DESIGN, SYNTHESIS, AND CHARACTERIZATION OF ELECTRON
TRANSPORTING DPP-BASED COPOLYMERS FOR APPLICATION IN ORGANIC
ELECTRONICS

A Dissertation
Presented to
The Academic Faculty

by

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In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy in the
School of Chemistry and Biochemistry

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DESIGN, SYNTHESIS, AND CHARACTERIZATION OF ELECTRON TRANSPORTING DPP-BASED COPOLYMERS FOR APPLICATION IN ORGANIC ELECTRONICS

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<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>( \sigma )</td>
<td>Conductivity</td>
</tr>
<tr>
<td>( \mu )</td>
<td>Charge carrier mobility, ( \text{cm}^2/\text{V} \cdot \text{s} )</td>
</tr>
<tr>
<td>( \mu_h )</td>
<td>Hole mobility mobility, ( \text{cm}^2/\text{V} \cdot \text{s} )</td>
</tr>
<tr>
<td>( \mu_e )</td>
<td>Electron mobility, ( \text{cm}^2/\text{V} \cdot \text{s} )</td>
</tr>
<tr>
<td>( \pi )</td>
<td>Bonding orbital</td>
</tr>
<tr>
<td>( \pi^* )</td>
<td>Antibonding orbital</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>Wavelength, nm</td>
</tr>
<tr>
<td>( \lambda_{\text{max}} )</td>
<td>Max wavelength, nm</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>BBL</td>
<td>Poly(benzobisimidazobenzophenanthroline)</td>
</tr>
<tr>
<td>BDT</td>
<td>Benzodithiophene</td>
</tr>
<tr>
<td>BGBC</td>
<td>Bottom gate/bottom contact</td>
</tr>
<tr>
<td>BGTC</td>
<td>Bottom gate/top contact</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk heterojunction</td>
</tr>
<tr>
<td>C*</td>
<td>Volumetric capacitance</td>
</tr>
<tr>
<td>C_{ox}</td>
<td>Capacitance of gate dielectric</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>d</td>
<td>Channel thickness, nm</td>
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<tr>
<td>D-A</td>
<td>Donor-acceptor</td>
</tr>
<tr>
<td>DPP</td>
<td>Diketopyrrolopyrrole</td>
</tr>
<tr>
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<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
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<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<td>$M_n$</td>
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<tr>
<td>MoO$_x$</td>
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<tr>
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<td>-------------</td>
</tr>
<tr>
<td>NDI</td>
<td>Naphthalene diimide</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>OECT</td>
<td>Organic electrochemical transistor</td>
</tr>
<tr>
<td>OFET</td>
<td>Organic field-effect transistor</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic light emitting diode</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic photovoltaic</td>
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<td>$\Delta T$</td>
<td>Change in transmission</td>
</tr>
<tr>
<td>TA</td>
<td>Transient absorption</td>
</tr>
<tr>
<td>TCB</td>
<td>1,2,4-trichlorobenzene</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>TGBC</td>
<td>Top gate/bottom contact</td>
</tr>
<tr>
<td>TGTC</td>
<td>Top gate/top contact</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet photoelectron spectroscopy</td>
</tr>
<tr>
<td>UV-vis</td>
<td>Ultraviolet-visible spectroscopy</td>
</tr>
<tr>
<td>$V_D$</td>
<td>Source-drain voltage, V</td>
</tr>
<tr>
<td>$V_G$</td>
<td>Gate voltage, V</td>
</tr>
<tr>
<td>$V_{\text{max}}$</td>
<td>Max voltage, V</td>
</tr>
<tr>
<td>$V_{\text{OC}}$</td>
<td>Open circuit voltage, V</td>
</tr>
<tr>
<td>$V_{\text{Th}}$</td>
<td>Threshold voltage, V</td>
</tr>
<tr>
<td>$W$</td>
<td>Channel width, nm</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zinc oxide</td>
</tr>
</tbody>
</table>
SUMMARY

Organic semiconducting polymers continue to be developed for electronics because of their low-cost and high processability which has led to large-area deposition techniques. That also have the advantage of being mechanically pliant, helping to realize the goal of flexible electronics. There are two main areas of research regarding semiconducting polymers: p-type (hole transporting) and n-type (electron transporting). In the past, there has been more development in the design and synthesis of p-type polymers over n-type due to their increased stability. The current drive is to design n-type materials with high electron mobilities that compare to the high hole mobilities of their p-type counterparts.

This thesis covers the development of n-type donor-acceptor polymers based on diketopyrrolopyrrole (DPP) moieties for application in OPVs, OFETs, and OECTs. Chapter 2 includes the complete design, synthesis, characterization, and electrical performance of DPP copolymerized with benzodithiophene (BDT). A family of polymers, pDPPTh-OSThBDT (P1), pDPPTz-OThBDT (P2), and pDPPTz-OSThBDT (P3), was designed to determine the impact of two key structural features, thiazole-flanked DPP and thioalkyl side chains, on the stabilization of frontier molecular orbital energy levels and electrical properties. When the two structural features are used together, they have been shown to have a combinatorial effect on energy level stabilization. Despite modest mobilities, OFET devices revealed the thiazole-flanked DPP is essential in achieving the desired n-type performance. OPV performance suffered when these materials were used with the common acceptor PC71BM due to poor miscibility. In the same manner,
photophysical tests showed that $\text{P3}$ demonstrates the strongest polaron and exciton formation, with $\text{P1}$ demonstrating less and $\text{P2}$ showing the least.

Chapter 3 covers the design of an n-type material for OECTs, a field with an even larger n-type to p-type discrepancy. To date there are only two main examples of n-type polymers for this application, with limited side chain development. This chapter coupled thiazole-flanked DPP containing a linear methyl ester side chain to bithiophene to yield $\text{pOMeDPPTz-BTh}$. The backbone was chosen as it has proven to generate high electron mobilities in OFETs, as demonstrated by the average electron mobility of $1.19 \times 10^{-2}$ cm$^2$/V·s. To obtain the desired OECT performance however, the side chain must be able to induce electronic charges through the collection of ionic charges from an aqueous electrolyte. Unsurprisingly, the methyl ester did not provide sufficient stability and ionic induction in aqueous environments. By saponifying the methyl ester into a potassium salt, the newly formed $\text{pK^+DPPTz-BTh}$ was found to be water soluble. Once filmed, an acid soak resulted in $\text{pCOOH-DPPTz-BTh}$ which has stronger hydrogen bonding and should result in the desired OECT performance.
CHAPTER 1. INTRODUCTION

1.1 Designing Organic Semiconducting Polymers

Organic semiconducting materials populate a well-established field in electronic devices for a multitude of benefits; unlike their inorganic counterparts, organic semiconductors are more economical, solution processable, and have the potential to generate flexible electronics due to the readily functionalized and fine-tuning capabilities of organic materials\(^1\)-\(^3\). The flexibility and solution processability allow for large scale device fabrication through processes such as roll-to-roll and inkjet printing, without the need for excessive processing temperatures that silicon-based electronics require\(^4\)-\(^9\). Though it is unlikely organic electronics will ever completely replace inorganic based electronics, the low-cost, light-weight, and easy processing of organic semiconductors make a compelling argument for the continued research into designing new organic materials as well as improving deposition methods.

Development in the field has already led to a myriad of applications of organic semiconductors into devices such as organic photovoltaics (OPVs)\(^10\)-\(^15\), organic light emitting diodes (OLEDs)\(^16\)-\(^19\), organic field effect transistors (OFETs)\(^20\)-\(^25\), energy storage systems\(^26\)-\(^28\), and sensors\(^29\)-\(^33\). Figure 1 depicts three examples of printed or flexible electronic devices used today that utilize organic semiconductors. Advances in organic semiconductors has led to wearable sensors, flexible commercialized solar panels, and conformal displays.
The focus of this thesis is to explore the optical, electronic, and morphological effects of various structural changes on electron transporting semiconducting polymers for various devices. The following will provide an introduction on semiconducting polymers and the devices they are applied in within this manuscript.

1.1.1 Molecular Design Features

The field of organic semiconductors has been dominated by two main subjects: conjugated small molecules and conjugated polymers. Conjugated small molecules are advantageous for their relatively easy synthesis and purification, as well as their ability to form homogenous, tightly packed arrays which can result in high charge carrier mobilities$^{37-39}$. On the other hand, conjugated polymers are often more soluble in common solvents, have smaller band gaps, and possess more attractive mechanical and thermal properties$^{40-44}$. What makes these materials attractive for electronic devices is their ability to transport charges through the conjugated bonds. Conjugation refers to a system of overlapping p orbitals, which allow electrons to be delocalized$^{45}$. This delocalization is what makes conductivity ($\sigma$) possible in organic materials once an outside bias is applied or the material is doped. Conductivity is directly related to the number of charges generated and their relative mobility ($\mu$).
With the addition of each conjugated bond \((n)\), new bonding \((\pi)\) and antibonding \((\pi^*)\) orbitals are added to the system. As Figure 2 depicts, the spacing between the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) gets smaller with the addition of each orbital. As \(n\) approaches infinity, the spacing between orbitals becomes difficult to distinguish and eventually they take on a similar delocalized band structure as that of inorganic materials. The delocalized band for occupied orbitals is known as the valence band and the unoccupied orbital band is the conduction band. The space between the top of the valence band (HOMO) and the bottom of the conduction band (LUMO) makes up the band gap \((E_g)\). The size of \(E_g\) plays a significant role in how much energy is required to generate excited charges, which directly correlates to the number of charge carriers that are produced. Details on the how to characterize \(E_g\) will follow in a later section.
Figure 2. Effect of conjugation length, n, on frontier molecular orbital energy levels and subsequent band formation as conjugation length approaches infinity.

This ability to minimize $E_g$ through polymerization is a huge contributor to the popularity of semiconducting polymers. Since the discovery of conducting polyacetylene in the 1970s$^{46}$, the field of semiconducting polymers has continued to grow, expanding on design principles for more effective charge transport and ease of processing. A major milestone was the introduction of conjugated aromatic rings into polymer backbones. Aromatic rings can planarize the polymer backbone, which is required for p orbitals to overlap and delocalize electrons between adjacent rings$^{47, 48}$. This subsequently leads to enhanced intramolecular charge transport down the individual polymer chains as well as intermolecular transport through $\pi-\pi$ stacking (Figure 3).
Figure 3. Illustration of typical charge transport along polymer backbone intramolecularly and between adjacent polymer chains intermolecularly.

There are myriad examples of aromatic rings that have been employed in various combinations to yield both hole and electron transporting semiconductors ranging from simple aromatic rings such as benzene\textsuperscript{49, 50} and thiophene\textsuperscript{51-53} to more complex derivatives such as benzodithiophene (BDT)\textsuperscript{54-57} and naphthalene diimide (NDI). A wide array of common donor (electron-rich/electron transporting) and acceptor (electron-poor/hole transporting) moieties is depicted in Figure 4. Examples of polymers employing these units began with homogenous polymers (ie. the same unit repeating), such as polythiophene. A hinderance of using homogenous polymers however, meant that modifications could alter the band gaps slightly, through the introduction of electron donating and withdrawing units,
but it was difficult to drastically alter both the HOMO and LUMO of a single moiety, and by extension the polymer.

![Donor Moieties](image)

![Acceptor Moieties](image)

**Figure 4.** Examples of common donor (top) and acceptor (bottom) monomers used in semiconducting polymers.

This progressed into the development of donor-acceptor (D-A) polymers, which are comprised of alternating D-A units that when copolymerized together, exhibit a smaller band gap (**Figure 5**). The polymer $E_g$ lowers as a result of the donor unit contributing to the HOMO while the acceptor contributes to the LUMO, thus reducing the band gap relative to either monomer individually. This enables scientists to individually modify HOMO and LUMO energy levels to target specific optical, electrical, or processing characteristics for desired device use.
Finally, the last aspect that must be considered when designing semiconducting polymers is processability. As polymers become more planar and molecular weights increase solubility typically decreases. To compensate for this, large linear or branched side chains are often employed on the polymer backbone\textsuperscript{59, 60}. Unfortunately, there is a drawback to using large side chains; as side chains get larger and bulkier, the planarity of the backbone can decrease, reducing intramolecular charge transport\textsuperscript{61}. Likewise, packing efficiency of polymer chains can decrease leading to diminished intermolecular charge carrier mobility. Thus, a balance must be obtained between solubility and charge carrier mobility.

1.1.2 Optical and Electronic Characterization

As the previous sections have discussed, the size of the $E_g$ and subsequent charge transport ability depends on structural design. The size of the $E_g$ is not the only factor of importance when considering polymer design, however. The relative energy of the $E_g$ is a direct relation to the material stability, both in the neutral and charged form. Before
discussing how to achieve stability in energy alignment, it is important to explain the optical and electronic characteristics that will be covered.

There are multiple ways to describe the electronic energy levels of semiconducting polymers, as can be seen in Figure 6. The optical properties of materials can be easily determined through absorption spectra to yield the optical gap, which is the energy for an excited electron to go from the ground state ($S_0$) to the first excited state ($S_1$). This is estimated through the onset of absorption in UV-vis spectra with equation (1).

$$E \ (eV) = \frac{1240}{\lambda}$$  \hspace{1cm} (1)

Figure 6. Illustration of the electronic energy levels in organic semiconducting polymers that can be found experimentally where $S_0$ is the ground state and $S_1$ is the first excited state. Adapted from reference\textsuperscript{62}.

When an electron is excited to a higher energy, it leaves behind a positively charged hole to which it is still bound, and together they are known as an exciton. In electronic devices, charges are collected separately which means the exciton must be separated.
Separating excitons typically requires more energy than the optical gap. This energy requirement is known as the exciton binding energy. The optical band gap and exciton binding energy together make up the materials $E_g$. The $E_g$, sometimes referred to as a transport gap, is thus the energy required to generate excitons and separate them for charge collection.

Experimentally the HOMO and LUMO are estimated by determining the ionization potential (IP) and electron affinity (EA), where ionization potential is the minimum energy required to remove an electron from the valence band of a neutral species and electron affinity is the change in energy when an electron is added a neutral species\textsuperscript{63, 64}. Cyclic voltammetry (CV) is the most common electrochemical method of indirectly estimating IP and EA\textsuperscript{65, 66}. The technique provides a quick approximation of oxidation and reduction potentials, which can be converted to IP and EA through the following equations:

\begin{equation}
E_{\text{IP}} = -(E_{\text{ox onset}} + 5.1)(\text{eV}) \\
E_{\text{EA}} = -(E_{\text{red onset}} + 5.1)(\text{eV})
\end{equation}

where both onsets have been corrected against the formal potential of ferrocene Fc$^+$/Fc. While the oxidation and reduction peaks are useful, there are a series of approximations that cannot be avoided when estimating IP and EA from CV including device setup and electrolyte choice\textsuperscript{67}. These assumptions have been discussed as it pertains to both small molecules and polymers\textsuperscript{68-71} and are more compelling when used in conjunction with other testing methods to corroborate the results. Likewise, for the discussions presented in this thesis, all CV results were performed outside of a glovebox in cells that had been bubbled through with nitrogen but were not airtight. The potential for oxygen and water to infiltrate the cells further highlights the need to verify any values obtained.
Ultraviolet photoelectron spectroscopy (UPS) is a direct method of estimating IP, as it excites valence electrons using ultraviolet photons under high vacuum and compares the kinetic energy of those electrons against that of the sample’s electron binding energy\(^7\). There is debate about the possible discrepancies of UPS estimated IP, as the work function on the surface of the material could differ from the bulk\(^6\), however there are significantly fewer assumptions involved than in CV. Similarly, the high vacuum the samples are under while performing the experiments precludes any interference from water or oxygen. Due to the nature of UPS in probing valence electrons only, it cannot be used to estimate EA as it inherently contains no electrons. Inverse photoemission spectroscopy (IPES) is used to directly measure EA of semiconducting materials by depositing electrons from an electron gun into the unoccupied states and measuring the energy of the photons as they decay\(^7\). While UPS and IPES are both more expensive and intensive tests than CV, IPES is a rare resource and often unattainable, thus highlighting the use of multiple estimation methods.

1.1.3 N-channel Dilemma

When semiconducting polymers are used in devices such as OFETs, they are conventionally described in two ways with respect to charge transport; hole transporting (p-channel device) and electron transporting (n-channel device). In some cases, materials can transport both holes and electrons and are characterized as ambipolar. Throughout the history of semiconducting polymers hole transporting materials have dominated the field largely due to higher device stability, especially in ambient conditions\(^25, 58, 73\). Meanwhile, electron transporting polymer design has not been as thoroughly studied due to poor stability and weak mobilities\(^74, 75\).
Electron transporting materials are not necessarily unstable in the neutral form, the instability issues derive from the electron doped anion form. Oxygen and water both readily oxidize the anions, as well as act as charge traps\textsuperscript{76, 77}. In addition, charge traps can form within the polymer itself, further reducing overall charge mobilities\textsuperscript{45, 78, 79}. Unlike in the case of hole transporting polymers, the work functions of the metal electrodes have a much higher charge injection barrier to overcome to inject charges in electron transporting materials. Research has determined the ‘ideal’ energy alignment of these semiconductors is to have EA’s no less than 4.0 eV to attain sufficient ambient stability\textsuperscript{80, 81}.

