,1,3-benzothiadiazole]-2’,2”-diyl) (P3HT-\( b \)-PFT6BT), we have demonstrated that small perturbations to the molecular structure can have a significant impact on intramolecular charge transfer (Chapter 3). In P3HT-\( b \)-PCT6BT, where a carbazole moiety is used as the electron-rich unit of the push-pull polymer electron acceptor, effectively no charge transfer is observed in chloroform solution (\( \varepsilon_0 = 4.81 \)). The driving force for exciton dissociation via hole
transfer, defined as the energy difference between the excited state of the acceptor and charge transfer (CT) state, is 0.25 eV. The energy of the singlet exciton is the optical bandgap measured by the absorption onset and the CT state energy is calculated using constrained density-functional theory. Moderately efficient charge transfer is observed in P3HT-\textit{b}-PFT6BT, which incorporates a relatively less electron-rich fluorene moiety in the acceptor. The driving force for hole transfer is increased to 0.29 eV. Approximately 10\% of excitons generated along P3HT-\textit{b}-PFT6BT block copolymer chains dissociate to a charge transfer state transfer state. In P3HT-\textit{b}-PPT6BT, we decrease the electron donating ability of the electron-rich unit in the acceptor further by incorporating a phenyl ring as the electron-rich unit of the acceptor block. The driving force in chloroform solution is increased further to 0.37 eV.

![Chemical structures of P3HT, PPT6BT, and P3HT-\textit{b}-PPT6BT. P3HT is a homopolymer composed of repeating electron-rich thiophene units. PPT6BT is an alternating push-pull copolymer composed of alternating electron-rich phenyl units and electron-deficient dithienylbenzothiadiazole (T6BT) units.]

\textbf{Figure 5-4:} Chemical structures of P3HT, PPT6BT, and P3HT-\textit{b}-PPT6BT. P3HT is a homopolymer composed of repeating electron-rich thiophene units. PPT6BT is an alternating push-pull copolymer composed of alternating electron-rich phenyl units and electron-deficient dithienylbenzothiadiazole (T6BT) units.

Additionally, P3HT-\textit{b}-PPT6BT was carefully designed to decouple energy transfer and charge transfer such that these processes could be monitored independently. In solution, energy transfer occurs predominately from P3HT to PPT6BT. The rate of energy transfer from a donor to an acceptor is directly proportional to the degree of spectral overlap, quantified by the overlap
The overlap integral for energy transfer from P3HT to PPT6BT is $5.9 \times 10^{13} \text{M}^{-1} \text{cm}^{-1} \text{nm}^4$ while the overlap integral for energy transfer from PPT6BT to P3HT is $5.9 \times 10^{11} \text{M}^{-1} \text{cm}^{-1} \text{nm}^4$ (Figure 5-3). Because the overlap integral for energy transfer from P3HT to PPT6BT is 2 orders of magnitude greater than the overlap integral for energy transfer from PPT6BT to P3HT, we assume the latter is negligible. Furthermore, in solution, charge transfer is expected to occur primarily via hole transfer from PPT6BT to P3HT. We have previously demonstrated that the electron-rich unit of the acceptor block disrupts electronic coupling between the strong electron donor (P3HT) and highly electron-withdrawing benzothiadiazole, preventing excited state electron transfer from P3HT to the acceptor almost completely (Chapter 3 and Chapter 4). Any charge transfer observed in P3HT-\textit{b}-PPT6BT chains is assumed to be the result of hole transfer from PPT6BT to P3HT. Thus, in isolated P3HT-\textit{b}-PPT6BT chains, we measure energy transfer from donor to acceptor and charge transfer from acceptor to donor.

**Synthesis and Chain Length Characterization**

Block copolymers were synthesized in two steps as reported previously. First a P3HT macroreagent was synthesized using a Kumada catalyst transfer polymerization (KCTP), resulting in end-functionalized P3HT. The PPT6BT block was added on in a chain extension reaction using Suzuki polycondensation. Successful chain extension and block copolymer synthesis is confirmed by unimodal gel permeation chromatography (GPC) absorbance traces (recorded at 420 nm) shifted to a higher molecular weight (lower retention time) relative to the P3HT macroreagent used (Figure 5-5).
By adjusting synthetic parameters, the chain length of each block can be systematically tuned. KCTP is known to follow a controlled chain-growth polymerization mechanism; the number-average degree of polymerization ($X_n$) can be tuned by altering the molar ratio of monomer to initiator (catalyst), “cat:mon”. By adjusting this ratio, P3HT macroreagents were synthesized with $M_n$ varying from 1100 – 5100 g mol$^{-1}$, corresponding to average P3HT contour lengths ($L_{P3HT}$) ranging from 2.6 – 12.2 nm. Different samples of P3HT are referred to as P3HT($x$), where $x$ denotes the $X_n$ of the sample. In addition to a high catalyst loading, for the low molecular weight P3HT(7) macroreagent, the acetone fraction was collected during Soxhlet purification to ensure a very low $L_{P3HT}$.

Under conditions employed here, Suzuki polycondensation follows a step-growth mechanism, making control of the molecular weight challenging. According to Carothers equation, the maximum attainable $X_n$ can be limited by using an asymmetric molar ratio of the two condensation monomers. In our reaction, the condensation monomers are functionalized phenyl (P)

**Figure 5-5:** GPC traces of the block copolymers (colored traces) overlaid with the P3HT macroreagent used (black traces). All traces are normalized to one for clarity.
and dithienyl benzothiadiazole (T6BT) moieties; the molar ratio “T6BT:P” is adjusted to tune the molecular weight of the PPT6BT block. Block copolymers were synthesized such that PPT6BT $M_n$ values range from 1500 – 7800 g mol$^{-1}$, corresponding to average PPT6BT contour lengths ($L_{PPT6BT}$) ranging from 3.3 – 16.4 nm. Synthetic details and molecular weight characterization are presented in Table 5-1 and Table 5-2. The block copolymers are named according to P3HT($x$)-$b$-PPT6BT($y$) where $x$ is the $X_n$ of the P3HT block and $y$ is the $X_n$ of the PPT6BT block.

