Investigating Heavy Atom Substitution on Perylene Diimides and Morphology Control Using Bulky Thiophene-Selenophene Block Copolymers

by

Huy Huynh

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Department of Chemistry
University of Toronto

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Abstract

The field of organic photovoltaics have seen significant growth over the last decade. In particular, bulk heterojunction devices are the currently favored device in organic photovoltaics due to the ability to optimize their active layer morphology. The active layer has the most potential for growth to produce devices with percent conversion efficiencies (PCE) in excess of 10%, which is the area that this thesis explores. For the n-type material, the atomistic substitution between S, Se and Te was investigated on a series of perylene diimide dimers linked with a 5-membered heterocycle. The optoelectronic properties are found to be virtually identical between the series with preliminary device data showing a PCE of 1.28%. Conversely, investigating morphology control of the active layer is also proposed using bulky phenyl-substituted thiophene-selenophene block copolymers. The bulky substituents are expected to compete with Se-Se and π-π interactions, which may lead to new and interesting morphology control.
Acknowledgments

The work accumulated in this thesis could not have been accomplished without the support and expertise from a large number of people in my life.

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<th>Definition</th>
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<tbody>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk heterojunction</td>
</tr>
<tr>
<td>CB</td>
<td>Chlorobenzene</td>
</tr>
<tr>
<td>CDCl₃</td>
<td>Deuterated chloroform</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>Chloroform</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DART-MS</td>
<td>Direct analysis real time mass spectroscopy</td>
</tr>
<tr>
<td>DCB</td>
<td>Dichlorobenzene</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DIO</td>
<td>1,8-diiodooctane</td>
</tr>
<tr>
<td>DME</td>
<td>Dimethoxyethanol</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>EQE</td>
<td>External Quantum Efficiency</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel permeation chromatograph</td>
</tr>
<tr>
<td>GRIM</td>
<td>Grignard metathesis</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>-------------</td>
<td>-------------</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>ICBA</td>
<td>indene-C 60 bis-adduct</td>
</tr>
<tr>
<td>iPrMgCl</td>
<td>Isopropylmagnesium chloride</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>$J_{sc}$</td>
<td>Short circuit current</td>
</tr>
<tr>
<td>$K_2CO_3$</td>
<td>Potassium carbonate</td>
</tr>
<tr>
<td>$K_3PO_4$</td>
<td>Potassium phosphate</td>
</tr>
<tr>
<td>KCTP</td>
<td>Kumada catalyst transfer polymerization</td>
</tr>
<tr>
<td>LiF</td>
<td>Lithium fluoride</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>M</td>
<td>Mole/litre</td>
</tr>
<tr>
<td>MALDI</td>
<td>Matrix-assisted laser desorption/ionization</td>
</tr>
<tr>
<td>mg</td>
<td>miligram</td>
</tr>
<tr>
<td>MgSO$_4$</td>
<td>Magnesium sulfate</td>
</tr>
<tr>
<td>mL</td>
<td>mililitre</td>
</tr>
<tr>
<td>NBS</td>
<td>n-bromosuccinimide</td>
</tr>
<tr>
<td>nBuLi</td>
<td>n-butyllithium</td>
</tr>
<tr>
<td>$\eta_e$</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>Ni(dppe)Cl$_2$</td>
<td>Dichloro(1,3-bis(diphenylphosphino)ethane)nickel</td>
</tr>
<tr>
<td>Ni(dppp)Cl$_2$</td>
<td>Dichloro(1,3-bis(diphenylphosphino)propane)nickel</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>NIS</td>
<td>N-iodosuccinimide</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic photovoltaics</td>
</tr>
<tr>
<td>P3HS</td>
<td>Poly(3-hexyl)selenophene</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3-hexyl)thiophene</td>
</tr>
<tr>
<td>P3PhT</td>
<td>Poly(3-phenyl)thiophene</td>
</tr>
<tr>
<td>PCBWM</td>
<td>Phenyl-C71-butyric acid methyl ester</td>
</tr>
<tr>
<td>PCE</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>Pd(PPh₃)₄</td>
<td>Tetrakis(triphenylphosphine)palladium(0)</td>
</tr>
<tr>
<td>PDI</td>
<td>Perylene diimide</td>
</tr>
<tr>
<td>PDOPT</td>
<td>Poly(3-(2,5-dioctyl-phenyl)- thiophene)</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>Polystyrene-sulfonic acid</td>
</tr>
<tr>
<td>PhI(OAc)₂</td>
<td>(Diacetoxyiodo)benzene</td>
</tr>
<tr>
<td>POPT</td>
<td>Poly(3-octylphenyl)thiophene</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>TD-DFT</td>
<td>Time dependant density functional theory</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal gravimetric analysis</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TOF</td>
<td>Time of flight</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>(\mu m)</td>
<td>Micrometre</td>
</tr>
<tr>
<td>(V_{oc})</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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</table>
Chapter 1
Introduction to Organic Photovoltaic Solar Cells

1 Demand for Alternative Energy

High global energy demands coupled with environmental concerns have driven the world away from typical environmentally damaging fossil fuels towards alternative energies such as hydro, nuclear, wind, and solar. Solar energy, in particular, is an attractive energy resource due to the large potential for harvesting solar radiation that can provide the world with energy several times over. Currently, the solar cell market is dominated by crystalline silicon wafer solar cells. However, the cost of silicon solar cells must be significantly reduced before this technology can reach mass market penetration. There are two main reasons why the price is currently too high; 1) pure high-grade silicon is required, which is expensive to purify, and 2) due to the poor spectral coverage and low absorption of silicon, thick wafer layers of approximately 400 to 180 µm are required. In fact, the silicon wafers account for up to 50% of the entire solar cell cost. Though studies are currently underway to solve these problems, researchers have begun to look into alternative materials that can replace silicon in solar cell technology.

One promising alternative is organic photovoltaics (OPV), which uses organic small molecules, dendimers, and polymers as the light harvesting material. This emerging technology has several advantages to their silicon counterpart. Firstly, molecular engineering of the organic molecules can easily be accomplished to fine-tune several properties such as the band gap, absorption and solubility. Furthermore, this material can be engineered to be more amorphous than crystalline, which opens up the opportunity to produce flexible solar cells. Another major advantage is that OPVs have a significantly reduced manufacturing cost and lower environmental impact. Highly developed organic materials are engineered to have high extinction coefficients with broad spectral profiles, which enables OPV to effectively have ~1000 thinner films than silicon wafers. Also, the organic materials are designed to be readily soluble, which opens up the possibility for cheap printing processes to manufacture solar cells.

With all of these advantages, there are still two main drawbacks with OPV, low efficiencies and short lifetimes. Indeed, before OPV can begin to rival crystalline silicon wafer solar cells as the dominate solar cell technology in the market, these two problems must be solved. Fortunately, the
potential advantages outlined here have spurred substantial international investment in this emerging and highly promising technology.

1.1 Organic Photovoltaic Device Architecture

The evolution of OPVs began with multilayer devices through sandwiching stacks of each component. Typically, the device architecture of OPVS are engineered with a transparent conducting layer, commonly a glass coated with indium tin oxide (ITO), which serves as the bottom electrode. Afterwards, this layer is coated with a polystyrene-sulfonic acid (PEDOT:PSS) layer, which facilitates hole injection/extraction by enhancing the surface contact with the active layer. This active layer, which will be expanded on in section 1.2, is deposited through inexpensive and simple techniques such as spin casting, screen printing, or spray coating. Afterwards, a thin layer of LiF is added to improve the electrode work function. Finally, the device is capped with an aluminum layer, which acts as the top electrode.

Figure 1-1 Schematic of bulk heterojunction device architecture (left) and the evolution of the active layer (right)

1.2 Active Layer Properties

The active layer is the most crucial component of OPV devices since it is responsible for harvesting and converting solar radiation into electricity. At first, the active layer was comprised only of a single layer polymer material. However, researchers quickly discovered that these devices performed poorly as the resulting photoexcited polymers failed to efficiently produce free charge carriers. Accordingly, the OPV architecture was improved through the addition of an electron acceptor (or n-type) material on top of the polymer, which is now known as the electron donor (or p-type) material, thus yielding bilayer devices (Figure 1-1). Now with an electron
accepting component, the electron donor upon photoexcitation can inject an electron into the LUMO of the electron acceptor. If the columbic attraction between the resulting positively charged polymer and negatively charged electron acceptor is overcome, free charge carriers in the form of holes, for the p-type material, and electrons, for the n-type material, are produced. Ideally, the free holes and electrons are able to migrate towards their respective electrodes leading to a potential. In reality, the morphology of the bilayer limit charge separation due to large domains of n-type and p-type materials and the limited interface between the two components.