1.2 Organic Field Effect Transistors

1.2.1 Device Structure

Organic field-effect transistors (OFETs) are electronic switches that manipulate electric fields to induce charge carrier conductivity in organic materials\textsuperscript{82}. There are four main configurations for OFETs: bottom gate/bottom contact (BGBC), bottom gate/top contact (BGTC), top gate/bottom contact (TGBC), and top gate/top contact (TGTC)\textsuperscript{21} (Figure 7).
Figure 7. Schematic representation of the four OFET architectures.

Each configuration is comprised of the same components, the semiconducting material, a dielectric layer, and the source, drain, and gate electrodes. In each case, the gate electrode is separated from the semiconductor by the dielectric layer. With respect to both bottom gate devices, the gate is applied directly onto the substrate, followed by the dielectric layer. The difference in bottom gate devices comes from the order of the source and drain deposition; bottom contact devices deposit the source and drain directly on the dielectric layer, with the semiconductor applied over them. Top contact configurations deposit the semiconductor on the dielectric layer, with the electrodes on top. Top gate configurations use the same BC/TC method but with the dielectric in between the semiconductor and the gate, which lies on top. Top gate electrodes serve the advantage of protecting the semiconductor from ambient degradation due to exposure of oxygen or water, however semiconductor film quality can be damaged in the deposition phases. The same is true concerning BGTC configurations, as the electrode deposition can compromise
the semiconductor film. For this reason, BGBC is chosen for all projects and discussions in this thesis as the device configuration to maintain film stability since ambient exposure can be regulated by processing and characterizing the devices in inert atmospheres.

BGBC source and drain electrodes are usually a metal, such as gold, which are applied through vapor deposition. Vapor deposition is done under vacuum at high temperatures, the cause of the concern for semiconductor film degradation in top contact configurations. Semiconducting polymers can generally be deposited through multiple methods such as spin-coating, blade-coating, ink jet printing, and spray coating. The gate electrode is typically a metal or conductor covered by an insulating dielectric layer. When a silicon gate electrode is used, the dielectric is commonly an oxide layer, such as SiO₂, but with the push to generate flexible devices, polymeric insulators such as poly(methylmethacrylate) (PMMA) are also employed. The dielectric layer has proven to have a dramatic impact on device performance as it can have negative impacts on semiconductor film morphology and subsequent charge carrier mobility values due to surface roughness and a difference in surface energies. These issues are often addressed with the use of surface treatments on the dielectric layer by growing self-assembled monolayers (SAMs) of organosilane compounds which increase the hydrophobicity of the surface.

1.2.2 Operation and Characteristics

There are two classifications for OFET operation, p-channel (hole transporting) and n-channel (electron transporting), which depend on the applied voltages and target charges. In both cases, the amount of current that flows through the semiconducting material between the source and drain, known as the source-drain voltage $V_D$, is dependent on the
voltage applied in the gate electrode, $V_G$. **Figure 8** depicts the inherent effects voltage changes have on the frontier molecular orbitals for both semiconductor classifications.

**Figure 8.** Ideal OFET orbital alignment to depict the effect of induced voltages on p- and n-channel materials, adapted from reference$^{21}$.

Initially, when $V_G = 0$, there is no bias induced in the semiconducting film, thus no charge mobility (**Figure 8**, leftmost image) meaning the device is “off”. In the case of p-channel materials, a negative $V_G$ raises the HOMO and LUMO such that the HOMO aligns with the fermi level of the electrodes, which take electrons from the HOMO leaving behind positively charged holes (**Figure 8**, top middle). When a $V_D$ is applied, the holes mobilize and are collected (**Figure 8**, top right), and the device is “on”. On the other hand, when a positive $V_G$ is applied, negative charges are induced in the semiconductor due to the lowering of the HOMO and LUMO such that the LUMO aligns with the electrode fermi
levels \((\text{Figure 8, bottom middle})\). When \(V_D\) is applied electrons can flow from the semiconductor into the electrodes \((\text{Figure 8, bottom right})\).

Of course, this is all describing an ideal situation, which is often not the case in real device performance. Semiconducting materials are prone to charge trapping, deriving from inherent polymer characteristics, structural defects in the film, or misalignment between energy levels of the polymer with the electrodes\(^{45,84}\). If these trap states are too deep, they can become immobile and need to be filled before charges become mobile. Filling these deep states typically results in the device turning “on” at a non-zero \(V_G\). To account for this, the voltage required to mobilize charges, the threshold voltage \((V_{\text{Th}})\), is reported. In general, charge traps in p-channel transistors lead to a positive change in \(V_{\text{Th}}\) whereas n-channel traps move \(V_{\text{Th}}\) negatively. After the trap states are sufficiently filled, the mobile charge carriers can move, generating a current, \(I_D\).

Arguably the most important parameter in OFETs is the charge carrier mobility, \(\mu\). When \(V_D\) is held constant, sweeping of \(V_G\) generates a current between the source and drain electrodes, \(I_D\). When \(V_D < |V_G - V_{\text{Th}}|\), \(I_D\) will scale linearly with \(V_D\) and the device is in the linear regime. Once \(V_D > |V_G - V_{\text{Th}}|\) the current becomes saturated, and the device is in the saturation regime. The equation for the linear regime is as follows:

\[
I_{LD} = \left(\mu_e C_{\text{ox}} \frac{W}{L}\right) \left( (V_G - V_{\text{Th}}) V_D - \frac{V_D^2}{2}\right)
\]

where \(C_{\text{ox}}\) is the capacitance of the gate dielectric material, and \(W\) and \(L\) are the width and length of the transistor channel. In the saturation regime, the current can be linearly related to \(V_G\) through the following equation:

\[
I_{SD} = \frac{W C_{\text{ox}}}{2L} \mu (V_G - V_{\text{Th}})^2
\]
The slope of the linear fit to equation (5) is $\mu$ and the x-intercept is $V_{Th}$. Typical BGBC transistors, p-channel (a) and n-channel (b), as well as a transfer curve can be seen in Figure 9.

**Figure 9.** Examples of BGBC transistors for p-channel (a) and n-channel (b) devices. Transfer curve (c) of p-channel polymer adapted from reference\textsuperscript{85}.

### 1.3 Organic Photovoltaics

The search for clean and renewable sources of energy is an ongoing battle. One commonly explored energy source is photovoltaic (PV) devices\textsuperscript{86-89}, also known as solar cells. Organic solar cells, comprised of either small molecules or polymers, are particularly intriguing as they can be fine-tuned to have a broad optical absorption and are commonly derived from earth abundant resources, thus offering the opportunity for affordable, large scale fabrication options\textsuperscript{11, 90-92}. Though they are generally viewed as being sustainable\textsuperscript{93-95}, their power conversion efficiency (PCE) has only reached a maximum of 18% to date, which falls below that of their inorganic competitors which have reached up to 47%\textsuperscript{96}. This largely stems from the fact that inorganics require less energy to excite charges, and have
longer exciton diffusion lengths\textsuperscript{97-99}, thus providing higher charge carrier mobilities than organics\textsuperscript{100}.

1.3.1 Device Structure

Device architecture for solar cells contain five key components: an indium tin oxide (ITO) coated glass substrate, two separate charge carrying interlayers, the active material, and a top electrode. The following will discuss an inverted device structure, as it the only architecture used in this dissertation. ITO is used as a conductor because of its transparency and commercial availability. Zinc oxide (ZnO) is spin coated on top to serve as the electron transporting interlayer (cathode). The active material is blade coated as the next layer, followed by molybdenum oxide (MoO\textsubscript{x}). MoO\textsubscript{x} acts as the hole transporting interlayer (anode) and is deposited in a thermal evaporator under vacuum. Finally, silver is used as the top electrode. All devices are tested under AM1.5G as the standard incident light.

Active material deposition can be broken down into three ways: multi-layer, interlocking combs, and bulk heterojunction (BHJ). Multi-layer was one of the first fabrication methods where the donor and acceptor would be layered on top of one another which was relatively easy to achieve through common deposition methods such as spin coating or blade coating. Unfortunately, exciton lifetimes are extremely small and are limited to traveling approximately 10nm in semiconducting polymers before they recombine which severely limits the domain sizes of each material. Films of each material would need to be limited to 20nm at max to allow for 100\% of charges to reach their perspective electrodes, which is not practical. From there, the concept of developing interlocking ‘combs’ to maximize the donor-acceptor interface was developed, but the method to achieve this, lithography, is very expensive and time consuming and generally
impractical for commercialization. Finally, BHJs became established where the donor and acceptor would be mixed before deposition. BHJs are by far the most practical of methods for maximizing donor-acceptor interfaces and subsequent exciton separation. One drawback to BHJs is separated charges can get lost or trapped trying to reach the electrodes, but fabrication parameters (ie. deposition method, solvent choice, D-A ratios, etc.) can be altered to limit this effect.

1.3.2 Operation and Characterization

Organic based solar cells function by absorbing photons from the solar spectrum to generate excited charges, which can then be collected. They are comprised of two main active materials, the donor and acceptor. The energy levels must align as seen in Figure 10 for charge transport to occur from one material to the other. For both the donor and acceptor material, the first step is for a photon to be absorbed. This creates an excited electron, which leaves behind a positively charged hole when it is excited to higher energy levels (step 2). At this point, the bound hole and electron are referred to as an exciton as they travel through the domain together (step 3). In the case of the donor material, once the exciton reaches the donor-acceptor interface the electron separates from the hole (step 4) into the acceptor material where it is collected at the cathode electrode (step 5). At the same time, the separated hole has traveled through the donor material to be collected at the anode.
Figure 10. Energy diagram for charge generation and collection in active materials of OPVs.

For efficient charge transport between the D-A materials the alignment of molecular orbitals must follow as depicted in Figure 10. Excited electrons will travel to decreased energies, thus if the donor LUMO was lower energy than the acceptor, the electrons would remain in the donor material and never reach the cathode. Holes travel in the inverse direction, increasing in energy to reach the anode, thus if the acceptor HOMO was higher energy than the donor the holes would remain in the acceptor material.

Solar cells are compared through power conversion efficiencies (PCE) which compare the actual power output of the device to the theoretical power that could be reached. PCE is calculated through the following equations:
\[
FF = \left( \frac{V_{\text{max}} \cdot J_{\text{max}}}{V_{\text{OC}} \cdot J_{\text{SC}}} \right)
\]  
(6)

\[
PCE = FF \times \left( \frac{V_{\text{OC}} \cdot J_{\text{SC}}}{P_{\text{in}}} \right)
\]  
(7)

Where FF is the fill factor, \( V_{\text{max}} \) and \( J_{\text{max}} \) are the max voltage and current, \( V_{\text{OC}} \) is the open circuit voltage, \( J_{\text{SC}} \) is the short circuit current, and \( P_{\text{in}} \) is the power of the incident light. An example of a typical output curve achieved when testing devices can be seen in Figure 11. The black curve depicts the current-voltage curve, where \( V_{\text{OC}} \) and \( J_{\text{SC}} \) are the values as the curve crosses the x- and y-axis. The theoretical max power is a product of \( V_{\text{OC}} \) and \( J_{\text{SC}} \) (blue square) while the max power observed is the product of \( V_{\text{max}} \) and \( J_{\text{max}} \) (green square). FF is the relative area the max power relative to the theoretical max. The higher the FF, the closer the device is to operating at the theoretical maximum.

![Figure 11](image.jpg)

**Figure 11.** Example current-voltage curve (black line) with theoretical power (blue dotted line) and max power (green dotted line) depicted.

### 1.3.3 Material Design Parameters

From the perspective of the active polymer material, factors that must be considered for polymer design include materials structure, associated optical absorption profile\(^{101,102}\),
electronic band gap, the nanoscale morphology of the active layer, and the device fabrication protocols. General active material structure design protocols follow that which was introduced in Chapter 1, section 1.1.1. As discussed, the aim is to utilize aromatic units with limited torsional angles to maximize charge transport throughout the polymer backbone and allow for \( \pi-\pi \) stacking induced intermolecular charge transport. Polymers for OPVs depend on the solar energy for charge generation, most of which within the visible light region, ranging from 380-700nm. As such, materials must be designed to maximize absorption within this range to allow for optical charge generation and absorption overlap with the partner material in the device. Electronic molecular orbital energy levels, mainly the HOMO and LUMO, must be designed to minimize energy barriers for exciton generation. Unfortunately, minimizing the gap results in smaller open circuit voltages \( (V_{oc}) \), which limit power levels for the device, so a balance must be attained between the two.

### 1.4 Photophysical Excitation

#### 1.4.1 Introduction

Photophysical responses in polymers provide information on excited states and structural features. For instance, photophysical tests can help determine the existence of excitons and polarons in semiconducting materials, which are essential for optical and electronic properties. As discussed in previous sections, an exciton is a negatively charged excited electron bound with the positively charged hole it generates when leaving ground state that together form a neutral excited state. A polaron is a charged excited state, which can move among excited states. Figure 12 depicts the frontier orbital energy levels of each type of excitation.
Figure 12. Example of neutral exciton and charged polaron excitations at the HOMO/LUMO energy levels adapted from reference\textsuperscript{104}.

Excitons are typically indicative of intramolecular charge transport because the electron and hole can delocalize across a few repeat units within a single polymer chain. They are not however, unlikely to travel and separate between $\pi$-$\pi$ stacks. Typically, when intermolecular charge transport is occurring it is due to polarons. Optical excitations can be used to demonstrate these occurrences through aggregative behavior of homopolymers\textsuperscript{105, 106}. J-aggregates describe materials that orient themselves in a head-to-tail manner, which correspond to intramolecular charge transport. They are seen in optical absorption spectra with a dominating $A_1$ absorption peak (lowest energy). H-aggregates thus describe intermolecular charge transport, typical of side-by-side alignment. Optical
spectra dominated by h-aggregates have a larger A₂ peak (higher energy). Figure 13 maps the difference in aggregation and optical signatures in a homopolymer.

**Figure 13.** Visual representation of a homopolymer optical spectra for J- and H-aggregates with pink polymer chain segments representing each packing style.

1.4.2 Basics of Pump-Probe Spectroscopy

These photophysical events happen on a time-scale of $10^{-15}$ to $10^{-12}$ seconds and can be detected through pump-probe transient absorption spectroscopy. First, an excitation pump pulse is absorbed by the sample generating excited states in the material. Shortly after the first pulse a second, much weaker pulse is used to generate the steady state absorption – it only excites to the lowest excited state to be subtracted from the first higher excitation pulse. There are three main spectral features that can be detected when plotting change in transmission vs energy or wavelength; the first is the ground state bleach (GSB), represented by a positive $\Delta T$, which is the result of the depletion of ground state ($S_g$) molecules as they become excited to the first excited state ($S_1$). Second in stimulated emission (SE), a negative $\Delta T$, which is when an excited electron in $S_1$ returns to $S_g$. In this case, the molecule is releasing a second photon in response to the pulse generated one,
which is also being collected by the detector. Finally, the last spectral signature of importance is photoinduced absorption (PA), also a negative $\Delta T$, the result of transition from excitation state to a further excitation.

**Figure 14.** Example of isolated and aggregated polymer chain TA spectra, with arrows indicating the change in transmission, adapted from reference\textsuperscript{103}.

Morphology of polymer chains play a big role in spectral signatures, as seen in **Figure 14.** For instance, polymer charge transport and resulting TA spectra will change based on the level of aggregation, especially from solution to film. In solution, polymer chains will be further apart which limits interchain charge transport. While very long polymer chains can generate intrachain polaron pairs – more than one polaron on the chain which can move independently along the backbone – the overall charge transport will still be limited, minimizing PA and SE peaks. On the other hand, while tightly packed polymer chains in film are more likely to have successful interchain charge transfer, they also have an increased chance of forming neutral polaron pairs between adjacent chains, which quenches SE. Thus, elucidating the ever-complex structure-
property relationship of semiconducting polymers and the importance of probing charge transport characteristics.

### 1.5 Organic Electrochemical Transistors

#### 1.5.1 Introduction to OECTs

Organic electrochemical transistors (OECTs), though similar to OFETs, differ in one major way; the doping method utilizes ionic charges from an aqueous electrolyte to induce electronic mobility in the active material. As discussed in previous sections, OFETs are processed solely from organic solvents and must be fabricated under inert atmosphere to prevent oxygen and water from degrading the device, which is especially true for electron transporting materials. OECT active materials should still be processable in organic solvents but be electrochemically stable in aqueous environments. Figure 15 depicts the device structure of an OECT.