**Table 5-1**: Synthetic parameters used to modulate molecular weight

<table>
<thead>
<tr>
<th>Cat:mon</th>
<th>T6BT:P</th>
</tr>
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<tbody>
<tr>
<td>P3HT(7)-$b$-PPT6BT(8)</td>
<td>0.05$^a$</td>
</tr>
<tr>
<td>P3HT(7)-$b$-PPT6BT(10)</td>
<td>0.05$^a$</td>
</tr>
<tr>
<td>P3HT(23)-$b$-PPT6BT(5)</td>
<td>0.025</td>
</tr>
<tr>
<td>P3HT(29)-$b$-PPT6BT(2)</td>
<td>0.02</td>
</tr>
<tr>
<td>P3HT(29)-$b$-PPT6BT(10)</td>
<td>0.02</td>
</tr>
<tr>
<td>P3HT(31)-$b$-PPT6BT(6)</td>
<td>0.02</td>
</tr>
</tbody>
</table>

**Table 5-2**: Molecular weight and size characterization of block copolymers

<table>
<thead>
<tr>
<th></th>
<th>P3HT $M_n$ (g mol$^{-1}$)</th>
<th>P3HT $L$ (nm)</th>
<th>PPT6BT $M_n$ (g mol$^{-1}$)</th>
<th>PPT6BT $L$ (nm)</th>
<th>Measured $r_\text{h}$ (nm)</th>
<th>Expected $r_\text{h}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT(7)-$b$-PPT6BT(8)</td>
<td>1100</td>
<td>2.6</td>
<td>5500</td>
<td>12.4</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>P3HT(7)-$b$-PPT6BT(10)</td>
<td>1100</td>
<td>2.6</td>
<td>7300</td>
<td>16.4</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>P3HT(23)-$b$-PPT6BT(5)</td>
<td>3900</td>
<td>9.4</td>
<td>3700</td>
<td>8.4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>P3HT(29)-$b$-PPT6BT(2)</td>
<td>4800</td>
<td>11.5</td>
<td>1500</td>
<td>3.3</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>P3HT(29)-$b$-PPT6BT(10)</td>
<td>4800</td>
<td>11.5</td>
<td>7300</td>
<td>16.4</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>P3HT(31)-$b$-PPT6BT(6)</td>
<td>5100</td>
<td>12.2</td>
<td>4200</td>
<td>9.4</td>
<td>5</td>
<td>4</td>
</tr>
</tbody>
</table>

$^a$ $^1$H NMR; $^b$ DLS; $^c$ freely-rotating wormlike chain model
Photoluminescence Quenching

Block copolymers were dissolved in chloroform at ~ 1 mg L⁻¹. At such low concentrations, there are no intermolecular interactions or aggregation of polymer chains. This is confirmed by multiangle dynamic light scattering (DLS) where we measure apparent hydrodynamic radii ($r_h$) consistent with isolated semiflexible chains (Figure 5-6). Assuming persistence lengths of roughly 3 nm for P3HT and 4 nm for PPT6BT, $r_h$ values of ~ 3 – 5 nm are estimated for isolated block copolymer chains in solution according to the freely-rotating worm-like chain model. ²⁵⁹, ³³⁹, ³⁴⁰

Figure 5-6: Multiangle dynamic light scattering of block copolymers in chloroform solution plot as the decay rate of the autocorrelation function ($\Gamma$) as a function of the scattering vector ($q$) squared. The slope of this line corresponds to the diffusion coefficient which is used to estimate the hydrodynamic radius in chloroform solution.

Steady state absorbance and emission spectra were recorded (Figure 5-7). Linear superpositions of P3HT and PPT6BT homopolymer absorbance and emission spectra nicely describe the block copolymer absorbance and emission spectra. The block copolymer spectra are deconvoluted to determine the individual contributions of each block to both absorbance and
emission. Using a previously reported method (Chapter 3), we quantify 1) the fraction of P3HT excited states that undergo energy transfer to the PPT6BT block ($f_Q$) and 2) the fraction of excitons generated on the block copolymer that dissociate to a charge transfer state, the CT state yield.

**Figure 5-7:** Steady state absorbance as molar absorptivity, $\varepsilon$, and photoluminescence spectra of dilute polymer solutions. Filled-in colored markers are the block copolymers, unfilled black markers are P3HT homopolymer, and unfilled gray markers are PPT6BT homopolymer. A linear superposition of the homopolymer spectra (solid black lines) describes the block copolymer spectra. Homopolymer spectra are scaled by their contribution to the linear superposition.
Exciton Diffusion as a Function of Chain Length

The strong dependence of $f_Q$ on the P3HT average contour length is used to estimate an exciton diffusion length along P3HT chains in chloroform solution (Figure 5-8). $f_Q$ data is fit using a one-dimensional diffusion equation (see Section 5.4 for details).\(^3\)^\(^3\)^\(^3\)\(^3\)\(^7\) Energy transfer is believed to occur by Förster resonance energy transfer and is therefore used to describe the boundary condition at the P3HT-PPT6BT donor-acceptor interface (Chapter 3).\(^2\)^\(^5\)^\(^5\) Previous studies have modeled exciton diffusion along P3HT chains linked to a fullerene electron acceptor moiety in solution, but cannot distinguish between energy transfer and charge transfer as the quenching mechanism at the donor-acceptor interface.\(^3\)^\(^3\)\(^5\) The block copolymers in this study were designed to monitor energy transfer and charge transfer independently, allowing for a more accurate model. We calculate an exciton diffusion length along the P3HT backbone of 2.5 nm.

![Graph showing fraction of quenched P3HT excited states ($f_Q$) as a function of the average contour length ($L_{P3HT}$). Red markers correspond to measured data and the dotted black line corresponds to the diffusion model assuming all P3HT quenching at the donor-acceptor interface is due to FRET.]

**Figure 5-8:** Fraction of quenched P3HT excited states ($f_Q$) as a function of the average contour length ($L_{P3HT}$). Red markers correspond to measured data and the dotted black line corresponds to the diffusion model assuming all P3HT quenching at the donor-acceptor interface is due to FRET.

Our results suggest that dihedral disorder in solution places bounds on exciton diffusion and localizes excited states to 2.5 nm segments along P3HT chains. There is evidence that
significant torsion along the backbone of conjugated polymers leads to localization of excited states. Furthermore, theoretical calculations have demonstrated that charge carriers are able to move relatively fast along straight segments of a polymer chain until reaching a sharp twist where they are deeply trapped by the vanishing hopping integral. There is evidence that, on very short time scales, structural disorder can broaden the distribution of exciton hopping rates and may initially enhance exciton diffusion; excitons preferentially hop downhill in energy. Nevertheless, at long time scales, after excitons have relaxed to low energy molecular subunits, structural disorder serves only to reduce overall exciton transport. Thus, at steady state, we assume exciton motion along a conjugated polymer chain is localized by torsion in a similar manner as electrons or holes. For P3HT chains well dispersed in chloroform, the dihedral potential suggests that every 2.5 nm there will be a 45° twist in the chain. At 45°, the matrix hopping element is approximately 70% of its maximum value and decreases rapidly to almost 0 as the dihedral angle approaches 90°. This suggests that a 45° twist in the chain creates a significant enough barrier to disrupt transport and confine excitons to approximately 2.5 nm segments along the P3HT backbone.