Bulk heterojunction devices (BHJ) are now the top choice for OPV, where a combined solution of the donor and acceptor materials are added to produce an interpenetrating layer of both. Under optimal processing conditions, intimately mixed domains of the n- and p-type materials form the active layer. With the appropriate control in morphology, the domains can be tuned to maximize the donor-acceptor interface area, while creating appropriately sized domains that facilitates hole and electron migration to their respective electrodes. However, it has recently been proposed that a third intermixed phase occurs at the donor-acceptor interface, where more pronounced mixing occurs between the donor and acceptor. Unfortunately, this third phase prohibits charge separation and therefore is currently an unavoidable morphological factor that reduces device performance in BHJ devices.

Figure 1-2 Mechanism of the active layer in organic photovoltaics

The events that occur within the active layer are illustrated in Figure 1-2. Upon photo irradiation, the donor absorbs a photon, which excites an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) to produce an exciton. If the LUMO
of the acceptor is ~0.3 eV lower, a sufficient driving force is achieved to induce efficient charge transfer and produce a cuolombically bound hole and electron pair between the donor and acceptor. If the columbic attraction is overcome, free charge carriers are produced. Due to differences in the metal work function, electrons are then able to migrate to the aluminum electrode, whereas the holes migrate towards the ITO electrode, thus completing the circuit to generate electricity.

1.3 Device Parameters

Of course, the most important part of OPVs is its efficiency in converting solar radiation into usable electricity. The percent conversion efficiency (PCE), \( \eta_e \), is found using equation (1), where \( V_{oc} \) is the open circuit voltage, \( J_{sc} \) is the short circuit current density, FF is the fill factor, and \( P_m \) is the intensity of incident light.

\[
\eta_e = \frac{V_{oc} J_{sc} FF}{P_m} \quad (1.1)
\]

The most common ways to analyze the parameters and performance of a device is through a current-voltage (I-V) curve.

![Figure 1-3 Representative J-V curve illustrating the parameters of equation 1.1](image)

As seen in equation 1.1, several key parameters are involved in producing high efficiency devices with many being a direct result from the electronics of the donor and the acceptor, as well as the resulting morphology when these two components are mixed in the active layer. These parameters
are most commonly illustrated in an I-V curve as seen in Figure 1-3. The $V_{oc}$ is indicative of the maximum voltage of the device and is derived from the difference in energy between the HOMO of the donor and the LUMO of the acceptor. However, charge recombination events ultimately lead to lower $V_{oc}$ values. Alternatively, the $J_{sc}$ represents the maximum current of the device and is affected by how well the device can create and transport charges. As a result, the absorption coverage, film thickness, surface area, and charge transport ability of the active layer all play an integral role in the $J_{sc}$. Lastly, the FF is a parameter that describes the “squareness” of the J-V curve and can be found from equation 1.2. This parameter is the least understood and describe the ease in the extraction of the photogenerated carriers by the electrodes.

Another common way to analyze device performances is through an external quantum efficiency (EQE) curve. The EQE curve is the ratio of the number of charge carriers generated in the solar cell as a function of wavelength. The EQE curve can illustrate which area of the solar spectrum is producing the highest efficiencies and which areas are not. The overall solar radiation distribution is shown in the left of Figure 1-4. Almost half of the photons that reach the Earth’s surface are in the visible region, which is where many solar cell devices typically exhibit high absorptions. However, researchers are now interested in producing more narrow band gap materials with broad absorption profiles. With narrow band gaps and broad absorption profiles, the organic materials would be able to harvest the large flux of photons in both the visible and near-infrared region.

Figure 1-4 Solar spectrum (left) and representative EQE curve (right), solar spectrum image modified from Heat Energy Island Group, Lawrence Berkeley National Laboratory
1.4 Fullerenes as the Quintessential Electron Acceptor

The ubiquitous n-type materials for current OPV devices are fullerene derivatives. Indeed, fullerene has proven to have many advantageous properties that allow for high OPV efficiencies. Such properties include having a deep-lying LUMO, which imparts high electron affinity character relative to that of the donor material. Furthermore, fullerene has a triply degenerate LUMO, which can be reversibly reduced with six electrons, thus emphasizing fullerene’s ability to carry and stabilize negative charge. In addition, fullerene has also been shown to undergo ultrafast photo induced charge transfer (~ca. 45 fs) with many potential donors with a significantly lower back transfer rate. Lastly, the three-dimensional structure of fullerene under optimal morphological conditions enables the unique ability for multidimensional charge transport. As a result, fullerene such as phenyl-C71-butyric acid methyl ester (PCBM) and indene-C 60 bis-adduct (ICBA) are at the forefront of high performing OPV with PCE in excess of 10%.

Unfortunately, there still remain many flaws when applying fullerene as the acceptor. Fullerene suffers from poor solubility, which requires further functionalization to allow fullerene to be solution processable. However, the functionalization of fullerene has proven to be difficult. Consequently, the electronic properties of fullerene are difficult to tune, which means the poor absorption profile of fullerene is difficult to remedy. However, the biggest drawback in using fullerene is that their synthesis and purification is extremely expensive and difficult. Through these flaws, researchers in the field of OPV are now aggressively seeking alternative electron acceptors, which can ideally mimic or even exceed the properties of fullerene at a considerably reduced price.

Figure 1-5 Chemical structures of fullerene (left), ICBA (middle) and PC71BM (right)
point. Research into finding an alternative to fullerene is the main focus of this thesis and will be elaborated in Chapter 2.
Chapter 2
Exploring Perylene Diimides for n-type Materials

2 Introduction

As stated in section 1.4, an important goal in the field of OPVs is finding a replacement to the widely used fullerene and its derivatives due to their lack of tunability, poor absorption profiles, and expensive purification. As an alternative, organic small molecules over the last decade have been capturing the attention of many groups since organic small molecules can be synthesized and purified easily, have good solubility, and can be tuned both electronically and morphologically through the addition of various functional groups and alkyl chains.

2.1 Perylene Diimide

Recently, perylene diimide (PDI) derivatives have surged in popularity as a potential n-type organic semiconductor due to their 1) good thermal, chemical, and light stability, 2) strong electron accepting ability, 3) exceptional electron mobility, 4) broad absorption profiles and high extinction coefficients, 5) high tunability of their optical and electrochemical properties though modifications at the bay region and 6) ability to tune their packing and solubility by modifying the imide position.21

![Perylene Diimide nomenclature.](image)

However, one of the largest hurdle that remains for the successful integration of PDI’s as the n-type material in OPV are the large aggregates that typically form using PDI-based systems. The cause of these large domains is due to the highly planar shape of PDI’s, which heavily promotes intermolecular $\pi-\pi$ stacking between the PDI molecules. Unfortunately the high degree of aggregation causes large PDI domains, which reduces the surface area of the donor-acceptor
interface. This consequently lowers the likelihood for charge separation since large domains impede the potential for exciton migration to the donor-acceptor interface. With typical maximum exciton diffusion length between 10-20 nm, it becomes clear that the large PDI aggregates in the µm range must be reduced.26

2.2 Recently Synthesized PDI

In order to limit the PDI domain size, several recent reports have attempted to synthesize twisted PDI units that can disrupt π-π interactions. The introduction of a linker group between the PDI’s causes the PDI’s to twist out of plane, which has proven to suppress the π-π interactions responsible for the large domains. For example, Zhao and co-workers have made a series of PDI dimers with various linker groups to compare the linker effect on their photophysical, electrochemical, and morphological properties.27

![Figure 2-2 Comprehensive study on linker effects on the resulting PDI dimer performance, data is from reference 27](image)

As seen in Figure 2-2, the PDI dimers all exhibit significantly improved PCE compared to the single PDI molecule under similar processing conditions. It appears that the LUMO of the PDI dimers remain virtually constant to the parent PDI (-3.74 eV). This effect is rationalized through DFT calculations of the LUMO, which shows the electron density delocalized about the PDI units with very little contribution from the linker. Conversely, the HOMO of the PDI dimers is raised by the electron donating linker (-5.86 eV to -5.54 eV) relative to the parent PDI (-5.99 eV). These
results reflect donor-acceptor systems where the LUMO is comprised mostly from the acceptor unit (PDI) and the HOMO from the donor (linker).\textsuperscript{28,29} Fortunately, PDIs have a well-placed LUMO that is capable of being easily reduced, yet still high enough to produce high $V_{oc}$ in devices. As a result, Zhao shows evidence that changing the linker in PDI dimers can be a good avenue towards maintaining the appropriately placed LUMO level, while being able to tune the HOMO level, which can reduce the band gap, and the active layer morphology.