![Figure 15. Visual representation of OECT device with charge generation at the polymer-electrode interface for a p-channel device, adapted from reference 109.](image)

OFETs only induce charges at the interface of the active material, whereas OECTs induce them throughout the bulk of the material. For the ions to penetrate beyond the interface of active layer, the material must be “soft” and able to withstand a change in volume and morphological alignment as the material swells. There is a catch with being too “soft” and swelling too much however, as the presence of ions and water in the material
channel can actually lower crystallinity, and by extension transconductance and switching speeds\textsuperscript{110,111}. Too much swelling could result in decreased charge mobility, too little could prevent charges from forming in the first place. Due to the 3D nature of charge generation and collection, mobility measurements are more extensive than OFETs. OECT mobility performance is described as transconductance ($g_m$) and calculated with equation (8):

$$g_m = \frac{Wd}{L} \mu C^* (V_{Th} - V_G)$$  \hspace{1cm} (8)

where $W$ is the channel width, $d$ is the channel thickness, $L$ is the channel length, $\mu$ is the charge carrier mobility, $C^*$ is the volumetric capacitance, $V_{Th}$ is the threshold voltage, and $V_G$ is the gate voltage. This equation can be broken into three key parts: the channel dimensions, active material characteristics ($\mu C^*$), and electrodes\textsuperscript{112-114}. Each portion can significantly change the resulting transconductance, thus highlighting the importance of reporting each component. Along with transconductance, other key parameters that should be reported are switching times, on-off ratios, and stability\textsuperscript{115}.

1.5.2 OECT Active Material Design

As it stands, there are still few definitive design parameters for OECT active materials, in part due to the transconductance dependence on device components as well as material performance. Typically, the goal is to attain highly crystalline polymers as they generally have better charge carrier mobility as a result of backbone planarity permitting intrachain transport and tightly packed $\pi$-$\pi$ stacking allowing interchain transport\textsuperscript{52,116,117}. In the case of OECTs however, when crystallinity was maximized it became apparent that ion injection into the film became strained, limiting ionic and electronic transport\textsuperscript{118}.

However, just as in the case of OFETs, hole transporting OECT polymers have been further developed than electron transporting polymers (Figure 16). This is again for
similar reasons in that hole transporting materials are more electrochemically stable in aqueous environments and often synthetically easier to achieve. The most renowned and applied hole transporting conducting polymer is poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS), with a transconductance as high as approximately 20 mS. PEDOT:PSS is incredibly stable, exhibits high volumetric capacitance, and is mechanically compliant, making it the leader in flexible and stretchable OECT devices\textsuperscript{119-121}. Other hole transporting materials based on polythiophenes, benzodithiophenes, and propylenedioxythiophene (ProDOT) have been developed with varying degrees of success\textsuperscript{122, 123}. One common theme amongst them is the use of hydrophilic side chains, primarily ethylene glycols, which allow for ion integration into the bulk of the film\textsuperscript{124}. Studies comparing the percentage of glycolated side chains against typical hydrocarbon confirmed the hydrophilic nature of the glycol groups drastically improved ionic transport\textsuperscript{125}. 
Figure 16. Examples of hole and electron transporting materials that have been used for OECTs.

There are two main electron transporting polymers that have been developed for OECT performance based on NDI and poly(benzobisimidazobenzophenanthroline) (BBL). Polymeric NDI has been designed with various percentages of hydrophilic vs hydrophobic side chains and confirmed similar results to that of the hole transporting materials in that hydrophilic side chains are necessary for sufficient ion penetration\textsuperscript{126-129}. Unfortunately, despite high capacitances and ion injection, the torsional flexibility among the NDI backbone led to poor electron mobility. On the other hand, BBL is a ladder polymer with high electron mobilities but due to the planar nature of the polymer and lack of side chain, the ion injection was slow, resulting in low switching speeds\textsuperscript{130}. These examples illustrate the complexity that comes with designing electron transporting materials for OECT performance; the polymer must have high charge carrier mobilities, high crystallinity, and
be stable to the electrochemical window of water while being soft enough to allow for ion penetration without absorbing so many ionic charges that electronic charge transport suffers. Needless to say, there is still much to learn in this field.
CHAPTER 2. FROM SYNTHESIS TO ELECTRONIC DEVICE FABRICATION: A MECHANISTIC STUDY OF DPP-BDT POLYMER FILMS

2.1 Introduction

Organic semiconducting polymers are a popular topic of research for their use in electronic devices, such as organic light emitting diodes (OLEDs), organic field effect transistors (OFETs) and solar cells\textsuperscript{20, 24, 131-134}. Relative to inorganic semiconductors, organic semiconductors offer an attractive advantage due to anticipated higher affordability, improved sustainability, easier large-scale fabrication, and the potential for use in flexible devices\textsuperscript{2, 4, 29, 90, 135, 136}. Substantial research has been conducted on the development of hole transporting materials\textsuperscript{58, 137, 138}, but the design of electron transporting counterparts and the inherent effects of molecular structure on electronic performance has yet to be as extensively explored, due in part to the complicated synthesis and relative instability of the materials\textsuperscript{21, 139}. Current research is aimed at designing new electron transport polymers with increased ambient stability and effective $\pi$-$\pi$ interactions, while limiting the size of bandgaps to optimize the number of charge carriers\textsuperscript{74, 75, 140-142}. Donor-acceptor (D-A) polymers are an attractive arena in semiconducting polymers as they present an advantageous opportunity of fine-tuning electronic energy levels\textsuperscript{143-145}.

In this manuscript, we analyze the use of thiazole-flanked dikteopyrrolopyrrole (DPP) as the acceptor moiety copolymerized with benzodithiophene (BDT) as the donor. DPP is a widely known acceptor that has been used in semiconducting small molecules and polymers alike for its relatively simple synthesis, semi-crystalline structure, and overall
stability\textsuperscript{146-150}. The electron deficiency of thiazole has been utilized to generate electron transporting polymers with decreased electron affinities (EA) and ionization potentials (IP) in naphthalene diimide\textsuperscript{151}, imide\textsuperscript{152, 153}, thienothiophene\textsuperscript{154}, and DPP\textsuperscript{155-158} polymers. Specifically, when DPP is flanked by thiazoles, the resulting structure exhibits a near zero torsional angle, due to a favorable pi orbital alignment between the thiazole-based sulfur and DPP-based oxygen\textsuperscript{159}. This in turn resulted in polymer backbones with extended planarization, coupled with increased quinoidal characteristics and effective charge carrier mobility for the polymers. BDT was chosen as the donor for its commercial availability, ease of functionalization, and planar structure\textsuperscript{56, 160-162}. To ensure solubility for ease of processing, the DPP moieties were designed to have a branched 2-octyldecyl side chain, while the BDT moieties utilized octyl-thiophene side chains that offer the potential to extend conjugation into a second dimension, facilitating charge carrier mobility\textsuperscript{163-165}. The impact of thioalkyl side chains vs simply alkylated thiophene substituents on BDT was examined as well, since thioalkyl units have been shown to lower the electron affinity in electronic band gaps, effectively increasing polymer stability\textsuperscript{57, 166}.

A set of polymers was designed to ascertain the efficacy of the electron deficient thiazole DPP and octyl-thiol side chains, and gauge whether the overall impact is additive. The first polymer \textbf{pDPPTz-OThBDT (P1)} combines thiazole DPP with BDT substituted with a purely hydrocarbon-based side chain. The next in the series, \textbf{pDPTh-OSThBDT (P2)}, applies the octyl-thiol side chain to BDT but uses thiophene-flanked DPP. The final polymer \textbf{pDPPTz-OSThBDT (P3)} combines thiazole DPP with octyl-thiol side chain substituted BDT, allowing examination of the impact of the described structural variations. Ionization potentials (IP) and electron affinities (EA) were estimated using cyclic
voltammetry and ultraviolet photoelectron spectroscopy (UPS). The photophysical and electronic properties of P1, P2 and P3 are reported, and their polaron formation is evaluated through transient absorption spectroscopy. OFET charge carrier mobilities were approximated allowing for an evaluation on the individual and combined impacts of each structural change on polymer performance. Finally, preliminary OPV performance is obtained using the common acceptor PC_{71}BM, including a morphological analysis and potential next steps.

2.2 Results and Discussion

2.2.1 Polymer Design and Synthesis

The general procedure for synthesizing the monomers and subsequent polymers can be found in Schemes 1-2 (synthetic details and characterization can be found in Experimental section). Stille coupling was used to copolymerize the target units under microwave conditions (1h, 160 °C). Soxhlet extraction was used for purification to yield the desired polymers, P1, P2, and P3.
**Scheme 1.** Schematic representation of the synthetic procedure for preparing monomers M1 and M2, and subsequent polymerization to afford P1.
Scheme 2. Schematic representation of the synthetic procedure for preparing monomers M3 and M4, and subsequent polymerization to afford P2 and P3.

Polymer molecular weight was determined via high-temperature gel-permeation chromatography (HT-GPC) at 135 °C using 1,3,4-trichlorobenzene as the eluent and polystyrene as the calibration standard. As presented in Table 1, the number average
molecular weights ($M_n$) are modest, ranging from 11-18 kDa, while the mass average molecular weight ($M_w$) reaches up to 57 kDa. It is important to note that the GPC curves for each of the polymers have a noticeable shoulder in the lower molecular weight region, suggesting the Soxhlet did not fully separate the smaller chains from the larger. This in turn explains the relatively large polydispersity indexes ($Đ$) for all three polymers of approximately 3.1-3.6. Despite that, these results are in the range of what is typically reported for DPP-BDT systems when using polystyrene as a calibration standard$^{55, 167-169}$.

**Table 1.** Molecular weight data as obtained from high temperature GPC at 135 °C using 1,2,4-trichlorobenzene as the eluent and polystyrene as the calibration standard.

<table>
<thead>
<tr>
<th></th>
<th>$M_n$ (kDa)</th>
<th>$M_w$ (kDa)</th>
<th>$Đ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>18.4</td>
<td>56.8</td>
<td>3.1</td>
</tr>
<tr>
<td>P2</td>
<td>17.2</td>
<td>57.1</td>
<td>3.3</td>
</tr>
<tr>
<td>P3</td>
<td>11.9</td>
<td>42.8</td>
<td>3.6</td>
</tr>
</tbody>
</table>

**Figure 17.** GPC characterization of P1 with TCB at 135 °C$^1$.

---

$^1$ High temperature GPC analysis done by Bronson Cox
Figure 18. GPC characterization of P2 with TCB at 135 °C².

Figure 19. GPC characterization of P3 with TCB at 135 °C³.

Thermal analysis was conducted using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA shows P1 is stable up to 374 °C, P2 is stable up to 387 °C, and P3 is stable up to 352 °C. DSC shows a slight endothermic transition for P1 from 50 to 85 °C, P2 from 55 to 85 °C and P3 from 60 to 90 °C, which is suspected to be possible side chain melting. There are no other thermal transitions of note in any of the polymers within the 25 to 300 °C range.

² High temperature GPC analysis done by Bronson Cox
³ High temperature GPC analysis done by Bronson Cox
**Figure 20.** Thermogravimetric analysis (TGA) of P1 in a nitrogen atmosphere (25 mL/min) at a heating rate of 10 °C/min.
Figure 21. Thermogravimetric analysis (TGA) of P2 in a nitrogen atmosphere (25 mL/min) at a heating rate of 10 °C/min.

Figure 22. Thermogravimetric analysis (TGA) of P3 in a nitrogen atmosphere (25 mL/min) at a heating rate of 10 °C/min.
Figure 23. DSC characterization curve of P1 from 25 °C to 300 °C based on third heating/cooling cycle in a nitrogen atmosphere with a nitrogen flow rate of 50 mL/min and a heating/cooling rate of 20 °C/min.

Figure 24. DSC characterization curve of P2 from 25 °C to 300 °C based on third heating/cooling cycle in a nitrogen atmosphere with a nitrogen flow rate of 50 mL/min and a heating/cooling rate of 20 °C/min.
Figure 25. DSC characterization curve of P3 from 25 °C to 300 °C based on third heating/cooling cycle in a nitrogen atmosphere with a nitrogen flow rate of 50 mL/min and a heating/cooling rate of 20 °C/min.
2.2.2 Optical and Electronic Properties

Figure 26. UV-vis spectra for P1, P2, and P3 both in solution (chloroform) and thin-film state.

Ultraviolet-visible (UV-vis) spectra were collected for P1, P2, and P3 in solution and solidified thin-films to estimate the optical band gap for each polymer ($E_{g,\text{opt}}$) (Figure 26). As can be seen by examination of Figure 26, P2 exhibited the lowest energy absorption maximum ($E_{\text{max}}^{\text{sol}}$) of 1.65 eV (750 nm) and lowest $E_{g,\text{opt}}^{\text{sol}}$ of 1.32 eV (941 nm) in solution and in a solidified thin-film (1.64 eV and 1.19 eV for $E_{\text{max}}^{\text{film}}$ and $E_{g,\text{opt}}^{\text{film}}$, respectively). The remaining polymers, P1 & P3 exhibit almost identical absorption spectra.
in solution. The same can be said of P1 & P3 in the solid film state, despite the curves shifting to a lower energy. In solution, $E_{\text{max}}^{\text{sol}}$ for P1 & P3 appears at 1.73 and 1.75 eV, respectively; while $E_{\text{g, opt}}^{\text{sol}}$ is 1.51 and 1.50 eV. As in the case of P2, in thin-films, $E_{\text{max}}^{\text{film}}$ (1.70eV for both) and $E_{\text{g, opt}}^{\text{film}}$ (1.35 and 1.33 eV) for P1 & P3 shift to slightly lower energy. The high intensity peaks in the lower energy range (1.5-2.0 eV) are attributed to polymer excitation, whereas the two less intense peaks at higher energy levels (2.7-3.6 eV) are likely due to individual monomer excitations. A summary of the optical excitation values is presented in Table 2.

P2 has the lowest energy $E_{\text{g, opt}}^{\text{film}}$ of 1.19 eV in the thin-film state compared to 1.35 and 1.33eV for the thiazole analogs, P1 and P3. The significantly smaller optical gap of P2 versus the thiazole polymers suggests that thiophene flanked DPP has a lower energy barrier to generate excited states. Taking into account that the only difference between P1 and P3 is the addition of the thioalkyl side chain in P3, the small difference in $E_{\text{g, opt}}$ both in solution and solidified thin-films between the polymers suggests that incorporating thiazole into the DPP-based polymer plays a stronger role in minimizing $E_{\text{g, opt}}$ than introducing thioalkyl side chain substituents. It is interesting to note that the max absorption for P2 has a smaller red shift of only approximately 0.01 eV in film state than either P1 or P3 (0.07 eV and 0.05 eV, respectively). The observed energy difference is likely due to the thiazole moiety, which allows for tighter π-π stacking than thiophene due to a decreased torsional angle between the flanking moiety and DPP\textsuperscript{157, 159}. 
Table 2. Polymer optoelectronic and electrochemical properties.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E_{\text{max,sol}}$ (eV)$^a$</th>
<th>$E_{\text{g,opt,sol}}$ (eV)$^a$</th>
<th>$E_{\text{max,film}}$ (eV)$^b$</th>
<th>$E_{\text{g,opt,film}}$ (eV)$^b$</th>
<th>$E_{\text{A}}$ (eV)$^b$</th>
<th>IP (eV)$^b$</th>
<th>$E_{\text{g,ec}}$ (eV)$^b$</th>
<th>IP$^{\text{UPS}}$ (eV)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>1.73</td>
<td>1.51</td>
<td>1.70</td>
<td>1.35</td>
<td>3.86</td>
<td>5.73</td>
<td>1.87</td>
<td>5.80</td>
</tr>
<tr>
<td>P2</td>
<td>1.65</td>
<td>1.32</td>
<td>1.64</td>
<td>1.19</td>
<td>3.68</td>
<td>5.65</td>
<td>1.97</td>
<td>5.63</td>
</tr>
<tr>
<td>P3</td>
<td>1.75</td>
<td>1.50</td>
<td>1.70</td>
<td>1.33</td>
<td>3.82</td>
<td>5.71</td>
<td>1.89</td>
<td>5.93</td>
</tr>
</tbody>
</table>

$^a$UV-vis absorption spectra of polymers in chloroform and blade coated with optical bandgap estimated from absorption onset using $E_{\text{g,opt}} = 1240/\lambda_{\text{onset}}$. $^b$Electrochemically estimated electron affinity, ionization potential, and bandgap as found through the oxidation and reduction potentials in CV. $^c$Ionization potential as estimated from UPS.

Figure 27. Electrochemical characterization of P1 polymer film under cyclic voltammetry (CV). P1 thin films were drop-casted on glassy carbon electrodes from chloroform solutions using TBAPF$_6$ (0.5M, propylene carbonate) as the electrolyte and Ag/Ag$^+$ (10nM AgNO$_3$/MeCN, 0.09 V vs Fc/Fc$^+$) for the reference electrode. Nitrogen was bubbled through cells for 10 minutes.
**Figure 28.** Electrochemical characterization of P2 polymer film under cyclic voltammetry (CV). P2 thin films were drop-casted on glassy carbon electrodes from chloroform solutions using TBAPF6 (0.5M, propylene carbonate) as the electrolyte and Ag/Ag+ (10nM AgNO3/MeCN, 0.09 V vs Fc/Fc⁺) for the reference electrode. Nitrogen was bubbled through cells for 10 minutes.
Figure 29. Electrochemical characterization of P3 polymer film under cyclic voltammetry (CV). P3 thin films were drop-casted on glassy carbon electrodes from chloroform solutions using TBAPF₆ (0.5M, propylene carbonate) as the electrolyte and Ag/Ag⁺ (10nM AgNO₃/MeCN, 0.09 V vs Fc/Fc⁺) for the reference electrode. Nitrogen was bubbled through cells for 10 minutes.