This interpretation is consistent with previous studies examining exciton diffusion in P3HT films. In the solid state, P3HT chains crystallize; the thiophene rings π-stack and the polymer chains become increasingly planar. As crystalline order is increased upon thermal annealing, exciton hopping rates and the exciton diffusion length, measured by photoluminescence quenching experiments, also increase. The exciton diffusion length increases from 3 nm in the “low crystallinity” as-cast film to 7 nm in the “high crystallinity” film after chains are recrystallized from the melt. In addition, earlier theoretical work suggests a dihedral angle greater than 40° is sufficient to effectively break conjugation and disrupt the electronic properties of polythiophene.

These results suggest that in designing non-fullerene acceptors for OPVs, chain planarity should be considered, particularly in the case of conjugated homopolymers. There is evidence to suggest that in some top-performing polymer/fullerene systems, exciton diffusion is not a
significant factor in the photocurrent generation mechanism. This could be due to the miscibility between fullerene and many amorphous conjugated polymers. When blended together, these materials form intimately mixed phases, unlike the pure donor-acceptor domains often illustrated. Thus, when an excited state is generated along the polymer chain, it is very likely to be generated near a donor-acceptor interface; no diffusion is required. This could differ in non-fullerene solar cells. As the degree of polymerization increases, the loss in entropy of mixing makes miscibility less likely. Assuming moderate molecular weights or greater, polymer blends will almost always phase separate. An n-type conjugated polymer electron acceptor will almost certainly not form an intimately mixed phase with a conjugated polymer electron donor. Furthermore, depending on the interaction energy of a particular oligomeric non-fullerene acceptor/polymer donor pair, blend morphology may consist of an intimately mixed phase or strongly segregated, pure domains. It has also been suggested that pure domains of electron donor and/or acceptor are necessary to achieve high performance. Thus, exciton diffusion will likely contribute to the mechanism of photocurrent generation in high-performance non-fullerene solar cells. Our results suggest that exciton diffusion is disrupted by significant twisting of aromatic rings along the backbone. Polymers and oligomers that have more rigid, planar backbones due to molecular design or intermolecular aggregation will likely facilitate longer exciton diffusion lengths.

**Exciton Dissociation as a Function of Chain Length**

Any quenching of excited states generated along either the P3HT block or the PPT6BT block not accounted for by energy transfer is assumed to be the result of intramolecular charge transfer and is therefore proportional to the CT state yield. CT state yield as a function of \( L_{P3HT} \) is presented in Figure 5-9a. The black dashed line starting at 0% that quickly saturates to about 20%
serves as a guide to the eye. When P3HT chains are very short (~ 2.6 nm), the CT state yield is only around 5%. This suggests that confining charge transfer states along short P3HT chains introduces an energetic penalty that disrupts charge transfer.

Conversely, charge transfer is mostly independent of the PPT6BT average chain length (Figure 5-9b). Again, the black dashed line serves as a guide to the eye. This result is unexpected. First, as the chains become longer, a drop in the CT state yield is expected due to limited access of excitons to the donor-acceptor junction. Nevertheless, the CT state yield remains at about 20% for \( L_{PPT6BT} \) ranging from approximately 3 – 16 nm. This result is consistent with a very long exciton diffusion length, possibly greater than 15 nm, along the PPT6BT backbone. There is evidence that push-pull polymers in solution can support relatively long exciton diffusion lengths, possibly as high as 10-15 nm, particularly when excited above the bandgap.\(^ {257,351,352} \) Although, confirmation of

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**Figure 5-9:** CT state yield as a function of both P3HT \( (L_{P3HT}) \) and PPT6BT \( (L_{PPT6BT}) \) average contour lengths. (a) As the average contour length of P3HT chains increases, the CT state yield quickly rises and saturates at almost 20%. (b) Charge transfer is largely independent of PPT6BT average contour length (blue markers), although it drops significantly when the P3HT block chain length is short (gray markers). The black lines in both plots serve as a guide to the eye.
this would require studies of high molecular weight PPT6BT blocks that could induce aggregation or chain-folding, potentially generating additional donor-acceptor contacts.

Furthermore, based on results shown in Figure 5-9a, a decrease in CT state yield might be expected as the average chain length of PPT6BT decreases. Our results demonstrate that when PPT6BT chains are very short \( L_{\text{PPT6BT}} \approx 3 \text{ nm} \), confinement effects are not observed and charge transfer remains very efficient with a measured CT state yield of 23%. In fact, our results suggest that even a single repeat unit of PPT6BT does not result in an energetic penalty due to confinement of the charge transfer state. This can be understood by considering the statistical nature of polymers and the step-growth mechanism used to synthesize PPT6BT. In P3HT(29)-b-PPT6BT(2), although the PPT6BT \( X_n \) is 2, approximately 40% of P3HT(29)-b-PPT6BT(2) chains are likely to be functionalized by a single PPT6BT repeat unit, referred to as P3HT-PT6BT (see Section 5.5 for details). 

Furthermore, assuming these P3HT-PT6BT chains do not effectively generate CT states, we calculate an expected CT state yield for the different \( X_n \) values of PPT6BT present in all the block copolymers examined. If these P3HT-PT6BT chains did not result in efficient exciton dissociation, we would expect a significant drop in the CT state yield and a measured value as low as 12% (Table 5-3). Nevertheless, the CT state yield measured for P3HT(29)-b-PPT6BT(2) is close to 23%. Thus, confinement effects are not observed even with a single push-pull functionality.