Another promising report by Yao and co-workers synthesized a PDI dimer using thiophene as the linker (Figure 2-3).\textsuperscript{30} Unlike the previous paper, this PDI dimer contains a 2-methoxyethoxyl group appended on to the 7 position of the PDI from the linker. This addition is likely due to their prior report that shows that the addition of the weakly solvophobic 2-methoxyethoxyl group to PDI enables elevated solubility, improved solution-processability, reduced aggregation, and optimal phase separation.\textsuperscript{31} As evidence that the twisting introduced by the thiophene linker, as well as by the 2-methoxyethoxyl group, can significantly reduce the aggregation of PDI, optical microscopic images are shown in Figure 2-3. A blended film of a bis-2-methoxyethoxyl PDI with a conjugated polymer based on alkylthiophene-2-yl-substituted benzo[1,2-b:4,5-b0]-dithiophene (PBDTTT-C-T) as the donor polymer shows large domains in the realm of 200 – 700 nm wide. Conversely,

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_3.png}
\caption{Optical microscopic images of blended films of parent PDI (top) and PDI dimer (bottom) with PBDTTT-C-T, images are from reference 30}
\end{figure}
blends using the PDI dimer produce significantly smaller domains of approximately 30 nm. Accordingly, the PCE improved dramatically from 0.13% to 4.03% going from the parent to the PDI dimer.

![Chemical structures of D1, D2, D3, D4, and D5](image)

**Figure 2-4 Recent reports in 2014 of twisted PDI molecules, D1 – D5, and the chemical structure of donors PBDTTT-C-TT and PBDTT-F-TT**

Just in 2014, an ever increasing number of PDI small molecules employing the twisted geometry approach to break up molecular packing and aggregation have been reported. A large PDI dimer, **D1**, using a bulky fused-ring indaceno[2-b:56, -b’]dithiophene as the linker produced a good PCE of 2.61% with P3HT. 32 Alternatively, **D2** was synthesized by fusing two PDI units together through the imide group, thus skipping the use of a linker entirely. 33 In this case, the twisting is enhanced giving a good PCE of 3.20% with PBDTTT-C-T. Intriguingly, a star-shaped PDI trimer, **D3**, was also reported shortly after yielding a good PCE of 3.22% thus marks the first time a PDI
trimer has been synthesized through the bay position (a PDI trimer using triphenyl amine through the PDI has been reported previously). $^{34,35}$Excitingly, D4, is recently reported with a PCE of 4.34% with PBDTTT-C-T.$^{36}$ Most recently, D5, was reported to have a high efficiency of 5.90% with PBDTT-F-TT setting the current benchmark for current non-fullerene small molecule acceptors.$^{37}$

These reports and more have made it abundantly clear that the favorable properties of PDI’s have captured the academic attention of many groups in the field of organic photovoltaics towards finding a replacement to the highly successful, yet highly expensive, fullerene.

2.3 Proposal

![Chemical structures of the dimeric PDI (left) and donor polymer PBDTTT-CT (right).](image)

Figure 2-5 Chemical structures of the dimeric PDI (left) and donor polymer PBDTTT-CT (right).

Herein, we report an atomistic study on a heterocyclic linker of a PDI dimer (Figure 2-5). It has been shown in the past that this strategy is effective in improving a material’s optical profile by red-shifting the absorbance as the atom is replaced from S to Se to Te.$^{38}$ However, we expect this phenomenon to not occur in this system due to the poor communication between the highly twisted PDI units and the heterocyclic linker. Fortunately, the electronic properties are already suitable for OPV applications. In this regard, we hope to study whether replacing S with Se and Te in the linker could improve the electron mobility due to the increased polarizability of the heavy atom. It has already been reported that replacing S with Se can increase the electron mobilities by a factor of 10 in conjugated copolymers due to the increased orbital overlap from the larger $\pi$-orbitals of Se compared to S.$^{39}$ Furthermore, the more polarizable Se atom introduces strong Se-Se interactions,
which has been shown in polymers to improve crystallinity and enhance interchain charge transport.40,41,42 Interestingly, no studies have been reported on whether the trend will continue with Te substitution. In this chapter, the optoelectronic properties and device performance of S-PDI, Se-PDI, and Te-PDI as the acceptor material is investigated with PBDTTT-C-T as the donor polymer.

2.4 Synthesis of PDI Dimers

![Figure 2-6 Synthesis of the PDI Dimers](image)

The synthesis of 1 was published previously.43 Synthesis of the PDI dimers was accomplished by Stille coupling with the corresponding stannylated heterocycle to produce S-PDI, Se-PDI, and Te-PDI. The products were fully characterized by $^1$H NMR, $^{13}$C NMR, and matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry. All products are soluble in common solvents such as dichloromethane, chloroform, and toluene. However, the solubility surprisingly appears to be less for Se-PDI and significantly less for Te-PDI, as compared to S-PDI.

It should be noted that S-PDI, Se-PDI, and Te-PDI are an inseparable mixture of the 1,7,1’,7’-, 1,6,1’,7’-, and 1,6,1’,6’- regioisomers, as illustrated in Figure 2-7. These regioisomers are the results of the dibrominated PDI that is synthesized in a mixture of the 1,6- and the 1,7- isomers with compositions varying batch to batch in typical 70:30 to 75:25 ratios. This contamination has typically been ignored by groups due to their extremely difficult separation.44
2.5 Characterization

Unsurprisingly, apart from the heterycyclic protons, the $^1$H NMR of S-PDI, Se-PDI, and Te-PDI are all very similar. The heterocyclic protons are shown in Figure 2-8, which shows a downfield shift from 7.47 to 7.58 to 7.94 ppm going from S to Se to Te, respectively. The spectra were obtained using concentrated solutions of each derivative at room temperature, which clearly illustrates their difference in solubility by comparing the peak intensities with the chloroform satellites.
The solution absorption profiles of all three dimers in chloroform is shown in Figure 2-9 and appears to be nearly identical. Only a small incremental red-shift is seen going from 563 to 565 to 568 for S-PDI, Se-PDI, and Te-PDI indicating that the atom substitution has only a small effect on the absorption profile. All the derivatives also show similarly high extinction coefficients of ~50 000 M⁻¹ cm⁻¹. Compared to the absorption in solution, thin film absorption of S-PDI, Se-PDI, and Te-PDI are blue-shifted and display similar absorption profiles with each other. Interestingly, Te-PDI has a shoulder peak that is not present in either S-PDI or Se-PDI. This causes the absorption profile to broaden compared to the near identical S-PDI and Se-PDI profiles.