EA and IP were estimated through the irreversible reduction and oxidation potentials in cyclic voltammetry (CV) (Table 2). The EA and IP were found to be 3.86 and 5.73 eV for P1, 3.68 and 5.65 eV for P2, and 3.82 and 5.71 eV for P3. The polymers with thiazole flanked DPP (P1 & P3) have almost identical electrochemical band gaps (E_{g,ec}) of 1.87 and 1.89 eV, while the thiophene flanked DPP, P2, demonstrates a larger E_{g,ec} of 1.97 eV.

Figure 30. UPS characterization of blade-coated P1 film on ITO-coated glass. Inset is zoomed-in on lower binding energy region of UPS spectrum.
Figure 31. UPS characterization of blade-coated P2 film on OTS-coated glass. Inset is zoomed-in on lower region binding energy of UPS spectrum.

Figure 32. UPS characterization of blade-coated P3 film on OTS-coated glass. Inset is zoomed-in on lower region binding energy of UPS spectrum.
Ultraviolet photoelectron spectroscopy (UPS) was another method used to estimate the ionization potentials of the polymer thin films due to the inherent uncertainty tied to the assumptions made in the conversion factors that relate redox potential calculations to solid-state ionization potentials in CV$^{62, 67}$. The ionization potentials are 5.80, 5.63, and 5.93 eV for P1, P2, and P3, respectively. These values are lower energy than those found with CV, but this is a consistent trend found in polymers$^{68, 170}$ due to the aforementioned assumptions made when calculating oxidation and reduction potentials, and the extreme vacuum samples are placed under when performing UPS measurements, which prevents any water or oxygen from impacting the IP values. The thiazole containing polymers, P1 and P3, have a notably larger decrease of IP in UPS relative to the thiophene DPP. This is likely due to the increased order of polymer chains in blade coated films for UPS compared to the drop cast films used in CV. This further supports the trend seen in UV-vis as thiazole polymers showed a larger shift in energy from solution to film than the thiophene polymer.

Without access to inversion photoemission spectroscopy (IPES), a rare and expensive machine, there is no way to estimate EA with the same level of certainty that UPS estimates IP$^{71}$. For this reason, Figure 33 maps the ionization potentials as found from UPS with the $E_{g, ee}$ calculated from CV to visually compare the energy levels of P1, P2, and P3 against the common acceptor unit PC$_{71}$BM.
Figure 33. Depiction of the electronic transport gaps of P1, P2, and P3 relative to PCBM, using IP found from UPS and electrochemical band gaps from CV.

Remarkably, P2 has the largest E_{g,ec} of 1.97 eV as found from CV. This indicates that despite its optical gap being the smallest, P2 has the largest electron-hole binding energy of approximately 0.78 eV, compared to 0.52 and 0.56 eV in P1 and P3. This in turn signifies that though P2 requires the least amount of energy to optically excite charges, it has the highest energy barrier to separate and subsequently collect charges, likely resulting in severely hindered OPV performance. IPs as found from UPS combined with the electrochemical E_{g,ec} from CV illustrate the vast difference between energy stabilization of thiophene-DPP and thiazole-DPP. As Figure 33 depicts, the electron affinities of P1 and P3 are similar to one another, with a difference of only 0.1 eV, while P2 lies 0.27-0.37 eV higher. This indicates that thiazole as a replacement for thiophene has a significantly stronger impact on lowering molecular energy levels than the presence of thiol containing side chains. In addition, these results further confirm that both structural changes stabilize
polymer energy levels and have a synergistic relationship. Frontier orbital alignment also show all three polymers have EAs higher than PC71BM, indicating they all could potentially function as donor materials when used with PC71BM. The change in energy from P2 to PC71BM of 0.5 eV is much larger than that of the thiazole polymers (0.27 and 0.17 eV for P1 and P3 respectively) suggesting there could be a larger driving force for electron injection from the donor to acceptor material.

2.2.3 OFETs

Organic field effect transistors (OFETs) were fabricated by blade coating the polymers from chloroform solution (10 mg/mL) to determine their charge carrier mobilities. The data presented in Table 3 demonstrates that each polymer has some degree of ambipolarity, and P2 is approximately 3.5 times better at moving charges than the thiazole analogs. The electron mobilities for P1, P2, and P3 are 8.3 x 10^{-5}, 8.1 x 10^{-4}, and 8.5 x 10^{-5} cm²/V·s, respectively; and the hole mobilities are respectively, 1.2x10^{-5}, 3.5 x 10^{-4}, and 2.1 x 10^{-5} cm²/V·s. It is clear P2 has a higher proclivity for hole transport than either thiazole polymer, as seen in Table 3 and Figure 34. The electron mobility values for P1 and P3 are approximately four times higher than their hole mobilities, indicating they are superior at transporting electrons. Transfer curves of P2 and P3 are shown in Figure 34 to demonstrate the stability of charge carrier mobility over six consecutive sweeps for thiophene vs thiazole analogs. P2 shows almost no change in mobility curves throughout
the sequence but P3 has a clear decline in the curves for holes with each cycle despite maintaining consistent electron counts.

![Transfer curves of six consecutive sweeps for P2 (left) and P3 (right) using a V_d of -80 V. Solid arrows represent forward sweep. P3 is representative of both thiazole containing polymers.](image)

**Figure 34.** Transfer curves of six consecutive sweeps for P2 (left) and P3 (right) using a V_d of -80 V. Solid arrows represent forward sweep. P3 is representative of both thiazole containing polymers.

**Table 3.** Average hole and electron charge carrier mobilities as found through BGBC OFETs in the saturation regime.

<table>
<thead>
<tr>
<th></th>
<th>Hole</th>
<th></th>
<th>Electron</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\mu_h$ (cm²/V·s)</td>
<td>$V_{th}$ (V)</td>
<td>$V_{th}$ (V)</td>
<td>$\mu_e$ (cm²/V·s)</td>
</tr>
<tr>
<td>P1</td>
<td>$1.2 \times 10^{-5}$</td>
<td>7</td>
<td>39</td>
<td>$8.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>P2</td>
<td>$3.5 \times 10^{-4}$</td>
<td>32</td>
<td>59</td>
<td>$8.1 \times 10^{-4}$</td>
</tr>
<tr>
<td>P3</td>
<td>$2.1 \times 10^{-5}$</td>
<td>0</td>
<td>23</td>
<td>$8.5 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

While the mobility values were modest, significant insight can still be ascertained from these tests. All three polymers demonstrate hysteresis in the reverse sweep for both holes and electrons, indicative of charge trapping. Six consecutive transfer curves (**Figure 34**) reveal that P2 is relatively stable with almost no change in hole or electron mobility over the course of the sequence. Similarly, P1 and P3 show relatively no change for electron mobility but there is a decrease in mobility in the negative voltage range. The
decrease in current coupled with the shifting threshold voltage is due to the bias-stress effect\textsuperscript{171}. While this results in an overestimation of hole mobilities, the stabilization of the electron mobilities in \textbf{P1} and \textbf{P3} paired with the low-lying frontier orbitals suggest they may function better as acceptor materials in OPVs, rather than donors.

\textbf{2.2.4 OPVs}

Solar cells were fabricated using an inverted structure of glass/ITO/ZnO/polymer:PC\textsubscript{71}BM/MoO\textsubscript{3}/Ag. The polymers were blade coated from chloroform (35 mg/mL) on a 40 °C heated stage at 25 mm/s. Solar cell device performance can be found in Table \textbf{4}. The average device efficiencies were modest at 0.19, 0.12, and 0.03 \% with fill factors of 41, 35, and 31 \% for \textbf{P1}, \textbf{P2}, and \textbf{P3}, respectively. $V_{\text{OC}}$ for the thiazole polymers are relatively similar (0.88 and 0.90 V for \textbf{P1} and \textbf{P3}), which is to be expected as it is a direct correlation to the difference of IP in the donor material and the EA in the acceptor material. \textbf{P2} demonstrates a smaller $V_{\text{OC}}$ of 0.53 V as a result of the higher IP as discovered in CV and UPS. $J_{\text{SC}}$ is where a drastic difference can be seen between the family of polymers, explaining the trend in PCE. \textbf{P1} demonstrates the highest average $J_{\text{SC}}$ of 0.53 mA/cm\textsuperscript{2}, followed by \textbf{P2} with an average of 0.37 mA/cm\textsuperscript{2}, and \textbf{P3} with an average of 0.12 mA/cm\textsuperscript{2}. The low $J_{\text{SC}}$ in \textbf{P3} could be explained by the preferred electron transport in the material, as found in OFET devices, but this does not explain how \textbf{P1} reached the highest $J_{\text{SC}}$. Likewise, despite showing the best hole transporting capabilities in OFETs, \textbf{P2} was not the best performing when used with PC\textsubscript{71}BM.
Table 4. OPV device characteristics of polymers with PCBM and DIO.

<table>
<thead>
<tr>
<th>Polymer/PCBM</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>0.53 ± 0.02</td>
<td>0.88 ± 0.02</td>
<td>41 ± 2</td>
<td>0.19 ± 0.02</td>
</tr>
<tr>
<td>P2</td>
<td>0.37 ± 0.32</td>
<td>0.53 ± 0.24</td>
<td>35 ± 2</td>
<td>0.12 ± 0.10</td>
</tr>
<tr>
<td>P3</td>
<td>0.12 ± 0.02</td>
<td>0.90 ± 0.02</td>
<td>31 ± 1</td>
<td>0.03 ± 0.01</td>
</tr>
</tbody>
</table>

Figure 35. Current density-voltage curve of 1:1 polymer blends with PCBM.

All polymer devices were also fabricated combining P1 and P3 as the acceptor materials each with P2 as the donor material. It was expected that their similar backbones would allow them to be miscible and possibly result in superior device efficiencies. Though they did result in smoother surfaces than when combined with PBCM (Figure 41 in Thin Film Surface Morphology), unfortunately there was no current observed for any of the devices so despite having an average $V_{OC}$ of 0.62 and 0.45 V for P1/P2 and P3/P2, there were no efficiency values to report.
2.2.5 Thin Film Surface Morphology

Atomic force microscopy (AFM) was used to probe the surface roughness of the neat polymer films as well as devices to ascertain if the surface morphology could be a factor in the low PCE values. It was already discovered that the polymers had poor solubility and would de-wet in any organic solvents other than chloroform, as depicted in Figures 36-38. As Figure 36 shows, the thin films are very smooth when coated from chloroform, with a height profile of only 3.9 nm between the three polymers. When p-xylene was used (Figure 37) P1 and P3 showed only a slight increase in height profile to 9 nm, but overall, still maintained relatively smooth films. P2 however showed large aggregates with a height profile reaching 64nm, believed to be the result of poor solubility. The opposite was true when films were formed in chlorobenzene as P2 showed relatively smooth and uniform films whereas P1 and P3 had clear de-wetting as noted by the speckled AFM profiles in Figure 38.
Figure 36. AFM images of each polymer blade-coated from chloroform (10mg/ml) at 40°C onto OTS-18 modified SiO$_2$ substrates.

Figure 37. AFM images of each polymer in p-xylene (10mg/ml) blade-coated at 90°C onto OTS-18 modified SiO$_2$ substrates.
Figure 38. AFM images of each polymer in chlorobenzene (10mg/mL) blade-coated at 90°C onto OTS-18 modified SiO$_2$ substrates. Inserts are provided for P1 and P3 to enhance the de-wetting effect.

Finally, the 1:1 polymer:PC$_{71}$BM blends in chloroform (35 mg/mL) on ZnO spin-coated glass substrates were analyzed in AFM (Figure 39). It is immediately apparent that there is large scale phase separation occurring for each combination, especially in the case of the thiazole polymers as the phase separation reached diameters of approximately 200nm for P1 and P3. With the average exciton diffusion length of semiconducting polymers being approximately 10nm, this indicates that roughly 90% of charges generated were undergoing recombination before they reached the donor-acceptor interface, which would certainly impede device efficiencies. In order to confirm the phase separation wasn’t a result of poor film deposition on ZnO, neat polymer solutions (35 mg/mL chloroform) were blade coated using the same blade coat parameters on ZnO coated substrates. As Figure 40 shows, the films are relatively smooth for each polymer, leading to the conclusion that the phase separation was a result of immiscibility of the polymers with PCBM.
Figure 39. AFM images of height (top) and phase (bottom) surface profiles for 1:1 ratios of P1, P2, and P3 with PCBM in chloroform (35 mg/mL) on ZnO coated glass substrates.

Figure 40. AFM images of height (top) and phase (bottom) surface profiles of neat polymer films (coated from 35 mg/mL chloroform solutions) on ZnO coated substrates.
**Figure 41.** AFM images of height (top) and phase (bottom) surface profiles of 1:1 P1/P2 (left column) and P3/P2 (right column) films (coated from 35 mg/mL chloroform solutions) on ZnO coated substrates.

### 2.2.6 Exciton Dynamics

Based on the optical excitation spectra in **Figure 26**, all three polymers are dominated by h-like aggregation, meaning they align side-by-side. This suggests that there should be more interchain charge transfer and heavy reliance on polaron formation over excitons. To probe the ability of each polymer to form polarons and excitons, transient absorption (TA) experiments were conducted on neat films of the polymers. The excitation wavelength was chosen as $E_{\text{max}}^{\text{film}}$ of the steady state absorption spectrum of the neat material (**Figure 26**). The TA spectra (**Figure 42**) are broken down into three distinct sections: yellow, blue, and red. The yellow and blue regions represent photoinduced absorption. The red region shows the ground state bleach that is consistent with the steady-
state absorption spectra. The yellow region shows that P1, P2, and P3 each have the same photoinduced absorption. The blue region of the spectra centered around 1.4 eV is distinct for each of the polymers. P3 has the most intensity, second to P1, while P2 has no intensity in this region.

**Figure 42.** TA spectrum of the neat materials\(^4\).

P1, P2, and P3 each have the same photoinduced absorption in the yellow region which is most likely due to the common DPP and BDT moieties in the polymer backbone. The blue region of the spectra centered around 1.4 eV however, is distinct for each of the polymers. P3 has the most intensity, with P1 showing slightly less, and P2 demonstrating no intensity. The presence of the two photoinduced absorption regions may indicate that due to the individual monomer moieties, each polymer has the ability to populate higher lying excited states and potentially create polarons or charge separated states to some extent.

\(^{4}\) TA spectrum taken and analyzed by Dr. Sarah Marques.
extent. The blue region indicates that **P3** and **P1** have a higher potential for forming these states than **P2**.

Combined with the bandgap energy calculation from the steady state UV-vis, electrochemical bandgap calculation and UPS, a cohesive electronic picture can be built around the influence of the thiazole and thiophene on the electronic structure. **P1** and **P3** have the lowest optical band gap which allows stabilization of the charges, hence the second photoinduced absorption peak that has a long-lived component. On the other hand, **P2** is not able to stabilize these longer-lived components. This would suggest by adding the thiazole, more electron density is introduced into the backbone stabilizing the excited states upon excitation, a characteristic not found in the case of the thiophene counterpart, **P2**. Comparing **P1** and **P3** though, besides energetic stabilization from the thiazole incorporation, **P3** seems to energetically stabilize more excited states due to the thiol alkyl group, possibly creating a more favorable conformation that allows for further stabilization of excited states.