**Table 5-3**: Fraction of P3HT-PT6BT chains and expected CT state yield assuming \( D = 2 \)

<table>
<thead>
<tr>
<th>PPT6BT ( X_n )</th>
<th>( x_p^a )</th>
<th>Expected CT(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.39</td>
<td>12%</td>
</tr>
<tr>
<td>5</td>
<td>0.18</td>
<td>18%</td>
</tr>
<tr>
<td>6</td>
<td>0.15</td>
<td>18%</td>
</tr>
<tr>
<td>10</td>
<td>0.09</td>
<td>19%</td>
</tr>
</tbody>
</table>

\(^a\) fraction of mono-functionalized P3HT chains; \(^b\) expected CT state yield if no CT observed from PPT6BT \( X_n = 1 \)
It has been shown that excited states generated on push-pull polymers are polarized and have significant charge transfer character.\textsuperscript{257,353-358} In a recent study comparing optoelectronic properties of conjugated homopolymers and push-pull polymers, it was found that the energy gap reduction with increasing oligomer chain length was much less pronounced in push-pull polymers.\textsuperscript{257} In conjugated homopolymers such as P3HT, it appears that intramolecular delocalization is required to promote efficient exciton dissociation to a charge transfer state. Nevertheless, due to the electronically different building blocks of push-pull polymers, excited states located along PPT6BT chains are polarized. Our results indicate that an extended conjugation length is not necessary for efficient charge transfer.

Oligomeric non-fullerene acceptors used in high-performance OPV devices consist of roughly 10 aromatic rings arranged in an alternating electron-rich/ electron-deficient pattern. Their architecture is reminiscent of low molecular weight push-pull polymers, making them push-pull oligomers. In P3HT-\textit{b}-PPT6BT, when the PPT6BT block is very short, ~3.3 nm on average, charge transfer appears to be just as efficient as when the chains are ~ 16 nm long. This suggests that devices incorporating push-pull oligomers will be able to generate free charges efficiently despite the limited conjugation length of the electron acceptor.

5.7 Conclusion

Using conjugated block copolymers composed of a conjugated homopolymer electron donor covalently linked to a push-pull polymer electron acceptor, this study examines the effect of polymer chain length on exciton diffusion and dissociation. An exciton diffusion length of ~ 2.5 nm is calculated for P3HT chains in chloroform solution. This corresponds to the approximate distance along the chain an exciton can travel before reaching a dihedral angle of 45°. This suggests
a sharp twist in chain disrupts exciton transport and more planar materials may facilitate longer
exciton diffusion lengths.

By quantifying intramolecular charge transfer as a function of the P3HT and PPT6BT block
average contour lengths, fundamental differences between conjugated homopolymers and push-
pull polymers are investigated. Our results demonstrate that in conjugated homopolymers, such as
P3HT, a conjugation length > 3 nm is required for efficient exciton dissociation. Below this contour
length, confinement of the charge transfer state wave function introduces an energetic penalty and
inhibits efficient charge transfer. In push-pull polymers, such as PPT6BT, efficient charge transfer
is observed even with very low chain lengths (≤ 3 nm). We suspect this is facilitated by the charge
transfer character of excited states along a polymer chain composed of alternating electron-
rich/electron-deficient units. Thus, we demonstrate that the push-pull character eliminates chain
length effects on exciton dissociation and in fact, enables single-site exciton dissociation.

This chapter is adapted from:

Chapter 6

Proposed Future Experiments, Summary, and Outlook

6.1 Proposed Future Experiments

Throughout this dissertation, we have established the use of conjugated block copolymers as interesting model systems. We have demonstrated that these materials can be judiciously designed for hypothesis-driven research to elucidate fundamental structure-property relationships regarding charge and energy transfer within organic materials. Nevertheless, we have only scratched the surface; there are virtually endless different block copolymer architectures that can be designed for interesting experiments. Here, we propose a few of the most logical extensions of this work.

Examining Low-Loss Organic Photovoltaics Using Conjugated Block Copolymers

High-performance organic photovoltaic devices can achieve very high external quantum efficiencies (EQE) and internal quantum efficiencies (IQE) that approach 100%.\textsuperscript{52,62,359,360} In these devices, nearly all absorbed photons are converted to free charges that are collected at the electrodes and thus, short-circuit current ($J_{SC}$) values are effectively limited only by absorbance of the active layer. Nevertheless, overall efficiencies of OPVs remain limited due in part to relatively high energy loss ($E_{loss}$). $E_{loss}$ of a photovoltaic cell is defined as the energy difference between the exciton ($E_{SI}$) and open-circuit voltage ($eV_{oc}$).

Donor-acceptor pairs utilized in high-performance OPV devices often have a significant energy offset of approximately 0.3 eV between the optical gap and the energy of the charge transfer
state \((E_{SI} - E_{CT})\). This is thought to provide a driving force for charge transfer.\(^3,106\) Additionally, empirical observations made by Janssen and coworkers have established an additional \(-0.6\ \text{eV}\) energy loss between \(E_{CT}\) and \(eV_{OC}\) that appears to be universal across many OPV devices, regardless of photoactive materials and active layer morphology.\(^{106}\) This additional loss is attributed to radiative and non-radiative recombination following exciton dissociation to a charge transfer state. Due to very low electroluminescence of most conjugated polymers, it is typically thought that non-radiative losses dominate this additional 0.6 eV energy loss.\(^{261,361}\) There are two components to the total \(E_{loss}\): 1) losses due to charge generation, \(E_{SI} - E_{CT}\), and 2) losses due to charge recombination, \(E_{CT} - eV_{OC}\) (Figure 6-1a).

With \(E_{SI} - E_{CT}\) values frequently around 0.3 eV and \(E_{CT} - eV_{OC}\) values typically around 0.6 eV, many high-performance OPV devices have an \(E_{loss}\) around 0.9 eV. There are examples of high-performance devices with low energy losses between the optical gap and charge transfer state, but material requirements that enable high EQEs with low driving forces remain quite elusive. Furthermore, the origins of performance-limiting non-radiative energy losses are poorly understood.\(^{261,361,362}\) It is particularly desirable to minimize these non-radiative losses as they are presumably more detrimental to device performance than radiative losses. In principle, photons emitted upon radiative recombination can be reabsorbed and split into free charges. Thus, radiative recombination does not necessarily result in significantly reduced photovoltaic performance.

We propose a series of donor-acceptor block copolymers to explore the complex interplay between driving forces, energy loss, short-circuit current, and open-circuit voltage. The block copolymers consist of a P3HT electron donor covalently linked to a push-pull polymer electron acceptor, yielding: poly(3-hexylthiophene)-block-poly-\(((9-(9-heptadecanyl)-9H-carbazole)-1,4-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl)\) (P3HT-b-PCDTBT), poly(3-hexylthiophene)-block-poly-\(((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl)\) (P3HT-b-PFTBT), and poly(3-hexylthiophene)-block-poly-\(((2,5-
dihexylphenylene)-1,4-diyl -alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) (P3HT-b-PPDTBT). By making small perturbations to the electron-rich unit of the acceptor block, we make small adjustments to the electronic properties of the materials and intramolecular donor-acceptor heterojunction. Importantly, we expect that high chemical similarities between the materials will result in similar solid state morphology. Thus, photovoltaic performance can be compared across different materials and results attributed predominately to differences in the electronic structure rather than film morphology.