Figure 2-9 Absorption Spectra in chloroform (left) and film (right) of S-PDI (pink), Se-PDI (red), and Te-PDI (blue)

Table 2.1 Optoelectronic properties of S-PDI, Se-PDI, and Te-PDI

<table>
<thead>
<tr>
<th></th>
<th>Sol. $\lambda_{\text{max}}$ [nm]</th>
<th>Film $\lambda_{\text{max}}$ [nm]</th>
<th>$\varepsilon_{\text{max}}$ [M⁻¹ cm⁻¹]</th>
<th>HOMO [eV]</th>
<th>LUMO [eV]</th>
<th>$E_{\text{g}}^{\text{cv}}$ [eV]</th>
<th>$E_{\text{g}}^{\text{film}}$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-PDI</td>
<td>563</td>
<td>544</td>
<td>50 998</td>
<td>-5.63</td>
<td>-3.68</td>
<td>1.95</td>
<td>1.90</td>
</tr>
<tr>
<td>Se-PDI</td>
<td>565</td>
<td>544</td>
<td>49 555</td>
<td>-5.61</td>
<td>-3.67</td>
<td>1.94</td>
<td>1.90</td>
</tr>
<tr>
<td>Te-PDI</td>
<td>568</td>
<td>551</td>
<td>48 268</td>
<td>-5.58</td>
<td>-3.67</td>
<td>1.91</td>
<td>1.80</td>
</tr>
</tbody>
</table>

a Measured by CV. DFT calculated values in parenthesis

The electrochemical properties of S-PDI, Se-PDI, and Te-PDI were investigated using cyclic voltammetry (CV) in solution using a Ag/AgI electrode in 0.1 M Bu₄NPF₆/CH₂Cl₂ at a scan rate of 100 mV s⁻¹. As seen in Figure 2-10, all three derivatives exhibit almost identical voltamograms.
The HOMO is estimated to be -5.63, -5.61, and -5.58 eV for S-PDI, Se-PDI, and Te-PDI, respectively. Conversely, the LUMO is found to be virtually identical for all the derivatives at -5.67 eV. It appears that the electronic properties are also being dominated by the PDI units and exchanging the heterocyclic atom has a negligible impact.

Figure 2-10 Cyclic voltammetry of S-PDI (pink), Se-PDI (red), and Te-PDI (blue), in DCM/0.1 M [nBu₄N][PF₆] at 100 mV s⁻¹.

Unlike the remarkably similar photophysical and electrochemical properties of S-PDI, Se-PDI, and Te-PDI, the stabilities of the derivatives are significantly different, as seen in the thermal gravimetric analysis (TGA) (Figure 2-11). Unsurprisingly, S-PDI has the best thermal stability with a 5% weight loss temperature under a nitrogen atmosphere of up to 389.9 °C. Conversely, Se-PDI decomposes at a significantly lower temperature at 274.8 °C followed by Te-PDI, which is the lowest at 226.3 °C. The trend shows that the thermal stability decreases significantly going into the heavier heterycles, which may be due to the decreased aromatic character of the heterocyclic linker between the PDI units.
2.6 Density Functional Theory Calculations

For a complete analysis of S-PDI, Se-PDI, and Te-PDI, time-depndant density functional theory (TD-DFT) is conducted on the PDI dimers. To simplify the calculation, the 2-ethylhexyl chain is replaced by a methyl group and the 2-methoxylethoxyl group is replaced by a methoxyl group. Calculations of the optimized geometry, molecular orbitals, and absorption profiles were conducted using the *Gaussian 09* program at the B3LYP level of theory with 6-311G(d) basis set for C, H, N, O, S and Se, and the LAN2DZ basis set for Te.

The optimized geometry of all three derivatives demonstrates that a significant dihedral angle exists between the PDI units resulting in a twisted confirmation. However, the relative twisting is approximately the same between the three PDI derivatives. The calculations also show that the PDI units have the largest contribution to the LUMO, which supports the experimental LUMO levels being identical regardless of the change in linker. Conversely, the HOMO has significant contributions from both the PDI units and conjugated linker backbone. Surprisingly, the linker’s heteroatom has close to 0 contributions in both the HOMO and the LUMO, which explains why exchanging the atom appears to have little effect on the PDI dimer’s optoelectronic properties.
Figure 2-12 The a) optimized geometry and b) LUMO (top) and the HOMO (down) of S-PDI$_2$ (left), Se-PDI$_2$ (middle), and Te-PDI$_2$ (right).
2.7 Preliminary Device Data

The preliminary organic photovoltaic device performances were studied on S-PDI and Se-PDI. The devices were constructed using the conventional architecture with an ITO substrate spin coated with a PEDOT:PSS layer followed by a spin coated solution containing the PDI dimer and PBDTTT-C-T. A LiF layer was then deposited and finally capped with an aluminum anode. According to reported results of similar systems, a 1:1 ratio of the donor and acceptor with various % of 1,8-diiodooctane (DIO) as the co-solvent with a 1:1 ratio of chlorobenzene (CB) and 1,2-dichlorobenzene (DCB) produced optimal results. \(^{36,30}\) The annealing temperatures and times were investigated and under similar conditions, it was found that annealing at temperatures above 70°C caused the PCE to decrease due to a decrease in the \(J_{sc}\). When comparing devices using Se-PDI that were annealed at 70°C and 100°C, the \(V_{oc}\) and FF remained nearly identical at 0.82 V and 33.21%, respectively. Conversely, the \(J_{sc}\) changed from 1.92 to 1.78 mA cm\(^{-1}\) when the sample was annealed at elevated temperatures, which suggests that higher temperatures may disrupt the crystallinity of Se-PDI.

### Table 2.2 Preliminary photovoltaic properties of S-PDI and Se-PDI

<table>
<thead>
<tr>
<th></th>
<th>Conc. In CB/DCB [mg/mL]</th>
<th>DIO [Vol %]</th>
<th>Anneal. [°C]</th>
<th>(V_{oc}) [V]</th>
<th>(J_{sc}) [mA cm(^{-2})]</th>
<th>FF [%]</th>
<th>Ave. PCE [%]</th>
<th>Standard Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-PDI</td>
<td>15:15 1:1</td>
<td>5</td>
<td>70</td>
<td>0.86</td>
<td>3.28</td>
<td>48.09</td>
<td>1.28</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>18:18 1:1</td>
<td>none</td>
<td></td>
<td>0.84</td>
<td>1.85</td>
<td>35.96</td>
<td>0.47</td>
<td>0.08</td>
</tr>
<tr>
<td>Se-PDI</td>
<td>15:15 2:1</td>
<td>2</td>
<td>70</td>
<td>0.80</td>
<td>2.62</td>
<td>40.36</td>
<td>0.77</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>10:10 2:1</td>
<td>2</td>
<td>70</td>
<td>0.82</td>
<td>1.92</td>
<td>33.21</td>
<td>0.48</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>10:10 2:1</td>
<td>100</td>
<td>1.78</td>
<td></td>
<td></td>
<td>33.01</td>
<td>0.44</td>
<td>0.06</td>
</tr>
</tbody>
</table>

The J-V and EQE curves for the best performing devices are shown in Figure 2-13. A 15:15 mg/mL of S-PDI and PBDTTT-C-T in a mixture CB/DCB with 5% DIO as the co-solvent annealed at 70°C produces the devices with a \(V_{oc}\) of 0.86 V, a \(J_{sc}\) of 3.28 mA cm\(^{-1}\) and a FF of 48.09% to yield an average PCE of 1.28%. Conversely, similar conditions except for using 2% DIO gave the best results for Se-PDI with a \(V_{oc}\) of 0.80 V, a \(J_{sc}\) of 2.62 mA cm\(^{-1}\) and a FF of 40.36% to yield a PCE of 0.77%. Both the acceptor and PBDTTT-C-T contribute to the photon-to-electron conversion to yield a broad EQE band from 300 to 800 nm. However, the device testing are still in the preliminary stages so direct comparisons between S-PDI and Se-PDI cannot be made at this time.
Figure 2-13 The preliminary studies of the J-V (a) and EQE (b) curves for the best performing devices fabricated from the 1:1 blended PDI and PBDTTT-C-T with [DIO]=5% for S-PDI and [DIO]=2% for Se-PDI

2.8 Work towards PDI tetramer

Further investigations into new types of PDI are also currently underway. Prior to the publication of D3 (Figure 2-4), the synthesis of the triphenylamine-cored PDI was attempted without the butoxyl group on the opposite bay position. To our surprise, the reaction conditions outlined in Figure 2-14 led to the crude synthesis of TPA-PDI$_2$ as the main product.