### 2.3 Conclusion

A family of semiconducting polymers, **pDPPTz-OThBDT**, **pDPPTh-OSThBDT**, and **pDPPTz-OSThBDT** (**P1**, **P2**, **P3**), were designed and prepared using Stille coupling of the substituted DPP and BDT moieties. The donor-acceptor polymers were devised to compare the effectiveness of thiazole-flanked DPP and thioalkyl thiophene side chains in stabilizing energy levels, enhancing charge transport characteristics, and ascertaining if the substituents have a symbiotic relationship. The thiazole containing polymers (**P1**, **P3**) show strong ambient stability with significantly lower EAs of 3.93 and 4.03 eV relative to the 3.66 eV EA of the thiophene analog (**P2**). Given the sole difference between **P1** & **P3** is
the addition of octylthiol side chains in P3, it is concluded that thiazole DPP plays a much stronger role in stabilizing electronic energy levels than the thioalkyl side chains, but they can work harmoniously. TA experiments offer a potential explanation for why solar devices were poor; P3 has the highest photoinduced absorption of the three materials but due to its low-lying EA and stronger electron mobility, would likely function better as an acceptor material rather than a donor. P2 fails to demonstrate any polaron formation in the 1.4-1.6 eV photon range, which would help explain why the all-polymer devices also failed. Finally, as P1 also predominately transports electrons and demonstrates polaron formation, it is suspected that efficiencies would increase if it were also used as an acceptor material, though it would likely result in slightly less efficient devices than P3. In the future, common donor materials should be chosen with analogous backbones to be combined with the thiazole polymers in OPVs, as the similarities may result in superior blending. While the goal of stabilizing electronic energy levels by the utilization of thiazole flanked DPP and thioalkyl side chains was realized, it did not result in superior charge carrier mobility, thus elucidating the perplexity of chemical design as it pertains to device performance. It would be interesting to use GIWAXS analysis on the set of polymers to determine the relative microscale crystallinity and compare it against the data presented. Moving forward, it could prove beneficial to pre-screen solar active materials using TA, both in the neat and blended forms, to determine the efficiency of polaron and exciton formation.
2.5 Experimental

2.5.1 Materials and Methods

Chloroform, dichloromethane, tetrahydrofuran (THF), dimethyl formamide (DMF), and toluene were purchased as anhydrous-grade solvents from Sigma-Aldrich. THF was distilled from sodium benzophenone in a solvent purification system (SPS). Starting materials were purchased from commercial suppliers and used without further purification. Sodium thiosulfate, 2-thiophenecarbonitrile, benzo[1,2-b:4,5-b’]dithiophene-4,8-dione (BDT), n-butyl lithium, trimethyltin chloride (1.0 M THF), 2-octyl-1-dodecanol, liquid bromine, sodium hydride, potassium tert-butoxide, 2-thiophenthiol, iron(III) chloride, tris(dibenzylideneacetone)-dipalladium (0) (Pd$_2$(dba)$_3$), and copper(I) iodide were purchased from Sigma-Aldrich. 2-cyanothiazole, 1-bromooctane, diethyl succinate, tin(II) chloride dihydrate, and 2-n-octylthiophene were purchased from Fischer Scientific. Triphenylphosphine, t-amyl alcohol, and potassium carbonate were purchased from Alfa Aesar. N-octadecyltrichlorosilane was bought from Gelest Inc.

$^1$H NMR spectra were recorded using a Varian Mercury V, 400 MHz nuclear magnetic resonance spectrometer. Solid state $^{13}$C NMR spectra were recorded using a Bruker AVIII, 300 MHz nuclear magnetic resonance spectrometer. Elemental analysis was conducted by Atlantic Microlab, Inc. Thermal analysis was conducted on a Perkin-Elmer Pyris-1 thermogravimetric analyzer (TGA) in a nitrogen atmosphere (25 mL/min) with a heating rate of 10 °C/min. Thermal transitions were measured with a TA Q200 Differential Scanning Calorimeter (DSC) in a nitrogen atmosphere (50mL/min) with a heating/cooling rate of 10 °C/min.
UV-vis absorption spectra were recorded on an Agilent 8453 UV-Visible Spectrophotometer. Polymer films were prepared by blade coating on a heated stage (40 °C at 25 mm/s) polymer solutions in chloroform (5 mg/ml) onto pristine SiO₂ glass substrates and OTS-18 pretreated glass covered substrates. The details can be found in the following section “2.2.2 Methods”.

Cyclic voltammetry (CV) spectra were performed using a three-electrode cell with a Princeton Applied Research 273 potentiostat/galvanostat under CorrWare control. The electrolyte was 0.5 M tetrabutylammonium hexafluorophosphate (TBAPF₆, Acros Organics, 8% recrystallized from hot ethanol) dissolved in propylene carbonate. A glass carbon electrode with drop-cast polymer film (1 mg/mL solution in chloroform) was used as the working electrode. A glassy carbon rod served as the counter electrode, and an Ag/Ag⁺ electrode (10 mM AgNO₃ and 0.5 M TBAPF₆ in acetonitrile, 0.09 V vs Fc/Fc⁺) was used as the reference. Nitrogen was bubbled through the cell for 10 minutes to perform the experiments in an inert atmosphere with scan rates of 50 mV/s.

Ultraviolet Photoemission Spectra (UPS) were measured on a Kratos Axis Ultra DLD XPS/UPS system with a He-I lamp radiation at 21.2eV. All samples were in electronic equilibrium with the spectrometer and were run at a base pressure of 10⁻⁹ Torr. The Fermi level was calibrated using atomically clean silver. Experiments were run at a 5 eV pass energy and 0.05 eV step size with the aperture and iris set to 55 μm. The secondary electron edge (SEE) and emission close to the Fermi level of the UPS curves were used to calculate the work function and subsequent IP for each polymer using the following equations:

$$\phi = hν - E_{cutoff}$$
\[ IP = h\nu - (E_{\text{cutoff}} - \varepsilon_{V_F}^F) \]

Where \( h\nu \), \( E_{\text{cutoff}} \), and \( \varepsilon_{V_F}^F \) represent the incident photon energy (HE I, 21.22 eV), the high binding energy cutoff, and the lowest binding energy point.

Bottom contact bottom gate OFETs were fabricated onto \( n \)-doped silicon wafers <100>. The silicon served as the gate electrode while a 300nm thick SiO\(_2\) layer served as the gate dielectric. Source and drain contacts were made using 3nm Cr as an adhesive layer and 50nm Au. These were made with a photolithography lift-off technique to ensure fixed channel dimensions of 50\( \mu \)m wide by 2mm long. The substrates were sonicated in acetone for 30 minutes, and then rinsed with acetone, methanol, and IPA in that order, and dried using an air gun. After 30 minutes in the UV/ozone, the substrates would soak overnight in a 1\( \mu \)L/mL solution of OTS-18 in anhydrous toluene. Polymer solutions of 10mg/mL in chloroform were then blade coated at 25 mm/s using a heated stage (40 °C) under ambient conditions.

All OFET measurements were conducted using a probe station in a nitrogen filled glovebox and an Agilent 4155C semiconductor parameter according to previous methods\(^{151}\). Mobility values were calculated from the following equation and the saturated regime in the transfer plots of \( V_G \) vs \( I_{SD} \) by extracting the slope of the linear range of the \( V_G \) vs \( I_{SD}^{1/2} \) plot:

\[ \frac{1}{\delta I_{SD}^2} \frac{\delta I_{SD}}{\delta V_G} = \left( \mu_e C_{ox} \frac{W}{2L} \right)^{1/2} \]

In this equation, \( I_{SD} \) is the source drain current (A), \( V_{SD} \) is the source drain voltage (V), \( V_G \) is the gate voltage (V) scanning from -80 to 80 V in the transfer plot, \( C_{ox} \) is the capacitance per unit area of the gate dielectric layer, \( W \) is the channel width, \( L \) is the
channel length, and $\mu_e$ is the electron field-effect mobility in the saturated regime (cm$^2$/V·s). The hole field-effect mobility, $\mu_h$, was calculated in the same manner. The threshold voltage, $V_{\text{TH}}$, was calculated by extrapolating $V_T = V_G$ at $I_{\text{SD}} = 0$ in the $V_G$ vs $I_{\text{SD}}^{1/2}$ curve. Averages were based off a minimum of 6 devices (6 channels per device) for each polymer.

Solar cells were fabricated using an inverted structure of glass/ITO/ZnO/polymer:PC$_{71}$BM/MoO$_3$/Ag. Glass substrates with patterned ITO were cleaned by sonication with sodium dodecyl sulfate in water, water, and IPA before being subjected to UV-ozone for 10 minutes. A solution of 0.11M ZnO in 2-methoxyethanol was spin coated onto the surface for 30 seconds at 4000rpm (approximately 30nm) and immediately heated at 150°C for 10 minutes. After the substrates cooled, the 1:1 polymer/PC$_{71}$BM solutions (35mg/mL in chloroform) were blade coated at 25mm/s with the stage heated to 45°C in ambient conditions. The substrates were transferred into an argon filled glovebox to have 15nm MoO$_3$ and 160nm Au electrodes deposited by vacuum deposition with 0.049cm$^2$ active pixels. The devices were tested in a nitrogen filled glovebox with an AM 1.5G illumination at 100mW/cm$^2$ generated using a Newport Oriel 69907 power supply connected to a 150 W xenon arc lamp with collimating lenses in a Newport Oriel 94021A simulator lamp housing. A 2410 Keithley SourceMeter® SMU Instrument was used to test J-V curves with a current sweep from -1 to 1 V. The known active area was used to convert the curve to current density. By plotting this against the voltage curve, the $J_{\text{SC}}$, $V_{\text{OC}}$, FF and PCE could be calculated. Averages were based off 8 devices of each polymer blend.
2.5.2 Synthetic Details

4,8-bis(5-octylthiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene (A): To a nitrogen filled round bottom flask, 2-octylthiophene (2.67g, 13.6mmol) was dissolved in 60mL THF and cooled in an ice bath. 2.5M n-BuLi (5.45mL, 13.6mmol) was added dropwise and stirred for 90 minutes. The reaction was then heated to 50°C and stirred 90 minutes, then brought back to room temperature. Benzo[1,2-b:4,5-b’]dithiophene-4,8-dione (1.00g, 4.54mmol) dissolved in THF was added to the reaction flask and stirred at 50°C for 90 minutes, then cooled back to room temperature. SnCl$_2$ 2H$_2$O (6.05g, 26.8mmol) was dissolved in 10% HCl (14mL) and added slowly to the reaction to be stirred overnight. The reaction mixture was poured on water & extracted in chloroform. The product was dried using MgSO$_4$, filtered and then condensed under reduced pressure. Finally, it was purified using silica gel column chromatography with 1:9 chloroform to hexane as the eluent, to yield A as a yellow solid(1.18g, 45%). $^1$H NMR (400MHz, Chloroform-$d$) $\delta$ 7.65 (d, $J = 5.7$ Hz, 1H), 7.45 (d, $J = 5.7$ Hz, 1H), 7.29 (d, $J = 3.5$ Hz, 1H), 6.91 (d, $J = 3.5$ Hz, 1H), 2.93 (t, $J = 7.7$ Hz, 2H), 1.78 (m, 2H), 1.47 (m, 10H), 0.91 (t, $J = 7.0$ Hz, 3H). Spectral data matches previously reported literature values.$^{172}$
(4,8-bis(5-octylthiophen-2-yl)benzo[1,2-b:4,5-b’dithiophene-2,6-diyl)bis(trimethylstannane) (M1): A (0.50g, 0.86mmol) was dissolved in 500mL dry THF under nitrogen and stirred in an ice bath for 30 minutes. 2.5M n-BuLi (0.92mL, 2.3mmol) was added dropwise over 25 minutes and the reaction was stirred 90 minutes at 0°C. The reaction was then brought to room temperature and stirred an additional 90 minutes. Trimethyl tin chloride (3.16mL, 3.16mmol) was added and stirred overnight. The reaction was poured over water, extracted in chloroform and washed with water. Mixture was dried using MgSO₄, filtered and condensed under reduced pressure. Product was recrystallized from an IPA-THF mixture, to yield a yellow solid M1 (115mg, 15%). ¹H NMR (400MHz, Chloroform-d) δ 7.69 (s, 1H), 7.32 (d, J = 3.5 Hz, 1H), 6.93 (d, J = 3.5 Hz, 1H), 2.95 (t, J = 7.7 Hz, 2H), 1.82 (m, 2H), 1.47 (m, 10H), 0.92 (t, J = 6.9 Hz, 3H), 0.47 (s, 9H). Spectral data matches previously reported literature values.¹⁷²

9-(bromomethyl)nonadecane (B): Triphenyl phosphine (15.6g, 59.5mmol) was dissolved in 30mL anhydrous DCM under nitrogen. The reaction was cooled to 0°C and Br₂ (2.58mL, 50.4mmol) was added dropwise. In a separate RBF, 2-octyl-1-dodecanol
(20.0mL, 56.1mmol) was dissolved in 20mL anhydrous DCM under nitrogen. Alcohol mixture was dropwise added to initial RBF while at 0°C, then brought to room temperature and stirred overnight. The solvent was removed under reduced pressure and then the product was extracted in hexane and filtered. The solvent was again removed and then solid was purified using silica gel column chromatography with hexane as the eluent. The product is a colorless oil, B (20.3g, quantitative). $^1$H NMR (400MHz, Chloroform-$d$) $\delta$ 3.45 (d, $J = 4.7$ Hz, 2H), 1.59 (m, 1H), 1.27 (m, 32H), 0.88 (t, $J = 6.9$ Hz, 6H). Spectral data matches previously reported literature values.$^{173, 174}$

3,6-di(thiazol-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (C): Sodium (0.51g, 22mmol) was cut under hexane and added to a 2-neck RBF with condenser and stir bar under nitrogen. 19.6mL t-amyl alcohol was added and stirred at 110°C overnight until sodium was fully dissolved. In a separate RBF, diethyl succinate (1.04mL, 6.30mmol) and 2-cyanothiazole (1.0g, 9.1mmol) were dissolved in 4.90mL t-amyl alcohol and degassed with nitrogen. The mixture was added to the sodium RBF slowly and refluxed at 120°C for 3 hours. Upon cooling to room temperature, the reaction was slowly precipitated in a mixture of 10.0mL glacial acetic acid, 245mL DI water and 122mL MeOH. Product was filtered using vacuum filtration and then washed with DI water and MeOH until solution ran clear. Product is a deep purple solid, C (1.07g, 78%). Anal. Calcd. for $C_{12}H_{16}N_4O_2S_2$
(%) C, 47.67; H, 2.00; N, 18.53; S, 21.21. Found (%) C, 46.61; H, 2.00; N, 17.06; S, 19.76. Spectral data matches previously reported literature values.157

\[
\text{2,5-bis(2-octyldodecyl)-3,6-di(thiazol-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (D):} \quad \text{A 2-neck RBF with stir bar and connected to a condenser was degassed with nitrogen. 30mL anhydrous DMF was added and purged with nitrogen for 10 minutes. C (1.0g, 3.3mmol) and 60\% oil suspension sodium hydride (0.34g, 8.4mmol) was added to the RBF and refluxed for 2 hours. The flask was cooled to room temperature, B (2.4g, 6.6mmol) was added dropwise, and the mixture was refluxed an hour. The reaction was cooled again and another portion of B (2.4g, 6.6mmol) was added and then refluxed for another hour. The mixture was cooled to room temperature, filtered and washed with chloroform. The mixture was dried under reduced pressure, re-dissolved in chloroform and washed with water 3 times. MgSO}_4 \text{ was used to dry the mixture, then filtered and the solvent was removed under reduced pressure. Silica gel column chromatography was run with a 6:4 hexane to DCM eluent. The product is a magenta solid, D (1.51g, 53\%).}
\]

\[\begin{array}{c}
\text{H NMR (400MHz, Chloroform-}d\text{) } \delta 8.05 (d, J = 3.1 \text{ Hz, 1H}), 7.70 (d, J = 3.1 \text{ Hz, 1H}), 4.35 (d, J = 7.4 \text{ Hz, 2H}), 1.86 (m, 1H), 1.34-1.14 (m, 32H), 0.86 (q, J = 6.9 \text{ Hz, 3H}). \\
\text{C NMR (400MHz, Chloroform-}d\text{) } \delta (\text{ppm}): 161.2, 155.3, 144.2, 138.0, 123.8, 110.5, 46.8, 37.8,
\end{array}\]
3.6-bis(5-bromothiazol-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (M2): To a nitrogen filled 2-neck RBF with condenser and stir bar was added D (0.50g, 0.58mmol), sodium borate (0.54g, 6.37mmol) in 12mL chloroform. In a separate RBF, Br₂ (0.31mL, 5.8mmol) was mixed with 12mL chloroform. The bromine solution was dropwise added to the initial RBF while at 0°C, and then refluxed for 12 hours. Sodium thiosulfate (2.75g, 17.4mmol) was dissolved in 11mL water and that mixture was added to the reaction once it cooled to room temperature. The reaction was stirred for 30 minutes and then washed with brine. The organic layer was dried using MgSO₄, filtered, and condensed under reduced pressure. Silica gel column chromatography was ran using 7:3 hexane to chloroform. The product was precipitated in cold MeOH to yield a purple-red solid, M2 (354mg, 60%). ¹H NMR (400MHz, Chloroform-d) δ 7.91 (s, 1H), 4.26 (d, J = 7.4Hz, 2H), 1.85 (m, 1H), 1.34-1.14 (m, 32H), 0.86 (q, J = 6.9 Hz, 3H). ¹³C NMR (400MHz, Chloroform-d) δ (ppm): 160.9, 156.3, 145.5, 136.9, 115.8, 110.7, 47.0, 37.9, 31.9, 31.4, 30.0, 29.7, 29.6, 29.4, 26.4, 22.7, 14.1. ESI mass calculated: 1019.45. Found: 1019.45.
2-(octylthio)thiophene (E): To a nitrogen filled 2-neck RBF with condenser and stir bar was added tert-butoxide (0.72g, 6.5mmol) in 5mL ethanol. In a separate RBF, 2-thiophenethiol (0.50g, 4.3mmol) was mixed with 2mL DCM. The DCM mixture was added dropwise to the initial RBF and stirred for 30 minutes in an ice bath. 1-bromoctane (0.74mL, 4.3mmol) was added to the RBF and refluxed for 2 hours. The mixture was washed with water 3 times and extracted in DCM. MgSO$_4$ was used to dry the mixture, which was then filtered and condensed down under reduced pressure. A silica gel column chromatography was run using 9:1 hexane to DCM to yield a colorless oil, E (0.98g, quantitative). $^1$H NMR (400MHz, Chloroform-$d$) $\delta$ 7.31 (dd, $J = 1.3, 5.4$ Hz, 1H), 7.09 (dd, $J = 1.3, 3.5$ Hz, 1H), 6.96 (dd, $J = 3.5, 5.4$ Hz, 1H), 2.79 (t, $J = 7.3$ Hz, 2H), 1.59 (m, 2H), 1.30 (m, 10H), 0.87 (m, 3H). Spectral data matches previously reported literature values.$^{175}$