**Preliminary Results:**

We fabricated OPV devices incorporating the block copolymers as the single active layer material. Similar processing conditions were employed for all devices in an effort to produce consistent film morphologies. Active layer morphology was investigated using resonant soft X-ray
scattering (RSoXS) and grazing-incidence wide-angle X-ray scattering (GIWAXS). Initial assessment of scattering profiles suggests qualitatively similar active layer morphology.

RSoXS can be used to characterize phase separation in polymer films with limited phase contrast.\textsuperscript{363} We use RSoXS to compare average domain spacing in the block copolymer films. Scattering profiles of all the block copolymers are qualitatively similar with a broad peak around 0.02 Å\textsuperscript{-1}, corresponding to a characteristic domain spacing of roughly 20-25 nm (Figure 6-2a).\textsuperscript{363} GIWAXS can be used to characterize preferential orientation of P3HT crystallites within the polymer film. Similar to RSoXS results, scattering profiles of all the block copolymers are qualitatively similar. GIWAXS vertical line profiles suggest P3HT chains preferentially oriented “edge-on” with respect to the substrate (Figure 6-2b).\textsuperscript{364} More in-depth morphological characterization is warranted, including: rocking scans from X-ray diffraction to obtain more comprehensive characterization of the orientation of P3HT crystallites, transmission electron microscopy (TEM) to examine morphology in real-space, and polarized-RSoXS to examine molecular orientation at the donor-acceptor interface.
Initial device results are presented in Table 6-1 and Figure 6-3. Data for P3HT-b-PFTBT devices is from a previously published study. Devices incorporating P3HT-b-PFTBT as the single active layer material exhibit the highest performance, while devices incorporating P3HT-b-PPDTBT perform more modestly, and devices incorporating P3HT-b-PCDTBT perform poorly. An in-depth study investigating the molecular origins of vastly different device performance resulting from slight chemical modifications would be very interesting. Qualitative inspection of suggests that while the active layers appear to have similar morphologies, devices have quite different $V_{OC}$ and $J_{SC}$ values. This begins to indicate that the electronic properties of these materials could yield information regarding both $E_{loss}$ and current generation processes in organic photovoltaic devices.

**Figure 6-2:** Morphology characterization of block copolymer thin films. (a) Resonant soft X-ray scattering profiles presented as scattering intensity ($I$) multiplied by the scattering vector ($q$) squared as a function of $q$. Data is offset for clarity. (b) Grazing-incidence wide-angle X-ray scattering (GIWAXS) scattering profiles in the out of plane direction of the block copolymers presented as $I$ vs $q$. 
To examine whether charge generation or charge recombination dominates \( E_{loss} \), it is necessary to characterize \( E_{CT} \). As an initial estimate, we consider the \( E_{CT} \) values in chloroform solution calculated in Chapter 3. As discussed in Chapter 4, \( E_{CT} \) depends strongly on the dielectric constant \( (\varepsilon_0) \) of the surrounding environment. We have previously used constrained density-functional theory (CDFT) to calculate \( E_{CT} \) in the block copolymers as a function of solvent dielectric constant (Chapter 4). \( \varepsilon_0 \) of chloroform (4.81) is similar to that of a P3HT film (3.3).\textsuperscript{58}

### Table 6-1: OPV device characterization.

<table>
<thead>
<tr>
<th></th>
<th>Efficiency (%)</th>
<th>( J_{SC} ) (mA/cm(^2))</th>
<th>( V_{OC} ) (V)</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT-( b )-PCDTBT</td>
<td>0.3 ± 0.02</td>
<td>1.27 ± 0.1</td>
<td>0.92 ± 0.03</td>
<td>0.28 ± 0.01</td>
</tr>
<tr>
<td>P3HT-( b )-PFTBT(^a)</td>
<td>3.1 ± 0.4</td>
<td>5.0 ± 0.3</td>
<td>1.23 ± 0.02</td>
<td>0.33 ± 0.01</td>
</tr>
<tr>
<td>P3HT-( b )-PPDTBT</td>
<td>1.0 ± 0.1</td>
<td>2.73 ± 0.1</td>
<td>1.03 ± 0.02</td>
<td>0.34 ± 0.02</td>
</tr>
</tbody>
</table>

\(^a\) From the literature\textsuperscript{144}

**Figure 6-3:** Current-voltage curves of OPV devices incorporating block copolymers in the active layer. P3HT-\( b \)-PFTBT data is taken from the literature.\textsuperscript{144}
Thus, we speculate $E_{CT}$ values in a chloroform environment calculated by CDFT may reasonably describe $E_{CT}$ values in block copolymer films.

Under these assumptions, we calculate very low (< 0.1 eV) driving forces for charge transfer ($E_{S1} - E_{CT}$, Table 6-2). This energetic offset yields losses due to charge generation. Thus, initial results suggest charge generation may not be a significant source of energy loss in these block copolymer devices. Energy loss due to charge recombination is characterized by $E_{CT} - eV_{OC}$. We estimate values of 0.9, 0.6, and 0.8 for $E_{CT} - eV_{OC}$ of P3HT-$b$-PCDTBT, P3HT-$b$-PFTBT, and P3HT-$b$-PPDTBT devices, respectively. These results begin to suggest that: 1) losses due to charge recombination could dominate $E_{loss}$ in these block copolymer devices; 2) devices incorporating P3HT-$b$-PFTBT may display significantly less recombination losses than P3HT-$b$-PCDTBT and P3HT-$b$-PPDTBT.

Table 6-2: Initial estimates for $E_{loss}$ and driving force for exciton dissociation in block copolymer OPV devices. All values presented in eV.