Figure 2-14 Synthesis towards TPA-PDI$_2$
As seen in Figure 2-15, the aromatic peaks of **TPA-PDI$_2$** can be assigned for all the aromatic protons. A strong singlet at 1.37 ppm is also a clear indication that the boronic ester still remains attached to the molecule. The compound was further verified using MALDI-TOF. The crude material was washed thoroughly with hot hexanes to remove any starting material from the reaction. Still, residual impurity peaks are observed, which is attributed to be from the originally desired tri-substituted PDI product, **TPA-PDI$_3$**. However, the reaction likely did not proceed to completion since both **TPA-PDI$_2$** and **TPA-PDI$_3$** began to crash out of the reaction mixture. In contrast, **D3** (Figure 2-4) was synthesized in toluene, which allowed for higher reaction temperatures, and the PDI units had butoxy groups, which would further enhance the solubility in these reaction conditions.$^{34}$ Regardless, the isolation of TPA-PDI$_2$ opens the door towards the synthesis of more complex PDI units with the boronic ester functional group.

Figure 2-15 The $^1$H NMR peak assignment for TPA-PDI$_2$ where the numbers in blue represent the expected integration
One avenue towards applying **TPA-PDI₂** is to form a large PDI tetramer with different linkers between the triphenylamine groups. Preliminary screenings using *Gaussian 09* at the B3LYP level of theory with 6-31G(d) basis set on potential molecules to react with **TPA-PDI₂** is shown in Figure 2-16. Unsurprisingly, the LUMO remains roughly the same for **G1-3** indicating that the LUMO of the tetramer is dominated by the PDI units. Conversely, the calculations show that the HOMO can be tuned by exchanging the linker.

![Figure 2-16 Proposal for a PDI tetramer with various donor linkers](image)

**Table 2.3 Screening of potential PDI tetramer at the B3LYP level of theory with 6-31G(d) basis set**

<table>
<thead>
<tr>
<th></th>
<th>HOMO /eV</th>
<th>LUMO /eV</th>
<th>Gap /eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPA-PDI₂</td>
<td>-5.33</td>
<td>-3.39</td>
<td>1.97</td>
</tr>
<tr>
<td>G1</td>
<td>-5.24</td>
<td>-3.46</td>
<td>1.78</td>
</tr>
<tr>
<td>G2</td>
<td>-5.21</td>
<td>-3.44</td>
<td>1.77</td>
</tr>
<tr>
<td>G3</td>
<td>-4.95</td>
<td>-3.46</td>
<td>1.49</td>
</tr>
</tbody>
</table>

### 2.9 Conclusions and Outlook

In conclusion, a series of PDI dimers, S-PDI, Se-PDI, and Te-PDI, with the atomistic exchange of S, Se, and Te in the linker group were successfully synthesized and fully characterized. All derivatives show broad absorption profiles between 400 – 700 nm, high extinction coefficients of \(\sim 50,000 \text{ M}^{-1} \text{ cm}^{-1}\), and well placed LUMO levels about -3.68 eV. It appears that the atom exchange in the linker has only a minimal effect on the optoelectronic properties. However, the thermal stabilities tested by TGA shows that the 5% weight loss temperature decreases from 389.9 to 274.8 \(\text{°C}\).
to 226.3 °C for S-PDI, Se-PDI, and Te-PDI, respectively, which is attributed to the decreased stability of the linker. Device studies are currently ongoing with preliminary results using a 1:1 blend of the PDI dimer with PBDDTTT-C-T to produce devices with a \( V_{oc} \) of 0.86 V, a \( J_{sc} \) of 3.28 mA cm\(^{-1}\) and a FF of 48.09% to yield a PCE of 1.28% for S-PDI and under similar conditions except for using 2% DIO gave the best results for Se-PDI with a \( V_{oc} \) of 0.80 V, a \( J_{sc} \) of 2.62 mA cm\(^{-1}\) and a FF of 40.36% to yield a PCE of 0.77%. Further studies towards using Te-PDI in a device and to improve overall device performances are currently underway. Testing the mobility of the resulting devices will be conducted to determine whether the exchange to heavier more polarizable atoms can improve the overall charge mobility of the devices. Furthermore, atomic force microscopy (AFM) images will be taken of the devices to determine whether the exchange in atoms can introduce new interactions that can change the blend morphology.

The synthesis of a PDI dimer with a triphenylamine core was also completed to yield a molecule with interesting further reactivity. Preliminary results using DFT calculations on potential PDI tetramers reveal that the LUMO is predominately based about the PDI units and that the HOMO can be tuned by exchanging the desired linker. These PDI tetramers are particularly interesting due to their 3 dimensional structures that may potentially be able to facilitate multidimensional charge transport in a similar fashion to fullerene.

**2.10 Experimental**

**General Considerations:** All reactions were performed in oven-dried glassware. All reagents were purchased from Sigma-Aldrich and used as received. DMF, THF and toluene were obtained from an Innovative Technology Pure Solv solvent purification system. Thin layer chromatography was performed on alumina plates pre-coated with Merck silica gel 60. Detection was achieved via irradiation by UV light. Flash chromatography was performed using SiliaFlash silica gel (Silicycle Inc.). All \(^1\)H and \(^13\)C NMR spectra were recorded on Varian Mercury 400, Varian Mercury 500, and Bruker Avance III 400 instruments at 25 °C. Chemical shifts (\( \delta \)) are expressed in parts per million (\( \delta \)) using residual solvent (\(^1\)H NMR \( \delta \) 7.26 ppm for CDCl\(_3\); \(^13\)C NMR \( \delta \) 77.16 ppm for CDCl\(_3\)) as reference.
A solution of 1,7-dibromoperylene diimide (2.5 g, 3.24 mmol) in dry DMF (163 mL) was prepared and allowed to stir for 10 minutes. Afterwards, anhydrous 2-methoxyethanol (1.28 mL, 16.2 mmol) and K₂CO₃ (2.24 g, 16.2 mmol) were added successively. The mixture was heated at 80 °C for 4 hours and then poured into water. The mixture was diluted with dichloromethane and washed with a 5% M solution of HCl and water three times. The DCM layer was dried over MgSO₄ and removed under vacuum. The resulting crude mixture was subjected to column chromatography using DCM:EA (50:1) as eluents to afford the desired product as a dark purple solid (1.0 g, 40%). Unreacted 1,7-dibromoperylene diimide was also recovered by column chromatography as the first eluted compound. ¹H NMR (400 MHz, CDCl₃, δ): 9.53 – 9.41 (m, 2H), 8.85 – 8.74 (s, 1H), 8.59 (d, J = 8.31 Hz, 1H), 8.52 (d, J = 8.18, 1H), 8.41 – 8.37 (m, 1H), 4.63 – 4.54 (m, 2H), 4.27 – 4.06 (m, 4H), 4.02 – 3.92 (m, 2H), 3.58 (s, 3H), 1.50 – 1.22 (m, 18H), 1.02 – 0.79 (m, 12H).