4,8-bis(5-(octylthio)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (F): To a nitrogen filled 2-neck RBF with stir bar was added E (0.50g, 2.2mmol) and 10mL THF. While in an ice bath, 2.5M n-BuLi (0.96mL, 2.4mmol) was added dropwise. The temperature was raised to 50°C and stirred for 20 minutes. In a separate RBF, benzo[1,2-
b:4,5-\textprime \)dithiophene-4,8-dione (0.16g, 0.73mmol) was dissolved in 10mL THF and purged with nitrogen. The mixture was added to the initial RBF and stirred at room temperature for 2 hours. In a third RBF was mixed tin dichloride dihydrate (1.15g, 5.11mmol), 1.56mL HCl and 0.52mL water. The initial RBF was cooled to 0°C and the tin solution was slowly added. The reaction was stirred at room temperature for 6 hours. The product was extracted in hexane and washed with water. MgSO$_4$ was used to dry the product, which was then filtered and condensed under reduced pressure. Silica gel column chromatography was run using hexane as the eluent to yield a light yellow solid, F (0.28g, 59\%). $^1$H NMR (400MHz, Chloroform-$d$) $\delta$ 7.62-7.61 (d, $J = 3.7$ Hz, 1H), 7.48 (d, $J = 3.7$ Hz, 1H), 7.33 (d, $J = 3.6$ Hz, 1H), 7.22 (d, $J = 3.6$ Hz, 1H), 2.93 (t, $J = 7.4$ Hz, 2H), 1.71 (p, $J = 7.4$ Hz, 2H), 1.54-1.28 (m, 10H), 0.90-0.86 (t, $J = 6.9$ Hz, 3H). Spectral data matches previously reported literature values.$^{176}$

![Chemical structure](image)

**4,8-bis(5-(octylthio)thiophen-2-yl)benzo[1,2-b:4,5-\textprime \)dithiophene-2,6-diyl]bis(trimethylstanne) (M3):** To a nitrogen filled 2-neck RBF with condenser and stir bar was added F (0.20g, 0.31mmol) dissolved in 40mL dry THF. The reaction vessel was cooled to -78°C and 2.5M n-BuLi in hexanes (0.29mL, 0.69mmol) was added dropwise and stirred for 30 minutes. The temperature was brought to 0°C for 30 minutes, and then
lowered back down to -78°C for another 30 minutes. 1M trimethyl tin chloride (0.90mL, 0.90mmol) was added and stirred for 20 minutes. The reaction was brought to room temperature and quenched with water. The mixture was extracted in hexane, dried using MgSO₄, filtered and condensed under reduced pressure. The product was recrystallized from a 1:1 IPA/ethanol mix to yield a yellow solid, M₃ (69mg, 23%). ¹H NMR (400MHz, Chloroform-d) δ 7.66 (s, 1H), 7.36 (d, J = 3.6 Hz, 1H), 7.24 (d, J = 3.6 Hz, 1H), 2.93 (t, J = 7.4 Hz, 2H), 1.77-1.70 (p, J = 7.3 Hz, 2H), 1.49-1.42 (m, 2H), 1.32-1.28 (m, 8H), 0.89-0.86 (t, J = 6.1 Hz, 3H), 0.48-0.34 (t, J = 27.5 Hz, 9H). Spectral data matches previously reported literature values.¹⁷⁶

3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (G): Sodium (0.83mg, 36mmol), a small amount of FeCl₃, and 66mL t-amyl alcohol were added to a dry 2-neck RBF under nitrogen and refluxed overnight at 110°C. Cyanothiophene (3.0mL, 32mmol) was added while still refluxing. Diisopropylsuccinate (2.2mL, 11mmol) was added to the mixture over 10 hours. The reaction was further refluxed for 12 hours. Upon cooling to room temperature, 35% HCl in methanol (0.6mL) was added to the mixture and stored overnight in the fridge. Precipitate was filtered and washed with methanol and water to yield a red solid, G (2.34g, 71%). ¹H NMR (400MHz, DMSO-d₆) δ 8.19 (dd, J = 3.8, 1.2 Hz, 1H), 7.94 (dd, J = 1.1, 5.0 Hz, 1H), 7.28 (dd, J = 3.8, 5.0 Hz, 1H). Anal. Calcd. for
C_{16}H_{8}N_{2}O_{2}S_{2} (%) C, 55.99; H, 2.68; N, 9.33; S, 21.35. Found (%) C, 55.89; H, 2.59; N, 9.20; S, 21.46.

2,5-bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (H): Potassium carbonate (1.40g, 10.0mmol), G (1.00g, 3.33mmol), and B (3.37g, 9.32mmol) were dissolved in 50mL anhydrous DMF in a dry 2-neck RBF under nitrogen. The reaction was refluxed 24 hours and then cooled to room temperature. Product was extracted in chloroform and washed with water and brine. The product was then dried using MgSO_{4}, filtered and concentrated under reduced pressure. A silica gel column chromatography was run using a 3:2 hexane/DCM mix. Finally, the product was recrystallized in IPA to yield a red solid, H (0.92g, 32%). \textsuperscript{1}H NMR (400MHz, Chloroform-\textit{d}) \delta 8.87 (dd, \textit{J} = 1.1, 3.9 Hz, 1H), 7.62 (dd, \textit{J} = 1.1, 5.0 Hz, 1H), 7.26 (dd, 3.9, 5.0 Hz, 1H), 4.03 (m, 2H), 1.90 (m, 1H), 1.24 (m, 32H), 0.86 (t, \textit{J} = 6.8 Hz, 6H). Spectral data matches previously reported literature values.\textsuperscript{177}
3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-
dihydropyrrolo[3,4-c]pyrrole-1,4-dione (M4): H (2.00g, 2.32mmol) dissolved in 15mL chloroform was added to an RBF under nitrogen and wrapped completely in foil. In a separate RBF, bromine (0.25mL, 4.8mmol) was dissolved in 5mL chloroform and then added dropwise into the initial RBF. The solution was stirred overnight at room temperature and then poured in 20mL saturated sodium sulfite solution. The product was extracted in chloroform and washed with water. The product was dried, filtered, and concentrated under reduced pressure. A silica gel column chromatography was run using 3:7 DCM/hexane. Finally, the product was precipitated in cold methanol to yield a purple solid, M4 (1.33g, 56%). $^1$H NMR (400MHz, Chloroform-d) δ 8.62 (d, $J = 4.2$ Hz, 1H), 7.21 (d, $J = 4.2$ Hz, 1H), 3.92 (d, $J = 7.7$ Hz, 2H), 1.87 (m, 1H), 1.24 (m, 32H), 0.86 (t, $J = 5.1$ Hz, 6H). Spectral data matches previously reported literature values.$^{177}$

\[ \text{M1, 15\%} \]

\[ \text{M2, 60\%} \]

\[ \text{P1, 87\%} \]

pDPPTz-OTHBDT (P1): M1 (90.5mg, 0.100mmol), M2 (102mg, 0.100mmol), tris(dibenzylideneacetone)dipalladium (2.73mg, 0.003mmol), triphenylphosphine (3.16mg, 0.012mmol), and a pinch of copper iodide were dissolved in anhydrous toluene (2mL) and anhydrous DMF (0.2mL) in an oven dried 5mL microwave vial under nitrogen. The vial was placed in a microwave reactor for 2 hours at 160°C at 250W power while stirring. The reaction changes from pink to dark green after polymerization. The polymer
was precipitated in methanol and purified in a cellulose Soxhlet thimble. The Soxhlet was run using methanol (24hr), acetone (24hr), ethyl acetate (12hr), hexane (24hr) and chloroform (12hr) in that order. The chloroform wash was concentrated and precipitated in methanol to yield 128mg of a dark green solid (87% yield). $M_n = 18.4$ kg/mol, $\mathcal{D} = 3.1$. $^{13}$C NMR (75 MHz, none) $\delta$ (ppm): 165.9, 160.6, 160.6, 157.4, 154.8, 146.4, 140.6, 137.7, 137.50 132.9, 129.0, 124.1, 124.1, 124.1, 111.5, 48.5, 33.8 33.1, 32.7, 32.5, 30.8, 30.4, 30.4, 23.8, 23.7, 23.6, 23.3, 14.9, 14.9, 14.8, 14.6. Anal. Calcd. for $C_{88}H_{130}N_4O_2S_6$ (%); C, 71.98; H, 8.92; N, 3.82; S, 13.10. Found (%): C, 72.10; H, 8.66; N, 3.70; S, 13.37.

**pDPPTh-OSThBDT (P2):** Prepared using the same procedure as P1 with the exception that the product came out in the hexane wash of the Soxhlet. The hexane wash was concentrated and precipitated in methanol to yield 88mg of a dark green solid (59% yield). $M_n = 17.2$ kg/mol, $\mathcal{D} = 3.3$. $^{13}$C NMR (75 MHz, none) $\delta$ (ppm): 165.3, 161.4, 161.3, 161.2, 160.9, 156.5, 147.9, 147.5, 147.1, 140.2, 138.3, 137.9, 137.6, 134.0 129.6, 112.3, 40.7, 37.2, 34.6, 32.7, 30.3, 30.2, 23.3, 23.2, 15.5, 14.5, 14.5, 1.2, 1.1. Anal. Calcd. for
C₉₀H₁₃₂N₂O₂S₈ (%); C, 70.63; H, 8.69; N, 1.83; S, 16.76. Found (%): C, 44.20; H, 7.94; N, 0.77; S, 5.38.

pDPPTz-OSThBDT (P3): Prepared in the same procedure as P1. The chloroform wash was concentrated and precipitated in methanol to yield 92mg of a dark green solid (60% yield). Mᵣ = 11.9 kg/mol, Ø = 3.6. ¹³C NMR (75 MHz, none) δ (ppm): 160.0, 160.0, 155.4, 155.2, 147.07, 144.8, 142.8, 142.1, 141.5, 140.5, 138.7, 137.0, 137.0, 133.2, 128.2, 122.5, 120.6, 111.6, 46.4, 45.9, 43.3, 40.2, 38.0, 36.4, 35.64 32.9, 32.8, 30.1, 30.0, 30.0, 23.4, 23.3, 23.3, 14.8, 14.5. Anal. Calcd. for C₈₈H₁₃₀N₄O₂S₈ (%) ; C, 68.97; H, 8.55; N, 3.66; S, 16.74. Found (%): C, 68.51; H, 8.30; N, 3.42; S, 15.92.
Figure 43. $^{13}$C NMR (75 MHz) spectrum of P1.$^5$

$^5$ Solid state NMR collected by Caria Evans.
Figure 44. $^{13}$C NMR (75 MHz) spectrum of P2.$^6$

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$^6$ Solid state NMR collected by Caria Evans.
Figure 45. $^{13}$C NMR (75 MHz) spectrum of P3.\(^7\)

\(^7\) Solid state NMR collected by Caria Evans.
CHAPTER 3. SIDE CHAIN ENGINEERING FOR OECT PERFORMANCE OF N-TYPE DPP POLYMERS

3.1 Introduction

The design of semiconducting active materials for organic electrochemical transistors (OECTs) is a budding field of research. The main challenge in designing new candidates is derived from the necessity of the active material to induce both ionic and electronic charge carrier mobilities from an aqueous electrolyte\textsuperscript{107}. Typically, organic electronic materials are not used in conjunction with aqueous systems due to the ability of water and oxygen to electrochemically degrade the material and generate charge traps. It has been shown, however, that the use of hydrophilic side chains can induce ion injection from an aqueous electrolyte to generate electronic charges. A common example employs ethylene glycol side chains attached to a hydrophobic backbone\textsuperscript{111, 124, 125}. To date, research has been dominated by the development of p-type materials due to their higher stability in ambient conditions relative to their n-type counterparts\textsuperscript{122, 178}.

Two major examples of n-type polymers for OECT performance have been demonstrated thus far: naphthalene diimide (NDI) based polymers with various hydrophilic side chains\textsuperscript{127, 179}, and poly(benzobisimidazobenzophenanthroline) (BBL), a ladder polymer with no side chains\textsuperscript{130}. Arguably the most important property both polymers demonstrate is electrochemical stability in aqueous environments – mainly, their EAs were lower than -4.0 eV. The NDI polymers demonstrated the importance of hydrophilic side chains for ion uptake, by modifying the ratio of hydrophilic to hydrophobic side chains\textsuperscript{129}.  

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OECT performance was achieved after over 50% of the side chains were hydrophilic, whereas any degree less functioned better as an OFET. The BBL polymer marks the importance of incorporating materials with high electronic transport, as the highly planar backbone in BBL enabled a higher transconductance than the NDI derivations\textsuperscript{130}. Unfortunately, the on/off switching speed for the BBL polymers was relatively slow, likely a result of slow ion uptake from the lack of hydrophilic side chains.

In this chapter, a DPP-based polymer is designed with a modifiable side chain for potential OECT use. The thiazole flanked DPP moiety is copolymerized with the donor unit bithiophene. Thiazole flanked DPP was chosen as the acceptor unit for its low-lying EA and high electron mobility in OFET devices\textsuperscript{157}. Bithiophene was chosen as the donor unit to raise the IP of the hybridized frontier molecular orbitals of the material and serve as a potential point of flexibility in the backbone for ion uptake. Methyl ester end groups were chosen for the side chains due to their ease of synthesis and can be saponified and hydrolyzed to yield a carboxylic acid, which has proven to be a viable side chain modification for OECTs\textsuperscript{180, 181}. Likewise, the ester groups have the potential to form hydrogen bonds, which could prove beneficial for ion uptake.

UV-vis was used to estimate the optical bandgap and evaluate the material’s preferred aggregate orientations. Cyclic voltammetry was used to estimate EA and IP, and subsequently generate the electrochemical bandgap. OFET charge carrier mobilities were measured and the data was coupled with AFM to analyze morphological changes on the surface of the devices. Finally, preliminary optical data on the potassium salt and subsequent carboxylic acid side chains allude to potential next steps.
3.2 Results and Discussion

3.2.1 Polymer Design and Synthesis

The general procedure for synthesizing the monomers and subsequent polymer can be found in Schemes 3-5 (synthetic details and characterization can be found in Experimental section). Stille coupling was used to copolymerize the target units under microwave conditions (1h, 160 °C). Soxhlet extraction was used for purification to yield the desired ester polymer, \( \text{pOMeDPPTz-BTh} \). Side chain saponification into a potassium salt yielded the polymer, \( \text{pK^+DPPTz-BTh} \), which can disperse in water. \( \text{pK^+DPPTz-BTh} \) can be deposited into films and acidified to yield the final carboxylic acid side chain polymer, \( \text{pCOOH-DPPTz-BTh} \). Due to poor solubility, molecular weights could not be determined through heated GPC, MALDI-MS, or NMR for the polymers, which is not uncommon in OECT materials\(^{123} \).
**Scheme 3.** Schematic representation of the synthetic procedure for monomer synthesis and subsequent polymerization to yield pOMeDPPTz-BTh.  

**Scheme 4.** Schematic representation of the post-polymerization potassium salt side chain modification to yield pK+DPPTz-BTh.

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8 Stannylated bithiophene acquired from Yadong Zhang.
**Scheme 5.** Schematic representation of the post-polymerization side chain acidification to yield the solvent resistant pCOOH-DPPTz-BTh.

TGA shows pOMeDPPTz-BTh is stable up to 371 °C (Figure 46) with only 0.15% weight loss due to water. DSC characterization (Figure 47) showed endothermic peaks at approximately 0 °C when heating mirrored by exothermic peaks at the same temperature upon cooling. These are likely the result of the side chains melting and recrystallizing. There are no other discernable thermal transitions until 400 °C, which is the result of polymer degradation.
Figure 46. Thermogravimetric analysis (TGA) of \textbf{pOMeDPPTz-BTh} in a nitrogen atmosphere (25 mL/min) at a heating rate of 10 °C/min.\textsuperscript{9}

\textsuperscript{9} TGA collected by Miguel Gonzalez
Figure 47. Differential scanning calorimetry (DSC) of pOMeDPPTz-BTh from -90 °C to 150, 200, 250, 300, 350, and 400 °C with the solid arrow representing heating and the dashed arrow representing cooling. Experiments were conducted under a flow of nitrogen with a flow rate of 50 mL/min and a heating/cooling rate of 10 °C/min.\textsuperscript{10}

\textsuperscript{10} DSC data collected by Alex Balzer.
3.2.2 Optical and Electrochemical Properties

**Figure 48.** UV-vis spectrum for pOMeDPPTz-BTh both in solution (1 x 10^{-6} M in 1,2,4-trichlorobenzene) and thin film state.