<table>
<thead>
<tr>
<th></th>
<th>Est. $E_{CT}^a$</th>
<th>$E_{S1} - eV_{OC}^b$</th>
<th>$E_{S1} - E_{CT}$</th>
<th>$E_{CT} - eV_{OC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT-$b$-PCDTBT</td>
<td>1.87</td>
<td>0.93</td>
<td>0.06</td>
<td>0.87</td>
</tr>
<tr>
<td>P3HT-$b$-PFTBT</td>
<td>1.83</td>
<td>0.73</td>
<td>0.10</td>
<td>0.63</td>
</tr>
<tr>
<td>P3HT-$b$-PPDTBT</td>
<td>1.86</td>
<td>0.92</td>
<td>0.09</td>
<td>0.83</td>
</tr>
</tbody>
</table>

$^a$ CDFT in chloroform; $^b$ optical gap of block copolymer

A closer examination of vastly different current values across the block copolymer devices may also be instructive. $E_{S1} - E_{CT}$ values presented in Table 6-2 suggest very low energetic driving forces for charge transfer of $\leq 0.1$ eV. To investigate this further, we characterize the EQE and IQE spectra of the devices. EQE is defined as the ratio of generated charges to incident light; IQE is defined as the ratio of generated charges to absorbed light. We measure significantly different EQEs and IQEs across the devices (Figure 6-4). IQE values were obtained using the transfer matrix formalism to calculate fraction of incident light absorbed by the active layer. Optical properties
of the block copolymers, $n$ and $k$, values were measured by Bryan Smith using spectroscopic ellipsometry. These preliminary results suggest there may be a correlation between $E_{S1} - E_{CT}$ and IQE. Although, our initial estimates for $E_{S1} - E_{CT}$ values span a range < 0.05 eV; it is surprising that such a small difference in driving force could yield such a significant difference in charge generation. These initial results lay the groundwork for what promises to be a very interesting investigation.

**Proposed Future Studies:**

First, more appropriate characterization of $E_{CT}$ will facilitate accurate characterization of $E_{S1} - E_{CT}$ and $E_{CT} - \psi_{OC}$. $E_{CT}$ can be measured using sensitive EQE measurements or photothermal deflection spectroscopy. Both of these techniques can be used to characterize sub-bandgap electronic transitions. Initial estimates suggest: 1) all block copolymer devices could have very low

![Figure 6-4: (a) External quantum efficiency (EQE) and (b) internal quantum efficiency (IQE) measurements of block copolymer OPV devices.](image)
$E_{SI} - E_{CT}$ values; and 2) very small differences in $E_{SI} - E_{CT}$ can result in significantly different efficiencies of charge generation (IQE). Additional characterization of other factors that influence device performance are warranted. In particular, characterization of charge mobility within the donor and acceptor domains. Local charge mobility can be probed using time-resolved terahertz conductivity measurements and bulk mobility can be probed through space-charge-limited current measurements or characterization of organic field-effect transistors. Further morphology characterization could also reveal subtle differences in film morphology between the block copolymers that may also contribute to different photovoltaic performance. An explanation for the different IQE values of the devices will facilitate closer examination into the origins of different $E_{loss}$ values.

Comparison between $E_{CT} - eV_{OC}$ values suggest that devices fabricated from P3HT-$b$-PFTBT may yield lower energy losses attributable to radiative and non-radiative charge recombination (0.6 eV) relative to devices incorporating P3HT-$b$-PCDTBT (0.9 eV) and P3HT-$b$-PPDTBT (0.8 eV). Investigation into the origin of this trend could yield very interesting results. Non-radiative losses are not well understood, but can be characterized indirectly using electroluminescence measurements. Radiative losses can be characterized using $J_{SC}$ and $E_{CT}$ measurements in addition to the reorganization energy.\footnote{360,361} These results could provide useful information regarding the molecular origins of non-radiative coupling between the charge transfer state and ground state that are detrimental to photovoltaic performance.

In summary, preliminary results suggest an in-depth study comparing photovoltaic performance of OPV devices incorporating these block copolymers will be very interesting. There are only subtle differences in the molecular structure between the block copolymers which yields qualitatively similar thin film morphologies. Despite mostly similar chemical and morphological properties, OPV device performance is vastly different. Small differences in chemical structure
yielding large differences in performance embodies the fundamental principle of organic electronics and presents an excellent opportunity for future research.

**Tuning Electronic Coupling Between Push-Pull Polymers to Examine Effects on Intramolecular Charge and Energy Transfer**

Materials utilized in high-performance OPVs are becoming increasingly complex, now including: push-pull polymers with tailored molecular orbital energies, nonfullerene acceptors that permit extensive design possibilities for the electron acceptor, and “two-dimensional” conjugated polymers with conjugated side chains. As a consequence, properties and processes at donor-acceptor heterojunctions are also becoming increasingly complex and convoluted. This dissertation establishes block copolymers as useful model systems to examine processes occurring at a donor-acceptor interface. Nevertheless, materials utilized in this work consist of a P3HT conjugated homopolymer electron donor covalently linked to a push-pull polymer electron acceptor. Extensive experimental work has demonstrated that linking the acceptor “push” or “pull” unit directly to P3HT has dramatically different effects on electronic coupling at the donor-acceptor interface.\textsuperscript{148,152} This in turn has a profound impact on charge transfer and recombination processes at the donor-acceptor interface. It may be informative to examine electronic coupling at the donor-acceptor interface between two push-pull polymers using a fully conjugated donor-acceptor block copolymer incorporating these more complex architectures.

All polymer solar cells incorporating a poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b’]dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-2-carboxylate-2,6-diyl)] (PTB7Th) electron donor blended with a poly[(N,N’-bis(2-octyldecylnaphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl)-alt-5,5’-(2,5-thiophene)] PNDIT electron acceptor have achieved efficiencies of nearly 6%.\textsuperscript{92} Nevertheless, preliminary results from
our group suggest devices incorporating a PTB7Th-b-PNDIT block copolymer as the photoactive material do not surpass 1% power conversion efficiency. PTB7Th-b-PNDIT block copolymer synthesis and device fabrication was performed by Dr. Youngmin Lee. Despite prior evidence suggesting conjugated block copolymers can microphase separate and therefore be used to enhance performance of OPV devices, initial results suggest that covalently linking the two push-pull polymers is detrimental to device performance.\textsuperscript{144} We speculate this is the result of strong electronic coupling at the donor-acceptor interface. PTB7Th is a push-pull polymer made up of alternating highly electron-rich benzodithiophene (BDT) and moderately electron-deficient thienothiophene (TT) moieties. PNDIT is also a push-pull polymer made up of electron-rich thiophene (T) and highly electron-deficient naphthalene diimide (NDI) moieties. These materials provide an excellent opportunity to systematically investigate the influence of electronic coupling at the donor-acceptor interface between two push-pull polymers. To this end, we propose the design, synthesis, and characterization of three donor-acceptor block copolymers in which electronic coupling between the donor and acceptor is systematically tuned.