A mixture of 1-bromo-7-methoxylethoxylperylene diimide (200 mg, 0.26 mmol), 2,5-bis(trimethylstannyl) thiophene (50.8 mg, 0.124 mmol), and Pd(PPh₃)₄ (14 mg, 0.0124 mmol) was dissolved in dry toluene (20 mL). The resulting mixture was heated to 100 °C for 36 hours, where a color change from dark red to dark purple occurred. Afterwards, the mixture was diluted with DCM and washed with water three times. The DCM layer was dried over MgSO₄ and removed under vacuum. The crude material was purified via column chromatography using DCM:EA (100:7) as eluent to yield the desired product as a dark purple solid (152 mg, 87%). ¹H NMR (400 MHz, CDCl₃, δ): 9.51 – 9.39 (m, 2H), 8.65 – 8.18 (m, 10H), 7.57 – 7.38 (m, 2H), 4.67 – 4.51 (m, 4H), 4.20 – 3.91 (m, 12H), 3.65 – 3.55 (m, 6H), 2.02 – 1.78 (m, 4H), 1.49 – 1.17 (m, 32H), 1.00 –
A mixture of 1-bromo-7-methoxylethoxylperylene diimide (300 mg, 0.391 mmol), 2,5-bis(trimethylstannyl) selenophene (85 mg, 0.186 mmol), and Pd(PPh₃)₄ (21.5 mg, 0.0186 mmol) was dissolved in dry toluene (30 mL). The resulting mixture was heated to 100 °C for 36 hours, where a color change from dark red to dark purple occurred. Afterwards, the mixture was diluted with DCM and washed with water three times. The DCM layer was dried over MgSO₄ and removed under vacuum. The crude material was purified via column chromatography using DCM:EA (100:7) as eluent to yield the desired product as a dark purple solid (180 mg, 64%). ¹H NMR (400 MHz, CDCl₃, δ): 9.55 – 9.43 (m, 2H), 8.77 – 8.21 (m, 10H), 7.66 – 7.50 (m, 2H), 4.70 – 4.52 (m, 4H), 4.21 – 3.89 (m, 12H), 3.66 – 3.55 (m, 6H), 2.01 – 1.77 (m, 4H), 1.46 – 1.18 (m, 32H), 0.98 – 0.78 (m, 24H). ¹³C NMR (126 MHz, CDCl₃) δ 164.00, 163.76, 163.59, 157.20, 153.70, 135.12, 134.33, 133.86, 133.44, 131.65, 131.42, 131.19, 129.50, 128.92, 127.92, 127.52, 123.98, 123.73, 122.49, 121.75, 121.55, 120.94, 118.00, 77.41, 77.36, 77.16, 76.91, 70.89, 69.47, 59.55, 44.54, 44.40, 38.14, 38.02, 30.85, 29.86, 28.93, 28.81, 24.27, 24.12, 23.21, 14.29, 10.81. MS (MALDI): m/z = 1505.6 [M+H]⁺.
A mixture of 1-bromo-7-methoxylethoxylperylenediimide (296 mg, 0.385 mmol), 2,5-bis(trimethylstannyl) tellurophene (95 mg, 0.188 mmol), and Pd(PPh$_3$)$_4$ (21.7 mg, 0.0188 mmol) was dissolved in dry toluene (30 mL). The resulting mixture was heated to 100 °C for 36 hours, where a color change from dark red to dark purple occurred. Afterwards, the mixture was diluted with DCM and washed with water three times. The DCM layer was dried over MgSO$_4$ and removed under vacuum. The crude material was purified via column chromatography using DCM:EA (100:7) as eluent to yield the desired product as a dark purple solid (70 mg, 24%). $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 9.55 – 9.43 (m, 2H), 9.05 – 8.22 (m, 10H), 8.04 – 7.86 (m, 2H), 4.70 – 4.52 (m, 4H), 4.21 – 3.89 (m, 12H), 3.66 – 3.55 (m, 6H), 2.01 – 1.77 (m, 4H), 1.46 – 1.18 (m, 32H), 0.98 – 0.78 (m, 24H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$: 163.56, 157.64, 153.35, 138.67, 133.67, 131.43, 131.13, 130.23, 129.46, 128.81, 128.41, 127.66, 123.79, 122.42, 121.71, 121.54, 118.08, 117.85, 70.91, 69.53, 69.45, 59.57, 44.38, 38.14, 38.01, 32.08, 30.98, 30.87, 29.86, 28.82, 24.26, 24.15, 23.25, 23.21, 22.85, 14.29, 14.25, 10.80, 10.74, 1.17. MS (MALDI): m/z = 1555.5 [M+H]$^+$. 

To a solution of tris(4-bromophenyl)amine (0.96 g, 2 mmol) in THF (40 mL) at -78°C was added nBuLi (3.69 mL, 6.6 mmol, 1.79 M) dropwise. The mixture was allowed to stir for 1 hour then 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.24 g, 6.6 mmol) was added. After 15 minutes, the mixture was warmed to room temperature and allowed to stir for an additional hour. The mixture was poured into water and extracted with chloroform. The organic layer was then dried over MgSO$_4$ and was concentrated to ~1 mL under reduced pressure. The concentrated solution was added to hot ethanol and allowed to recrystallize overnight at 0°C to produce the desired product as a white solid (380 mg, 31%). NMR (400 MHz, CDCl$_3$, $\delta$): 7.68 (d, J = 8.82 Hz, 2H$_2$), 7.07 (d, J = 8.83, 2H), 1.34 (s, 12H).
A mixture of 1-bromoperylene diimide (334 mg, 0.48 mmol), tris(4-(4,4,5,5-tetramethyl-1,3,2-dixoaborolan-2-yl)phenyl)amine (100 mg, 0.16 mmol), and Pd(PPh₃)₄ (16.8 mg, 0.014 mmol) was dissolved in THF (20 mL). To this mixture, a solution of K₂CO₃ (2M, 10 mL) was added and the resulting mixture was heated to 80°C overnight. After cooling to room temperature, the mixture was filtered and washed with water. The black solid was collected and washed repeatedly with hot hexanes to remove unreacted starting material to yield a crude black solid mixture of TPA-PDI₂ and TPA-PDI₃.
Chapter 3
Thiophene-Selenophene Copolymers

3 Introduction

Organic conjugated polymers are a class of organic electronic materials that excel as the semiconducting layer in OPV and organic thin film transistors (OTFT). Specifically, conjugated polymers are applied successfully as the p-type material in OPV for a variety of reasons. For example, their highly conjugated backbone allows for narrow band gap materials, thus yielding materials that are capable of harvesting low energy solar radiation. Furthermore, a significant advantage of conjugated polymers is that their optoelectronic, and morphological properties can be fine-tuned through a variety of strategies. In this chapter, factors allowing for morphology control are studied.

3.1 Morphology Control

As stated in section 1.2, the morphology of the active layer plays a crucial role in developing high performance devices. It is well accepted that processing conditions have a large impact on the resulting morphology of the active layer. For example, thermal annealing films is a common strategy to induce phase separation resulting in pure domains and increased crystallinity; the former enhances charge separation and reduces charge recombination, whereas the latter improves charge transport.45,46 Other popular strategies are solvent annealing and the addition of additives.47,48,49

However, our interests reside in morphology control through direct modification of the polymer. Many parameters of a polymer contribute to the morphology. Firstly, the molecular weight plays a significant role since larger molecular weight polymers tend to form longer more interconnected fibrils, which are better suited for charge transport through charge transfer between fibrillar bundles.50 Interestingly, a recent report in our group by Gibson, Seferos, and co-workers suggests that larger polymers are not necessarily better, but rather an intermediate molecular weight range is the most desirable.51 Secondly, the regioregularity of the polymer plays an important factor as well. Polymers with higher regioregularity are able to pack in a regular solid-state arrangement and are thus more crystalline resulting in improved charge transport properties. Thirdly, variations
in the functional groups and alkyl chains of the polymers can alter the intermolecular interactions of the polymers and can affect the interlayer spacing significantly.

A more recent strategy for morphology control is through the synthesis of block copolymers, which is the connection of two chemically distinct polymers by a covalent bond. Under this condition, the copolymers are known to spontaneously phase separate due to the distinct interactions of each block.

3.2 Kumada Catalyst Transfer Polymerization

The exploration of conjugated polymers begins with poly(3-hexylthiophene) (P3HT), easily the most well studied conjugated polymer. Historically, the synthesis of P3HT has undergone a variety of ever-changing conditions such as electrochemical polymerization, Suzuki coupling, Stille coupling, and the McCullough method. However, the current most popular conditions are via Kumada catalyst transfer polymerization (KCTP). These conditions begin with the addition of an alkyl Grignard to 2,5-dibromo-3-hexylthiophene, which is known from quenching studies that the Grignard preferentially adds to the less sterically hindered 5-position in a 75:25 ratio, compared to the 2 position. Fortunately, the sterically encumbered Ni catalyst selectively reacts with the main metathesized product at ambient conditions. An initial defect occurs where a tail to tail linkage forms upon reductive elimination of the Ni catalyst. However, the rest of the polymerization cycle occurs selectively in a head to tail fashion, yielding P3HT with typically over 99% regioregularity. If so desired, it was found that this initial tail to tail defect can be circumvented by externally initiating the Ni catalyst.
Figure 3-1 Metathesis and polymerization of 2,5-dibromo-3-hexylthiophene

KCTP produces P3HT in high yields with good regioselectivity. Most notably, the groups of McCullough and Yokozawa both studied the mechanism of KCTP and found that upon reductive elimination, an associative pair forms between the Ni catalyst and the extended monomer$^{57,50}$. When this occurs, the chance for reinsertion of the Ni catalyst with the same growing polymer chain becomes probable. Ultimately, the results are quasi-living characteristics for KCTP producing polymers with low polydispersities and a molecular weight that is dependent on catalyst loading.