UV-vis of the solution and thin film for pOMeDPPTz-BTh in 1,2,4-trichlorobenzene (TCB) (Figure 48) shows there is a change in peak absorption intensity from solution to film. In solution $A_1$ and $A_2$ are approximately the same intensity at 775 and 701 nm, respectively but in film the $A_2$ peak decreases relative to $A_1$. Due to the limited solubility of the material, the solution was heated to 70 °C to determine if there was any change in absorption while in TCB. The heated solution had no notable change from the room temperature solution, suggesting the material was fully solubilized. The optical band gap $E_{g\text{opt}}$ was estimated to be 1.41 eV, as shown by the values presented in Table 5. It is interesting to note that the material has a wider absorption range, and subsequent higher absorption onset in solution than when in film. The wider absorption range coupled with
the unchanging peak maxima suggests that the material can adopt more conformations in solution than in film.

**Table 5.** UV-vis absorption characteristics of pOMeDPPTz-BTh in solution and thin film.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\lambda_{\text{max}}^{\text{sol}}$ (nm)</th>
<th>$\lambda_{\text{max}}^{\text{film}}$ (nm)</th>
<th>$\lambda_{\text{max}}^{\text{sol}}$ (nm)</th>
<th>$\lambda_{\text{max}}^{\text{film}}$ (nm)</th>
<th>$E_g^{\text{opt}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pOMeDPPTz-BTh</td>
<td>775</td>
<td>775</td>
<td>701</td>
<td>702</td>
<td>1.41</td>
</tr>
</tbody>
</table>

CV was conducted on pOMeDPPTz-BTh in organic and aqueous environments to determine the reduction and oxidation potentials, and subsequently estimate EA and IP. In organic solvents ([Figure 49](#)), there are two reduction peaks with onsets at -1.43 and -1.59 eV, which are reversible over multiple cycles. The same can be said of the oxidation potentials, which were also found to be reversible at 0.73 and 0.94 eV. The reversibility suggests good charge carrier stability when in organic solvents and leads to an estimation of EA and IP of 3.67 and 5.83 eV. Unfortunately, the EA is not below the desired 4.05 eV for electrochemical stability in aqueous environments, as confirmed by little to no response when in an aqueous environment (see Appendix, [Figure 58](#)). Future tests conducted by Brian Khau will determine if saponification of the ester end group on the side chain into a carboxylic acid results in ionic charge accumulation, and subsequent electronic charge transport in aqueous environments.
Figure 49. Cyclic voltammograms of pOMeDPPTz-BTh polymer films in organic electrolyte, using a scan rate of 50 mV/s between -2.2 V and 1.0 V. pOMeDPPTz-BTh thin films were drop-casted on glassy carbon electrodes from 1,3,5-trichlorobenzene solutions using TBAPF$_6$ (0.1M, propylene carbonate) as the electrolyte and an Ag/Ag$^+$ pseudoreference (10mM AgNO$_3$/MeCN, 0.09 V vs Fc/Fc$^+$) for the reference electrode.$^{11}$

3.2.4 OFET Performance

Table 6. Electron transport properties of pOMeDPPTz-BTh in the linear regime on different surface modified BGBC OFET devices$^a$.

<table>
<thead>
<tr>
<th>Surface Modification</th>
<th>Average $\mu_e$ (cm$^2$/V.s)</th>
<th>Maximum $\mu_e$ (cm$^2$/V.s)</th>
<th>$V_{Th}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>$1.2 \pm 0.3 \times 10^{-2}$</td>
<td>$1.6 \times 10^{-2}$</td>
<td>$37 \pm 4$</td>
</tr>
<tr>
<td>OTS$^b$</td>
<td>$5.9 \pm 1.7 \times 10^{-3}$</td>
<td>$8.3 \times 10^{-3}$</td>
<td>$31 \pm 14$</td>
</tr>
<tr>
<td>HMDS$^b$</td>
<td>$7.8 \pm 2.6 \times 10^{-3}$</td>
<td>$1.0 \times 10^{-2}$</td>
<td>$40 \pm 3$</td>
</tr>
<tr>
<td>FDTS$^b$</td>
<td>$1.3 \pm 2.3 \times 10^{-3}$</td>
<td>$7.4 \times 10^{-3}$</td>
<td>$36 \pm 7$</td>
</tr>
</tbody>
</table>

$^a$OFET characterization results and standard deviations are based on a minimum of six devices for each surface modification. $^b$Devices demonstrated poor coating abilities.

$^{11}$CV data collected by Brian Khau.
Organic field-effect transistors were made by blade coating 10 mg/mL of the material in TCB on a heated surface (200 °C) at 25 mm/s onto various self-assembled monolayers (SAMs). Transfer and output curves can be seen in Figures 50-51 with tabulated electron mobility ($\mu_e$) values in Table 6. Average $\mu_e$ were $1.2 \times 10^{-2}$ cm$^2$/V·s for unmodified devices, and 5.9, 7.8, and $1.3 \times 10^{-3}$ cm$^2$/V·s for OTS, HMDS, and FDTS modified devices. Threshold voltages were all relatively similar at 37, 31, 40, and 36 V for unmodified, OTS, HMDS, and FDTS devices.

Remarkably, the highest average electron mobility of $1.2 \times 10^{-2}$ cm$^2$/V·s was achieved when no SAM was deposited. Typically, electron transporting materials experience charge trapping with high work function materials (i.e. the untreated SiO$_2$ devices) and need to be modified to enhance film coating and reduce charge trapping$^{75,182}$. This is commonly reduced by the addition of hydrophobic SAMs, such as OTS, HMDS, and FDTS. In the case of pOMeDPPTz-BTh however, the most hydrophobic SAM, FDTS, resulted in the lowest average $\mu_e$ of $1.3 \times 10^{-3}$ cm$^2$/V·s. The unmodified devices demonstrated the most consistent mobility values, as seen by the small deviation. All three modified surfaces had significantly larger standard deviations, a result of the poor and inconsistent film qualities. Another key thing to note is that the devices all operated solely in the linear regime. This is likely the result of a large energy offset between the LUMO in the organic material with the Fermi level of the metal electrodes$^{183}$. 

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Figure 50. Transfer curves (a and c) and output curves (b and d) for pOMeDPPTz-BTh blade-coated on unmodified SiO$_2$ (a and b) and OTS (c and d) modified OFET devices in the linear regime.
Figure 51. Transfer curves (e and g) and output curves (f and h) for pOMeDPPTz-BTh blade-coated on HMDS (e and f) and FDTS (g and h) modified OFET devices in the linear regime.

3.2.3 Thin Film Surface Morphology

Surface morphologies of pOMeDPPTz-BTh thin films on OTS, HMDS, or FDTS modified OFET devices were compared against thin films coated directly on untreated SiO₂ devices. As can be seen in Figure 52, the macroscale morphology for the untreated SiO₂ have a surface roughness of 36.4 nm across a 25 μm² area. Upon zooming in to a 2.5 μm² area however, virtually no surface features can be detected, resulting in a surface roughness of only 1.7 nm. The surface morphologies for HMDS and FDTS (Figure 53) visually appear the same as the unmodified devices for both 25 and 2.5 μm² areas, but the roughness
is roughly double that of the SiO$_2$ (84.4 and 70.9 nm for HMDS and FDTS, respectively). OTS modified surfaces demonstrate the worst film qualities, with surface roughness of 97.6 nm in a 25 μm$^2$ area. This is suspected to be the result of de-wetting, as noted by the large gaps in the smaller 2.5 μm$^2$ area.

Figure 52. AFM surface height (top row) and phase (bottom row) profiles of pOMeDPPTz-BTh thin films blade coated on unmodified SiO$_2$ OFET devices (left) and OTS (right) modified OFET devices.
3.2.5 Potential for OECT Application

Due to the preference for pOMeDPPTz-BTh to coat on hydrophilic SiO$_2$ over hydrophobic SAMs, it is believed that the carboxylic acid side chain will be even more hydrophilic, and demonstrate superior ionic induction relative to the ester, possibly resulting in the desired OECT performance of ionic and electronic charge transport capabilities. The ability of the potassium salt material, pK$^+_{DPPTz-BTh}$, to solubilize in water allows films to be made, which can then be acidified to produce the desired carboxylic acid, pCOOH-DPPTz-BTh. Initial UV-vis of pK$^+_{DPPTz-BTh}$ dissolved in water and drop cast thin film, as well as the acidified film to produce pCOOH-DPPTz-BTh can be seen in Figure 54. Absorption data and estimated optical gaps can be found in Table 7.
Figure 54. UV-vis absorption spectra of pOMeDPPTz-BTh [Ester] in solution (TCB) and thin film, pK⁺DPPTz-BTh [K⁺] in solution (water) and thin film, and pCOOH-DPPTz-BTh [COOH] in thin film.

Table 7. UV-vis absorption characteristics of pK⁺DPPTz-BTh in solution (water) and thin film, and pCOOH-DPPTz-BTh in thin film.

<table>
<thead>
<tr>
<th>Material</th>
<th>A₁</th>
<th>A₂</th>
<th>( \lambda_{\text{max}}^\text{sol} ) (nm)</th>
<th>( \lambda_{\text{max}}^\text{film} ) (nm)</th>
<th>( \lambda_{\text{max}}^\text{sol} ) (nm)</th>
<th>( \lambda_{\text{max}}^\text{film} ) (nm)</th>
<th>( E_g^{\text{opt}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pK⁺DPPTz-BTh</td>
<td></td>
<td></td>
<td>805</td>
<td>762</td>
<td>734</td>
<td>700</td>
<td>1.35</td>
</tr>
<tr>
<td>pCOOH-DPPTz-BTh</td>
<td></td>
<td></td>
<td>-</td>
<td>798</td>
<td>-</td>
<td>736</td>
<td>1.33</td>
</tr>
</tbody>
</table>

The \( E_g^{\text{opt}} \) for pK⁺DPPTz-BTh and pCOOH-DPPTz-BTh are estimated to be 1.35 and 1.33 eV. As Figure 54 depicts, there is a general red shift from the ester side chain to the potassium salt side chain, both in solution and in thin film. Likewise, the potassium film also has a smaller absorption onset wavelength relative to its solution state, just as the ester side chain demonstrated. This suggests that the change in conformation from solution...
to thin film is not dependent of the side chain modification, but rather the backbone of the material.

Interestingly, \( pK^+\text{DPPTz-BTh} \) in solution behaved more like the thin film of \( p\text{OMeDPPTz-BTh} \) with \( A_1 \) intensity higher than \( A_2 \). This changes however, in the thin film of \( pK^+\text{DPPTz-BTh} \) as the relative peak ratios decreases. The decreased peak definition is likely the result of the crude drop cast film, as opposed to the smooth blade coated film of \( p\text{OMeDPPTz-BTh} \). After being submersed in dilute hydrochloric acid solution, the newly formed \( p\text{COOH-DPPTz-BTh} \) film shows a small red shift relative to the potassium side chain thin film. Again, the drop cast thin film shows little peak separation, which is to be expected of a post-film modification. Further tests regarding the potential of \( p\text{COOH-DPPTz-BTh} \) to function as the active material in an OECT will be conducted by Brian Khau.

3.3. Conclusion

A thiazole flanked DPP has been coupled with bithiophene to yield a donor-acceptor polymer with modifiable side chains for potential use in OECTs. The initial polymer, \( p\text{OMeDPPTz-BTh} \), contains a methyl ester end group on the linear side chains of DPP, which has achieved electron mobility values as high as \( 1.6 \times 10^{-2} \text{cm}^2/\text{V} \cdot \text{s} \) in OFET devices, despite limited solubility. Interestingly, the highest and most consistent mobility values were achieved without any surface modification to the \( \text{SiO}_2 \) OFET devices. Hydrophobic SAMs, which are often employed to increase film quality and lower charge trapping, resulted in poor film qualities and lower average electron mobilities. Unfortunately, the EA was not below the desired 4.05 eV for electrochemical stability in the presence of water, as was demonstrated by the poor CV response of \( p\text{OMeDPPTz-} \)
BTh in water. However, it is likely that the carboxylic acid side chain in pCOOH-DPPTz-BTh will demonstrate stronger currents in aqueous environments. Taking advantage of the post-polymerization modifiable side chains, polymers can easily be multipurposed - utilized in both organic and aqueous devices. This could lead to a relatively quick and easy way of building a library of direct comparisons of OFET and OECT performance, ultimately speeding up the ongoing development of design parameters for n-type OECT materials. Future efforts should be focused on designing polymer backbones with electron affinities below 4.05 eV before optimizing side chain length and modifications.

3.4 Experimental

3.4.1 Materials and Methods

Chloroform, dichloromethane, tetrahydrofuran (THF), dimethyl formamide (DMF), and toluene were purchased as anhydrous-grade solvents from Sigma-Aldrich. THF was distilled from sodium benzophenone in a solvent purification system (SPS). Starting materials were purchased from commercial suppliers and used without further purification. Sodium thiosulfate, n-bromosuccinimide, concentrated sulfuric acid, liquid bromine, sodium hydride, tris(dibenzylideneacetone)-dipalladium (0) (Pd$_2$(dba)$_3$), and copper(I) iodide were purchased from Sigma-Aldrich. Diethyl succinate, tin(II) chloride dihydrate, potassium hydroxide, pentadecanolide, and 2-cyanothiazole were purchased from Fischer Scientific. Triphenylphosphine, hexamethyldisilazane, perfluorodecy1trichlorosilane, t-amyl alcohol, and potassium carbonate were purchased from Alfa Aesar. N-octadecyltrichlorosilane was bought from Gelest Inc.

$^1$H NMR spectra were recorded using a Varian Mercury V, 400 MHz nuclear magnetic resonance spectrometer. Solid state $^{13}$C NMR spectra were recorded using a
Bruker AVIII, 300 MHz nuclear magnetic resonance spectrometer. Elemental analysis was conducted by Atlantic Microlab, Inc. Thermal analysis was conducted on a Perkin-Elmer Pyris-1 thermogravimetric analyzer (TGA) in a nitrogen atmosphere (25 mL/min) with a heating rate of 10 °C/min. Thermal transitions were measured with a TA Q200 Differential Scanning Calorimeter (DSC) in a nitrogen atmosphere (50 mL/min) with a heating/cooling rate of 20 °C/min.

UV-vis absorption spectra were recorded on an Agilent 8453 UV-Visible Spectrophotometer. pOMeDPPTz-BTh polymer films were prepared by blade coating on a heated stage (200 °C at 25 mm/s) polymer solutions in TCB (10 mg/ml) onto pristine SiO₂ glass substrates. pK⁺DPPTz-BTh polymer films were prepared by drop casting from water and heating at 65 °C until dried.

Cyclic voltammetry (CV) was performed at scan rates of 50 mV/s using a Gamry Reference 3000 Potentiostat/Galvanostat using a three-electrode setup. The working electrode consisted of a glassy carbon electrode with dropcast polymer film (1 mg/mL solution in 1,2,4-trichlorobenzene); the counter electrode comprised of Pt flag, flamed with a butane torch. For the aqueous measurements, the electrolyte was 0.1 M NaCl in Millipore water, using a standard Ag/AgCl reference (3 M aqueous inner solution, BASI). For the organic measurements, the electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆, Acros Organics) dissolved in propylene carbonate, where TBAPF₆ was recrystallized in hot ethanol prior to use. A pseudoreference was made in-house by immersing an Ag wire in 0.1 M AgNO₃ /acetonitrile and was calibrated as 0.09 V vs the ferrocene/ferrocenium redox couple. Argon was bubbled through the electrolyte.
for 10 minutes to remove residual oxygen prior to data collection and perform the experiments in an inert atmosphere.

Bottom contact bottom gate OFETs were fabricated onto n-doped silicon wafers <100>. The silicon served as the gate electrode while a 300 nm thick SiO₂ layer served as the gate dielectric. Source and drain contacts were made using 3 nm Cr as an adhesive layer and 50 nm Au. These were made with a photolithography lift-off technique to ensure fixed channel dimensions of 50 μm wide by 2mm long. The substrates were sonicated in acetone for 30 minutes, and then rinsed with acetone, methanol, and IPA in that order, and dried using an air gun. Devices without SAMs were coated without UV-ozone. Devices using SAMs were subjected to 30 minutes in the UV/ozone and soaked overnight in a 1 μL/mL solution of either OTS-18, perfluorodecyltrichlorosilane, or hexamethyldisilazane in anhydrous toluene. Polymer solutions of 10 mg/mL in TCB were stirred overnight at 85 °C and blade coated at 25 mm/s using a heated stage (200 °C) under ambient conditions.