Structures in Figure 6-5 will be targeted. We will attempt to leverage an exciting new synthesis technique, direct (hetero)arylation polymerization (DHAP). DHAP has been developed over the past several years by Leclerc and coworkers for the synthesis of certain conjugated polymers.\textsuperscript{366-368} In this reaction, aromatic C-H bonds are directly coupled with aryl halide bonds (Scheme 6-1). While it is less developed and provides less chemical versatility compared to Suzuki and Stille coupling, DHAP eliminates additional reaction steps necessary to introduce boronic ester or alkyl stannane functional groups. Importantly, DHAP is amenable to the synthesis of thiophene-based polymers and, when applicable, eliminates the need for highly toxic organotin reagents. The reaction requires an “active C-H bond” that is pseudo acidic. For example, the C-H bond at the 2 or 5 position of a thiophene ring. Any other aromatic C-H bonds present in the reaction mixture must be significantly less reactive than this “active C-H bond”.
We propose a synthesis scheme for the targeted block copolymer structures using a series of DHAP reactions. First, PTB7Th and two different batches of PNDIT homopolymer will be synthesized to examine the effect of electronic coupling between two push-pull polymers.

**Figure 6-5:** Targeted structures that will be synthesized to examine the effect of electronic coupling between two push-pull polymers.

**Scheme 6-1:** Direct (hetero)arylation polymerization forms $sp^2$ hybridized carbon-carbon bonds by coupling a non-functionalized aromatic core (A) with a dihalogenated aromatic core (B).

$$n \text{H-A-H} + n \text{X-B-X} \rightarrow \text{A-B}_n + 2n \text{HX}$$

We propose a synthesis scheme for the targeted block copolymer structures using a series of DHAP reactions. First, PTB7Th and two different batches of PNDIT homopolymer will be
synthesized using two independent (DHAP) reactions; these materials will later be used as macroreagents to form the block copolymers (Scheme 6-2). In an attempt to maximize the likelihood of protonated chain ends, excess BDT will be used in the synthesis of macroreagent 1. Next, two different PNDIT macroreagents will be synthesized using an excess of NDI (2) or T (3) monomers to maximize the likelihood of brominated (2) or protonated (3) chain ends.

**Scheme 6-2:** Proposed synthesis scheme for macroreagents 1, 2, and 3 utilizing DHAP. Only expected major products are shown.

![Scheme 6-2](image)

PTB7Th-b-PNDIT triblock copolymer will be synthesized using a DHAP reaction between 1 and 2. We will attempt to incorporate a precise 1:2 stoichiometric ratio of macroreagents 1 and 2 to facilitate triblock copolymer formation. Nevertheless, the possibility of synthesizing diblock or multiblock copolymers will remain. Importantly, using this scheme the coupling at the donor-acceptor interface is controlled regardless of whether diblock or multiblock copolymers form.
The second and third targeted materials are PTB7Th-Ph-PNDIT and PTB7Th-bPh-PNDIT; a single phenyl or biphenyl moiety will be used as a conjugated linking unit between 1 and 3 in a two-step reaction (Scheme 6-3). In the synthesis of PTB7Th-\textit{b}-PNDIT, first, precisely 2.0 equivalents of 1-bromo-4-iodobenzene will react with 1 in a DHAP reaction, to yield 4. We suspect the greater reactivity of iodine with respect to bromine groups on the phenyl ring will encourage formation of 4 and prevent two chains of 1 from reacting with a single 1-bromo-4-iodobenzene. Once this reaction has been allowed to go to completion, the reactor will be charged with 2.0 equivalents of 3 which should result in PTB7Th-Ph-PNDIT. Synthesis of PTB7-bPh-PNDIT will be synthesized using an analogous reaction. 1 will react with 2.0 equivalents of 4-bromo-4’-iodobiphenyl to yield 5. Then 2.0 equivalents of 3 will be added to yield PTB7-bPh-PNDIT. It is possible that synthesis of these structures will require extensive optimization of reaction conditions. Nevertheless, DHAP is a very interesting and exciting technique that we would like to explore and leverage for the synthesis of conjugated block copolymers with and without aromatic linking groups.

**Scheme 6-3**: Proposed synthesis scheme for block copolymers PTB7Th-\textit{b}-PNDIT, PTB7Th-Ph-PNDIT, and PTB7Th-bPh-PNDIT.
Once block copolymers synthesis is complete, we will examine the effects of tuning electronic coupling at the donor-acceptor interface, specifically how it influences charge transfer. This will be accomplished using a UV-vis spectrophotometer and fluorimeter equipped with a photomultiplier tube with detection limits extending into the near-infrared region. We will apply the same procedure described throughout this dissertation to examine processes occurring at the donor-acceptor interface. Specifically, we will examine the influence of electronic coupling between donor and acceptor on charge and energy transfer. These interesting materials could be used in many other experiments as well. Transient absorption spectroscopy could be used to examine polaron formation in isolated chains and other excited state processes. Nanoparticles could be synthesized and steady state and transient absorption spectroscopy could be used to examine the influence of intermolecular interactions on a block copolymer composed of two push-pull polymers. The materials could also be cast into films and used in the active layer of OPV devices to examine the influence of electronic coupling at the donor-acceptor heterojunction on photovoltaic performance. While optimization of the synthetic protocol for these materials may prove challenging, systematically tuning electronic coupling between two push-pull polymers will yield interesting model materials to study charge and energy transfer occurring at a donor-acceptor interface.

Investigating Fundamental Photophysics of a Triblock Copolymer with an Energetic Cascade

It has been proposed that cascading energy levels within the active layer of an OPV device may facilitate charge separation.\textsuperscript{78,81} This process has also been observed in photoactive, covalently linked small molecules.\textsuperscript{42,45} It would be very interesting to study the photophysics of a triblock copolymer designed to funnel charges from one chain end to the other. Due to the complex
photophysics and synthetic limitations of conjugated polymers, realizing such a material will not be trivial. We propose the structure in Figure 6-6a, poly(3-hexylthiophene)-block-poly(2,6-(4,4-dialkyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene)-block-poly-((2,5-dihexylphenylene)-1,4-diyl-alt-[4,7-bis(3-hexylthiophen-5-yl)-2,1,3-benzothiadiazole]-2',2'-diyl) (P3HT-b-PCPDT-b-PPT6BT), as a possible candidate.