### 3.3 Block Copolymer Synthesis

Advantageously, the quasi-living nature of KCTP opens up the door for the synthesis of block copolymers. An illustration on the mechanism towards block copolymer synthesis is shown in Figure 3-2 using 2,5-dibromo-3-hexylthiophene and 2,5-dibromo-3-hexylselenophene as the monomers. To synthesize the first block, the metathesized thiophene monomer is allowed to react to completion through the first polymerization cycle. At this point, the P3HT block acts as a macroiniator for the addition of the Grignard activated selenophene monomer, thus beginning the second polymerization cycle. Assuming all prior thiophene monomer has already reacted and that the Ni catalyst remains strongly associated with the growing chain, polymers are formed where there is a block of pure P3HT linked covalently with a block of pure poly(3-hexylselenophene) (P3HS).
The best evidence for the formation of block copolymers is found in the gel permeation chromatography (GPC) traces of the polymers. Typically, a GPC trace of an aliquot of the polymerization reaction is taken after the complete consumption of the first monomer and before the addition of the second monomer. This trace is compared with the overall GPC trace once the second monomer is completely consumed. If block copolymers were to form, the GPC trace would show a new trace at a higher molecular weight and that the previous trace should be absent. Further evidence can be found in $^1$H NMR, which should appear relatively clean with most of the protons having the same chemical environment within the same block, with only a small fraction differing at the diblock junction.

### 3.4 Proposal

The addition of a phenyl-substituent at the 3-position of thiophene has been a well-studied strategy to tune the optoelectronic and morphological properties of poly(3-phenylthiophene) (P3PhT). For
example, poly[3-(4-n-alkyl) phenylthiophene] are one of the most well-studied phenyl-substituted thiophenes exhibiting broad red-shifted absorption profiles and higher $V_{oc}$ when compared to P3HT. Importantly, polymers with alkyl chains on the 4 position of the phenyl substituent are shown to be compatible with KCTP, which allows the possibility for the synthesis of block copolymers.\textsuperscript{58,59,60,61,62}

Furthermore, phenyl-substituted systems with various types, position, and number of substituents on the phenyl ring has been well studied in the past.\textsuperscript{63} Aasmundtvei and co-workers studied the structural order of various P3PhT derivatives by X-ray diffraction (XRD).\textsuperscript{64} Interestingly, they found that P3PhT with para-substituents tend to have the lowest degree of crystallinity. Conversely, substituents at the ortho position of the phenyl group are more crystalline and poly(3-(2,5-dioctyl-phenyl)-thiophene) (PDOPT) where there are substituents at both the ortho and meta position of the phenyl ring exhibits the highest crystallinity. Interestingly, they also found that the bulky group of PDOPT separates the interchain polymer distance by 1.48 nm, which suggests that $\pi-\pi$ interactions should not be possible in this system. With this in mind, a recent study found that the crystallization of PDOPT is directed by the packing of the side chain, rather than through typical $\pi-\pi$ interactions of the backbone.\textsuperscript{65} With this consideration, it would now be interesting to investigate how this elevated interchain distance is affected in block-copolymers.

Figure 3-3 Block copolymer targets.

As the previous work in our group has shown, block copolymers of P3HT and P3HS phase separate into areas rich in sulfur and areas rich in selenium as a result of the strong Se-Se interactions and can be tuned by varying the monomer ratios and relative side chains.\textsuperscript{66,67,42,68,69,70} This study will investigate how the Se-Se interactions behave when bulky phenyl substituents are incorporated into the backbone through the synthesis of PB1, PB2, and PB3. It is expected that the strength of the $\pi-\pi$ interactions of the polymer backbone and the Se-Se interactions will vary significantly depending on the substituent affecting the resulting interchain distance in both the face to face and
edge to edge directions. Through this strategy, we expect that the competing forces of the phenyl-substituents with the π-π and Se-Se interactions can be a new avenue towards controlling polymer morphology.

The proposed structural model of PDOPT by Aasmundtveit, which was supported by XRD data, has been reproduced in Figure 3-4. This model shows that the phenyl ring lies perpendicular to the thiophene ring. Incidentally, the alkyl chains on the 2,5 position of the phenyl ring interdigitate perpendicular to the thiophene ring and is measured to be 1.48 nm. As a result, π-π interactions between the thiophene backbone would not be possible. Assuming this structural model is accurate for PB3, it would be predicted that π-π and Se-Se interactions would not be possible meaning spontaneous phase separation of the thiophene and selenophene blocks would not occur to the same degree. Looking back to PB1 under the same structural model, the d-spacing would appear to be significantly increased with the alkyl chain para on the phenyl substituent. Furthermore, the distance between the face-on polymers would be significantly smaller and may have more pronounced π-π and Se-Se interactions. Lastly, PB2 may carry similar properties of both polymers such as the large d-spacing of PB1 with an increased face to face distance due to the ortho alkyl chain. As such, it is expected that all three proposed block copolymers will differ significantly in terms of their resulting morphologies.

Figure 3-4 Structural model of PDOPT of the a) face on and b) edge on view relative to the thiophene backbone. For clarity, the alkyl chains are hidden in a) and hydrogens are hidden in both a) and b). The sulfur atom is yellow and the carbon atoms are grey. Images adapted from reference 64
Ultimately, the prediction of polymer morphologies is still extremely challenging at this point. However, the proposed properties of PB1, PB2, and PB3 appear reasonable given the background of previously reported P3PhT and a study such as this where the effect of bulky substituents on the Se-Se interactions and phase separation of block copolymers remains elusive to the community.

### 3.5 Progress to date towards PB1

![Figure 3-5 Synthesis of 2-bromo-5-iodo-3-(4-octyl)phenylselenophene](image)

The progress of this project is still in the preliminary stages towards the synthesis of PB1, PB2, and PB3. The synthesis of 3-iodoselenophene, 4-octylphenylboronic acid, and 2-bromo-5-iodophenylthiophene have been reported previously.\(^5^9,7^1\) The synthesis of 3-(4-octyl)phenylselenophene was accomplished through Suzuki coupling with 4-octylphenylboronic acid. 3-(4-octyl)Phenylselenophene was treated with NBS in THF, followed by NIS in chloroform and acetic acid, to finish the 2-bromo-5-iodo monomer.

The synthesis of poly(3-(4-n-octyl) phenylthiophene) POPT has already been reported using standard Kumda coupling conditions. However, the polymerization is reported to require 65°C reaction temperature over 12 hours, which indicates that the bulky phenyl substituent significantly decreases the polymerization kinetics. In our case, even after the synthesis and purification of both the analogous 2-bromo-5-iodo thiophene and selenophene monomers, polymerization under the reported conditions failed to produce polymers of any appreciable molecular weights or yields.
Different polymer conditions at different temperatures and reaction times failed to yield polymers. The use of more active catalysts such as Ni(dppe)Cl$_2$ and Ni(MesAn)Br$_2$ also failed to produce polymers.

Figure 3-6 Failed polymerization attempts

To investigate if the metathesis step is the problem, 2-bromo-5-iodo-3-(4-phenyl)selenophene was treated with iPrMgCl at room temperature for 1 hour and quenched with dilute HCl. The $^1$H NMR of this reaction (Figure 3-7) shows that the Grignard has good selectivity for the iodinated 5 position with no indication that the brominated 2 position was substituted. Still, leftover monomer was present with 85% conversion to the metathesized species using 0.95 equivalence of the Grignard. However, incomplete metathesis is typical and a significant amount of the monomer was still converted, which should still be sufficient to produce polymers of appreciable molecular weights.\textsuperscript{72}

Figure 3-7 Metathesis acid quenching experiment of 2-bromo-5-iodo-3-(4-octyl)phenylthiophene after 1 hour using 0.95 eq. of iPrMgCl
A recent reason for the failed polymerization step is postulated to be due to the inseparable contamination of the 2-bromo-4,5-iodo heterocycle, however only circumstantial evidence is found in the $^1$H NMR. The integration for the phenyl protons appear to correlate well with each other and with the alkyl protons. However, the thiophene proton integrates at a lower value. If contamination with the 4,5 iodo product is the case, the integration would appear similar as to what is seen here where all the protons appear to integrate well, save for the thiophene proton, which would be slightly lower. For the selenophene monomer the selenophene peak also integrates at a lower than expected value. If we look at the synthesis of the monomers, an overnight reaction using an excess of NIS at 50°C was conducted, which may be sufficient conditions to iodinate the less reactive 4-position of the heterocycle. To investigate if this was the case, Direct Analysis Real Time mass spectroscopy (DART-MS) was done on both samples. However, no evidence was found of the postulated contaminated species, though this could simply be due to having a small amount of the contaminate present.