All OFET measurements were conducted using a probe station in a nitrogen filled glovebox and an Agilent 4155C semiconductor parameter according to previous methods. Mobility values were calculated from the following equation and the linear regime in the transfer plots of V_G vs I_LD by extracting the slope of the linear range of the V_G vs I_LD plot:

\[
I_{LD} = \left( \mu_e C_{ox} \frac{W}{L} \right) \left[ (V_G-V_{Th})V_D - \frac{V_D^2}{2} \right]
\]

In this equation, I_LD is the source drain current (A), V_D is the source drain voltage (V), V_G is the gate voltage (V) scanning from -80 to 80 V in the transfer plot, C_ox is the capacitance per unit area of the gate dielectric layer, W is the channel width, L is the
channel length, and $\mu_e$ is the electron field-effect mobility in the linear regime ($\text{cm}^2/\text{V} \cdot \text{s}$). The threshold voltage, $V_{\text{Th}}$, was calculated by extrapolating $V_{\text{Th}} = V_G$ at $I_{\text{LD}} = 0$ in the $V_G$ vs $I_{\text{LD}}$ curve. Averages were based off a minimum of 6 devices (6 channels per device) for each polymer.

3.4.2 Synthetic Details

**Methyl 15-hydroxypentadecanoate:** To a nitrogen filled round bottom flask with stir bar and condenser, pentadecalacetone (5.00 g, 20.8 mmol) was dissolved in 50mL methanol. Five drops of concentrated sulfuric acid was added to the RBF and the reaction was stirred at reflux overnight. The product was condensed under reduced pressure and redissolved in DCM and filtered through a silica plug. The product was again condensed under reduced pressure to yield a white solid (5.55g, 98%). $^1$H NMR (400MHz, Chloroform-$d$) $\delta$ 3.66 (s, 3H), 3.63 (t, $J = 6.7$ Hz, 2H), 2.28 (t, $J = 7.5$ Hz, 2H), 1.67-1.49 (m, 4H), 1.25 (s, 20H). Spectral data matches previously reported literature values.$^{184}$

**Methyl 15-bromopentadecanoate (Br-15-OMe):** To a single neck RBF with stir bar is added methyl 15-hydroxypentadecanoate (10.0 g, 36.7 mmol) dissolved in 200mL DCM. The mixture is bubbled through with nitrogen for 15 minutes. Triphenylphosphine
(12.1 g, 45.9 mmol) and sodium bicarbonate (0.26 g, 3.1 mmol) are added, and the mixture is cooled in an ice bath to 0 °C. NBS (8.50 g, 47.8 mmol) is added slowly over 20 minutes and the reaction is stirred for an hour at room temperature. Saturated sodium bisulfate is added to the reaction and stirred for 15 minutes. The product is washed with DI water, dried over MgSO₄, filtered and concentrated under reduced pressure. The dried product is dissolved in hexane:ethyl acetate 20:1 and refluxed for thirty minutes. The product is filtered out using the same hexane:ethyl acetate mixture and concentrated under reduced pressure. A silica gel column is run using the same mixture as the eluent to yield a while solid as the product (9.98 g, 81%). ¹H NMR (400MHz, Chloroform-d) δ 3.67 (s, 3H), 3.41 (t, J = 6.9 Hz, 2H), 2.31 (t, J = 7.6 Hz, 2H), 1.83-1.89 (q, J = 7.7 Hz, 2H), 1.60-1.65 (m, 2H), 1.40 (m, 2H), 1.26-1.30 (m, 18H). Spectral data matches previously reported literature values.¹⁸⁴

Dimethyl 15,15’-(1,4-dioxo-3,6-di(thiazol-2-yl)pyrrolo[3,4-c]pyrrole-2,5(1H,4H)-diyl)dipentadecanoate (OMeDPPTz): A 2-neck RBF was degassed and refilled with nitrogen with a stir bar and condenser. Bithiazole-DPP (1.0 g, 3.3 mmol) and NaH (0.34 g, 8.4 mmol) were dissolved in 30 mL anhydrous DMF and heated at 150 °C for two hours. The reaction mixture was cooled to room temperature and Br-15-OMe (2.2
g, 6.6 mmol) was added to the reaction and stirred at 80 °C for 6 hours. The reaction was again cooled to room temperature and another portion of **Br-15-OMe** (2.2 g, 6.6 mmol) was added and stirred at 80 °C for 6 hours. After cooling to room temperature, the reaction was filtered, washed with chloroform, and condensed under reduced pressure. The product was redissolved in chloroform and washed with DI water three times, before being dried with MgSO₄, filtered, and concentrated under reduced pressure. Silica gel chromatography was run using DCM as the eluent, and the product was precipitated from methanol to yield an iridescent purple solid (0.91 g, 34%). **¹H NMR (400MHz, Chloroform-d) δ 8.07 (d, J = 3.2 Hz, 1H), 7.72 (d, J = 3.2 Hz,1H), 4.40 (t, J = 7.6 Hz, 2H), 3.66 (s, 3H), 2.30 (t, J = 7.6 Hz, 2H), 1.74-1.58 (m, 4H), 1.41-1.26 (m, 20H).** **¹³C NMR (400MHz, Chloroform-d) δ (ppm): 174.3, 160.9, 155.3, 144.5, 137.5, 123.9, 110.5, 51.4, 42.8, 34.1, 29.7, 29.6, 29.5, 29.2, 29.1, 26.8, 24.9.** ESI mass calculated: 811.45. Found: 811.45.

**Dimethyl 15,15'-(3,6-bis(5-bromothiazol-2-yl)-1,4-dioxopyrrolo[3,4-e]pyrrole-2,5(1H,4H)-diyl)dipentadecanoate (Br-OMeDPPTz):** OMeDPPTz (0.50 g, 0.62 mmol) was added to a 2-neck RBF with stir bar and condenser and dissolved in 50 mL chloroform. The vessel was bubbled through with nitrogen for thirty minutes. Sodium bicarbonate (0.57 g, 6.8 mmol) was added to the reaction and the whole setup was cooled...
in an ice bath to 0 °C. While the reaction vessel cooled, a separate RBF was charged with 10 mL chloroform, liquid bromine (0.33 mL, 0.98 mmol) and bubbled through with nitrogen for thirty minutes while also cooling in an ice bath. The bromine mixture was added dropwise to the initial reaction vessel and then refluxed at 60 °C overnight. If TLC revealed the reaction has not reached completion another portion of bromine (0.10 mL dissolved in chloroform) would be added, and reflux would continue. Once the reaction if finished, it would be cooled to room temperature and saturate sodium thiosulfate would be stirred in for 30 minutes. The product would be washed with brine, dried with MgSO₄, filtered and condensed under reduced pressure. Silica gel chromatography would be run using DCM as the eluent, adding a splash of acetone as needed. The product was concentrated, then precipitated from methanol to yield a deep purple solid (0.12 g, 22%).

\(^1\)H NMR (400MHz, Chloroform-d) δ 7.94 (s, 1H), 4.32 (t, J = 7.5 Hz, 2H), 3.66 (s, 3H), 2.30 (t, J = 7.6 Hz, 2H), 1.74-1.58 (m, 4H), 1.41-1.26 (m, 20H). \(^1^3\)C NMR (400MHz, Chloroform-d) δ (ppm): 174.4, 160.7, 156.3, 145.8, 136.6, 115.86, 51.4, 43.0, 34.1, 29.7, 29.6, 29.5, 29.2, 29.1, 26.8, 24.9. ESI mass calculated: 967.27. Found: 967.27.

\textbf{pOMeDPPTz-BTh: Br-OMeDPPTz (0.387 g, 0.400 mmol), stannylated bithiophene (0.197 g, 0.400 mmol), tris(dibenzylideneacetone)dipalladium (10.9 mg, 0.012 mmol), triphenylphosphine (12.6 mg, 0.048 mmol), and a pinch of copper iodide were}
dissolved in anhydrous toluene (4 mL) and anhydrous DMF (0.4 mL) in an oven dried 10 mL microwave vial under nitrogen. The vial was placed in a microwave reactor for 1 hour at 160°C at 250 W power while stirring. The reaction changes from pink to dark green after polymerization. The polymer was precipitated in methanol and purified in a cellulose Soxhlet thimble. The Soxhlet was run using ethyl acetate (24 hr), acetone (24 hr), chloroform (24 hr), toluene (24 hr) and trichlorobenzene (24 hr) in that order. The trichlorobenzene wash was concentrated and precipitated in methanol to yield 268 mg of a dark green solid (69 % yield).

\[
\text{pK}^+\text{DPPTz-BTh: pOMeDPPTz-BTh (50 mg)} \text{ was stirred overnight in 10 mL of 2M KOH in methanol at 45 °C. The solution was cooled to room temperature and the polymer was centrifuged at 6000 RPM for 10 minutes in methanol. Methanol was decanted off and the polymer was centrifuged with methanol three times. Any remaining solvent was dried off under reduced pressure to yield the water-soluble product.}
\]
pCOOH-DPPTz-BTh: Drop cast films of pK*DPPTz-BTh were submerged in a dilute HCl water solution for 15 minutes. The film was rinsed with DI water and dried using a nitrogen air gun.
CHAPTER 4. CONCLUSIONS AND FUTURE WORK

4.1 Conclusions

This thesis examines the design, synthesis, and characterization of electron transporting donor-acceptor DPP-based co-polymers and their subsequent application in OFETs and OPVs.

Chapter 1 served as an introduction into organic semiconductors and the various design aspects and characterization techniques that must be considered for high performance organic electronics. Specifically, the difficulties behind designing electron transporting polymers was assessed as it pertains to OFETs, OPVs, and OECTs.

Chapter 2 compared the stabilization effect and charge transport characteristics of two structural features - thiazole-flanked DPP and thioalkyl side chains - in a family of polymers. Of the three polymers, pDPPTz-OTHBDT (P1), pDPPTh-OSThBDT (P2), and pDPPTz-OSThBDT (P3), the thiazole-flanked polymers P1 and P3 showed more stabilization than P2, indicating the electron deficient thiazole moiety has a larger effect on lowering frontier molecular orbitals than thioalkyl side chains. Ultimately, combining thiazole with thioalkyl side chains resulted in a combined lowering of the frontier molecular orbitals. The high-lying molecular orbitals of P2 afforded p-type charge carrier characteristics, in contrast to the n-type charge carrier characteristics of P1 and P3. Due to the preferred electron transporting nature of the thiazole-flanked DPP polymers and their poor miscibility with PC_{71}BM, future research should focus on using thiazole-flanked DPP materials as acceptors in OPVs. Finally, transient absorption spectroscopy provided further
proof for the poor OPV performances, establishing a potential method for screening OPV active materials in the future. These results highlight the complexity of semiconducting polymer design, as it pertains to various device performances.

In Chapter 3, modifiable methyl ester side chains on a thiazole-flanked DPP monomer are coupled with bithiophene to yield an electron transporting material, pOMeDPPTz-BTh. Post-polymerization modifications afforded a water soluble pK+DPPTz-BTh and subsequent solvent resistant pCOOH-DPPTz-BTh. While limited solubility due to the linear side chain restricted characterization techniques, electron mobilities of up to $1.6 \times 10^{-2} \text{cm}^2/\text{V} \cdot \text{s}$ were obtained for the initial methyl ester side chain. Electrochemical characterization of pOMeDPPTz-BTh resulted in an estimated electron affinity of 3.67 eV, which unfortunately was not low enough for the desired OECT electrochemical stability in the presence of water. Nonetheless, the preference of the methyl ester side chain to film on hydrophilic surfaces is a promising indicator that modifying the side chain into a carboxylic acid could result in a material with electrochemical stability in the presence of water for OECT devices. As the design principles for electron transporting materials for OECTs is still in early stages, this method of post-polymerization side chain modification is a relatively quick way of potentially obtaining dual purpose materials to develop a catalog of direct comparisons between organic (OFET) and aqueous-based (OECT) active materials.

4.2 Future Work

4.2.1 DPP-BDT Polymers

The results shown in Chapter 2 show the complexity of semiconducting polymer design as it pertains to desired electronic and optical features. It was proven that thiazole-
flanked DPP and thioalkyl side chains work harmoniously to stabilize frontier molecular orbitals. This is useful for future studies specifically aimed at frontier molecular orbital stabilization as it outlines the synergistic impact of electron deficient moiety placement and strength. The set of polymers did have modest molecular weights, so it would not only be fruitful to attempt expanding the polymer chains, but possible altering the position of the structural changes in question. Specifically, the placement of where the thioalkyl side chain attaches to the BDT moiety. Replacing a single carbon in a pure hydrocarbon side chain with sulfur could prove a relatively simple way of making minor adjustments to the frontier molecular orbital levels. In a similar fashion, replacing electron rich units with thiazole is a more impactful method of decreasing frontier molecular orbitals. Given the DPP and BDT moieties chosen for this family of polymers are both relatively strong donors and acceptors, it could prove beneficial to replace the alkylated thiophene units on BDT with thiazole, to decrease the electron density in that moiety as a whole and further stabilize the polymers.

Unfortunately, the electronic and optical device performance was not as high as desired with these polymers but there is still much to be learned and used. For instance, the thiazole unit is essential for dominantly electron transporting behavior in OFETs. When the electron charge carrier mobility is combined with the significantly lower lying orbitals, it suggests that the thiazole polymers would likely perform better as acceptors rather than donors in OPVs. On a similar note, it is hard to determine if the immiscibility of the thiazole polymers with PC71BM was due to the low molecular weights of the polymers or inherent structural incompatibility of the materials. Looking forward, solar studies should not only include morphological analysis – from surface roughness using AFM to microstructural
order with GIWAXS – to guide material designs and donor-acceptor combinations, but they should also use transient absorption to ascertain the efficacy of the neat and blended materials to form the polarons and excitons that are essential for OPV performance. Transient absorption would provide a means of pre-screening newly synthesized materials, saving time in solar device fabrication and optimization. This could also be used to screen active material application techniques, from spin coating and blade coating to spray coating, and determine how they impact solar device performance. Furthermore, it would be beneficial to see how already established materials perform in transient absorption, and if they follow expected trends.

4.2.2 OECT Synthetic Designs

The electron mobility values attainable of \textbf{pOMeDPPTz-BTh} despite limited solubility is very promising for future side chain development of n-type devices. Specifically, it would be interesting to see if the carboxylic acid modification of the side chain provides sufficient hydrophilic interactions for OECT device operation. Successful examples of carboxylic acid side chains have already been demonstrated using p-type polymers poly(3-hexylthiophene) and 3,4-propylenedioxythiophene (ProDOT), but none to date have been utilized in n-type polymers. CV scans of \textbf{pCOOH-DPPTz-BTh} are to be conducted soon by Brian Khau to determine if the linear carboxylic acid functionalized side chain has electrochemical stability in aqueous electrolytes and warrants further testing as an OECT active material. Likewise, it could begin the inevitable discussion on the influence of side chain length as it pertains to how far the ionic inducing unit is from the backbone and the impact on OECT performance. The relative insolubility of this particular
polymer suggests the side chains will likely need to be longer and branched for sufficient solubility, which could ultimately hinder ionic induction.

As discussed previously, the current design principles for electron transporting OECT active materials are actively being sought. Arguably, the only truly defined feature is the importance of having an electron affinity below 4.05 eV for sufficient electrochemical stability in aqueous environments. Beyond that, there are still concerns about how to find the ideal balance between ionic and electronic charge transport, as it pertains to device transconductance, change in volume, on/off switching speeds, etc. NDI-based polymers have been leading the field as far as backbones go thus far, with BBL-based polymers as the only other example. This thesis aimed to expand this area by designing a donor-acceptor polymer with thiazole-flanked DPP as the main electron transporting moiety. The polymer unfortunately did not attain the desired electron affinity, likely the result of pairing DPP with a donor unit. Future work should aim to pair known electron transporting moieties together. Bithiazole for example, in place of bithiophene, is more electron deficient and would result in a lower electron affinity. Similarly, polymerizing thiazole-flanked DPP with itself could prove sufficient in lowering the hybridized electron affinity. While OFET performance does not yet have a direct correlation to OECT performance, using polymer backbones with established high electron mobilities could provide a quicker path to high performing OECTs.

Despite the high electron affinity of the polymer discussed in this manuscript, the modifiable side chain is highly noteworthy and should be employed in future endeavors to design n-type materials for OECTs. The materials would in essence be dual purpose, employable in organic and aqueous devices. Part of the delay in concrete design parameters
for n-type OECT active materials is the fact that OECTs devices contain significantly more variables than OFETs, making it hard to definitively claim how a specific structural change impacted performance. If the polymer could be employed in an OFET and OECT however, it would provide a potential means of at least assessing electronic charge carrier mobilities between the devices. On that note, the length and bulk of the modifiable side chains could be further expanded to optimize the balance between ionic and electronic charge carrier mobilities as well. With the design of n-type materials for OECTs still being relatively new, the key to defining concrete parameters is to utilize what is known from similar fields and continue to build on it.
APPENDIX

Figure 55. UV-vis of pOMeDPPTz-BTh in a poor solvent, toluene, heated at 70 °C and allowed to cool to room temperature.
Figure 56. Cyclic voltammograms of pOMeDPPTz-BTh polymer films in aqueous electrolyte, using a scan rate of 50 mV/s between -0.8 V and 0.8 V. pOMeDPPTz-BTh thin films were drop-casted on glassy carbon electrodes from 1,2,4-trichlorobenzene solutions using NaCl (0.1M, water) as the electrolyte and Ag/AgCl (3 M aqueous NaCl inner solution, BASI) for the reference electrode.\textsuperscript{12}

\textsuperscript{12} CV data collected by Brian Khau
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