P3HT-b-PCPDT-b-PPT6BT will be synthesized in three steps (Scheme 6-4). In the first reaction, P3HT will be synthesized using a KCTP reaction with an external initiator, o-tolyl-Ni(dppp)-Br according to a previously reported method.\textsuperscript{197} Importantly, external initiation will ensure unidirectional growth by capping the non-living chain end with an o-methylphenyl group. Once all P3HT monomer has been consumed, the reactor will be charged with PCPDT-MgCl monomer. The reaction will be quenched with acid, yielding o-tolyl-P3HT-b-PCPDT-H.\textsuperscript{197} In the second reaction, the PCPDT chain end will be brominated using NBS.\textsuperscript{369} In the third reaction, PPT6BT will be added on using a Suzuki polycondensation reaction, yielding the triblock

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structure.png}
\caption{(a) Proposed structure of a triblock copolymer with an energetic cascade. (b) A cartoon illustrating the possibility of charge separated states in isolated block copolymer chains.}
\end{figure}
copolymer P3HT- \(b\)-PCPDT- \(b\)-PPT6BT. Formation of multiblock copolymers cannot be ruled out, but connectivity between the blocks will be controlled.

**Scheme 6-4:** Proposed synthesis scheme for P3HT- \(b\)-PCPDT- \(b\)-PPT6BT.

We speculate that this triblock copolymer will generate an energetic cascade in which holes are funneled from PPT6BT to PCPDTBT to P3HT. Expected energy level characterization is presented in Table 6-3. There are two polymer-polymer interfaces in the triblock copolymer; one junction joins P3HT and PCPDT, the other joins PCPDT and PPT6BT. \(E_{si}\) and HOMO values for PCPDT were obtained from the literature.\(^{107}\) DFT HOMO calculations for P3HT and PPT6BT were completed by Jason Munro. \(E_{CT}\) values are approximated assuming \(E_{CT}\) can be estimated to a first approximation as by the energy difference between the donor HOMO and acceptor LUMO plus an additional energetic term to account for Coulombic binding.\(^{106}\) Using these assumptions, we expect roughly equivalent driving forces of approximately 0.3 eV for hole transfer from PPT6BT to
PCPD T and PCPDT to P3HT. According to conclusions drawn in Chapter 4, these driving forces may enable an efficient route for holes to travel from PPT6BT to P3HT. Additionally, we estimate a very significant driving force for electron transfer from P3HT to PCPDT. Furthermore, inspection of absorbance and emission spectra of the individual homopolymers, we believe there could be efficient energy transfer from both P3HT and PPT6BT to PCPDT. It is unclear how these processes may influence hole transfer.

**Table 6-3:** Energy level estimations of P3HT-\textit{b}-PCPDT-\textit{b}-PPT6BT. All values are in eV.

<table>
<thead>
<tr>
<th>Donor</th>
<th>Acceptor</th>
<th>Est. $E_{CT}$</th>
<th>$E_{SID} - E_{CT}$</th>
<th>$E_{SIA} - E_{CT}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT</td>
<td>PCPDT</td>
<td>1.5</td>
<td>0.8</td>
<td>0.3</td>
</tr>
<tr>
<td>PCPDT</td>
<td>PPT6BT</td>
<td>1.9</td>
<td>-0.1</td>
<td>0.3</td>
</tr>
</tbody>
</table>

HOMO and $E_{SI}$ values for PCPDT were obtained from the literature\cite{197}

P3HT-\textit{b}-PCPDT-\textit{b}-PPT6BT will be examined using the procedure we have developed to monitor charge transfer within individual block copolymer chains. As discussed above, this will be accomplished using a UV-vis spectrophotometer and fluorimeter equipped with a photomultiplier tube with detection limits extending into the near-infrared region. Another very interesting experiment would be to examine whether or not charge separation occurs. If holes are funneled to P3HT, electrons are funneled to PPT6BT, and all blocks have a contour length on the order of 10 nm, this could result in electron-hole separation of roughly 10-30 nm along a single block copolymer chain (Figure 6-6b). Transient absorption spectroscopy will be used to examine whether or not signatures of hole polarons are present in isolated triblock copolymer chains. Examining the photophysics of a triblock copolymer designed to incorporate an energetic cascade will be an exciting project, particularly the possibility of observing charge separated states in isolated block copolymer chains.
6.2 Summary and Future Outlook

This dissertation establishes and demonstrates the use of conjugated block copolymers as model systems for fundamental studies of the charge generation mechanism in organic photovoltaics. In Chapter 3, we establish block copolymers as interesting and effective model systems. The covalent linkage enables studies of model donor-acceptor interfaces at length scales ranging from isolated chains, where the solvent establishes the local environment, to nanoparticles, which offer a way to control intermolecular interactions, to bulk films with model morphologies. Small perturbations in the chemical structure reveal consequences to charge and energy transfer in donor-acceptor systems.

In Chapter 4, we adjust the molecular structure at the donor-acceptor interface and dielectric environment to systematically tune energy levels that make up the driving force for charge transfer. In isolated block copolymer chains, a significant energetic offset is necessary to facilitate exciton dissociation at a donor-acceptor interface. In block copolymer films, intermolecular interactions are introduced and charge transfer is in enhanced, even in materials with a low energetic driving force. This demonstrates the importance of both enthalpic and entropic driving forces for exciton dissociation. In Chapter 5, we use block copolymers to examine the influence of chain length on exciton dissociation. We find that a “push-pull” architecture can facilitate efficient charge transfer in materials with limited conjugation lengths.

It is our hope that results established throughout this work will help further development of organic electronics, particularly organic photovoltaics. Fundamental studies in this field are challenging and often employ films of conjugated materials with complex, difficult to characterize morphological and energetic properties. This work utilizes an alternate approach. We design simple, well-defined systems for fundamental studies in solution, removing variables that arise in the solid state. Our experimental procedures can be adapted to future studies. Establishing a
comprehensive understanding of charge and energy transfer within organic materials, and then using this to guide the rational design of new materials for organic electronics is an enormous task. We hope this dissertation can contribute to this effort.
Appendix

Letters of Permission for Use of Copyright Materials and Acknowledgement of Funding Sources

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Tuning the synthesis of fully conjugated block copolymers to minimize architectural heterogeneity

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Publications
1. Aplan, M.P.; Lee, Y; Munro, J; Grieco, C; Seibers, Z; Kilbey, S.M.; Dabo, I; Wang, Q; Asbury, J.B.; Gomez, E.D. “Revealing the importance of energetic and entropic contributions to the driving force for charge photogeneration”, Submitted. 2018.

Presentations

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