![Figure 3-8 Evidence for monomer contamination with the 4,5-diiodo species](image)

**Figure 3-8 Evidence for monomer contamination with the 4,5-diiodo species**

To remedy this potential contamination, different conditions are proposed to synthesis the monomers in Figure 3-9. These conditions are more commonly used to iodinate the 5 position at
room temperature. Compared to NIS, PhI(OAc)$_2$ with I$_2$ are more mild conditions, which is likely not strong enough to iodinate the 4 position.

![Figure 3-9 Alternative pathway for the iodination of 2-bromo-3-(4-octyl)phenylthiophene](image)

**3.6 Expected complications towards PB1**

Although the synthesis of the homopolymers has been unsuccessful thus far, their completed synthesis should be only a matter of time. However, there are factors that we must be aware of towards the synthesis of the block copolymers. As discussed earlier, longer reaction times and elevated temperatures are required to polymerization POPT and its alkyl derivatives. Unfortunately, these conditions also make it more likely for the Ni catalyst complex to dissociate. If this event occurs, chain extension for the second block would not proceed efficiently causing the polymerization reaction to form new homopolymers, rather than chain extension towards block copolymers. In the literature, there have been examples of block copolymers of P3HT and 4-alkylphenyl substituted thiophenes.$^{62,73}$ However, these examples occur using P3HT as the macroinitiator, which is well known to associate strongly with the Ni catalyst at room temperature, thus circumventing the risk of the Ni catalyst dissociating from the first block. In our case, neither blocks are expected to form strong association complexes with the Ni catalyst at elevated temperatures due to the steric demands of the phenyl substituent meaning we may not have the advantage of a strongly associated macroinitiator.

**3.7 Expected complications towards PB2 and PB3**

In particular, the synthesis towards PB2 and PB3 will have the most difficulties since the positions of the alkyl chains significantly congest the surrounding area for oxidative addition of the Ni catalyst. Prior to this year, the synthesis of these bulky polymers through non-living polymerization conditions have only been reported since KCTP using the typically used Ni(dppp)Cl$_2$ and Ni(dppe)Cl$_2$ catalysts failed using the bulkier monomers.
Fortunately, PDOPT was recently synthesized under KCTP conditions for the first time thanks to a Ni catalyst with a hybrid P,N ligand, Ni(dppy)Cl₂. With Ni(dppy)Cl₂, PDOPT was successfully synthesized in high regioregularity with good catalyst dependence on molecule weight, which reinforces the quasi-living character of the polymerization. Furthermore, the dispersities range from good to moderately low (1.10 to 1.98), which is an indicator that the catalyst forms a strong association complex with the polymer. If this is true, using this catalyst may be a good strategy to synthesis PB1, PB2, and PB3.

![Figure 3-10 Successful polymerization of PDOPT using a hybrid P,N ligand](image)

### 3.8 Conclusions and Outlook

The synthesis towards PB1, PB2, and PB3 are currently ongoing. Results thus far indicate that the polymerization of these bulky phenyl monomers is more difficult than the comparatively steric free alkyl monomers. The recent report using KCTP to synthesize PDOPT in high regioregularity and good polydispersities is promising that the quasi-living polymerization of these bulky monomers may indeed be possible. If synthesized, the block copolymers should display interesting morphological features that are dependent on the substituents. For example, PB1 will be the have the lowest amount of sterics in the face to face direction, which should allow for π-π and Se-Se interactions to contribute to the morphology and will have the long alkyl chains in the 4 position that should reduce the d-spacing of the copolymers. Conversely, PB3 will have the most sterics in the face to face direction, which should diminish, or even completely remove, the potential for π-π and Se-Se interactions, but should have a significantly smaller d-spacing due to no alkyl chains in the para position. For PB2, a relative combination of both a large d-spacing and diminished π-π and Se-Se interactions is expected. Even though it has been well known that the block copolymers of thiophenes and selenophenes spontaneously phase separate due to Se-Se interactions, no studies thus far have attempted to analyze the competition that would occur between the Se-Se interactions and new interactions imparted by selective substituents. In doing
this study, a new form of morphology control can potentially be obtained, which can be used to further tune the morphology in the active layer of OPVs.

3.9 Experimental

A solution of 1-bromo-4-n-octylbenzene (2 g, 7.43 mmol) in THF (15 mL) was cooled to -78 °C. To this solution, nBuLi (5.20 mL, 8.17 mmol, 1.57 M), was added dropwise and the resulting solution was stirred at -78 °C for 1 hour. At the same temperature, triisopropyl borate (3.43 mL, 14.86 mmol) was added and the solution was stirred for 30 minutes. The solution was then warmed to room temperature and allowed to stir overnight. Water was added to the solution and was diluted with ethyl acetate and washed with 5% HCl and brine. The resulting ethyl acetate solution was dried over MgSO4 and removed under vacuum to yield a sticky white solid. The solid was taken up in minimal hexane and was added to a stirring solution of water for 1 hour. The resulting mixture was filtered to yield as a white flakey solid (1.39 g, 80%). 1H NMR (400 MHz, CDCl3, δ): 8.15 (d, J = 8.03 Hz, 2H), 7.34 (d, J = 7.94 Hz, 2H), 2.70 (t, J = 7.67 Hz, 2H), 1.67 (quin, J = 7.21 Hz, 2H), 1.32 (m, 10H), 0.88 (t, J = 6.78 Hz, 3H).

A mixture of 3-iodoselenophene (1.18 g, 4.59 mmol), 4-octylphenylboronic acid (1.5 g, 6.43 mmol), and Pd(OAc)2 (52 mg, 0.23 mmol) was dissolved in dimethoxyethane (47 mL) in a 3 neck flask equipped with a condenser. To this solution was added K3PO4 (4.68 g, 22 mmol) and the resulting mixture was refluxed at 90 °C overnight. The resulting mixture was allowed to cool to room temperature and diluted with DCM. After washing with brine, the DCM layer was dried over MgSO4 and evaporated under reduced pressure. The resulting crude brown oil was subjected to
column chromatography using hexane:EA (100:1) as the eluent to afford the desired product as a pale yellow oil (1.18 g, 81%). $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 8.13 – 7.97 (m, 2H), 7.66 (dd, $J = 1.85$, 5.04 Hz, 1H), 7.50 (m, 2H), 7.20 (m, 2H), 2.62 (t, $J = 7.67$ Hz, 2H), 1.63 (quin, $J = 7.00$ Hz, 2H), 1.32 (m, 10H), 0.88 (t, $J = 6.78$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$, $\delta$): 144.82, 142.11, 134.80, 130.69, 129.85, 128.97, 126.72, 124.79, 35.84, 32.09, 31.65, 29.69, 29.54, 29.46, 22.87, 14.30. HRMS-DART: calc. 321.1122, found 321.1128.

A solution of SePhC8 (1.56 g, 4.89 mmol) in THF (13.2 mL) was cooled to 0 °C. To this solution was added NBS (0.913 g, 5.13 mmol) slowly and stirred at 0 °C for 1 hour. The solution further stirred at room temperature for an additional 4 hours. The solution was quenched with water and diluted with diethyl ether and washed with saturated Na$_2$S$_2$O$_3$ (aq), KOH (aq), and brine. The diethyl ether solution was dried over MgSO$_4$, and evaporated under reduced pressure. The crude oil was filtered through silica using hexanes as the eluent to afford the desired product as a colorless oil (1.72 g, 92%). $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 7.50 – 7.45 (m, 2H), 7.29 (d, $J = 5.37$ Hz, 1H), 7.26 – 7.22 (m, 2H), 7.03 (d, $J = 5.64$, 1H), 2.66 (t, $J = 7.79$ Hz, 2H), 1.65 (quin, $J = 7.21$ Hz, 2H), 1.43 – 1.22 (m, 10H), 0.89 (t, $J = 7.49$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$, $\delta$): 144.05, 142.63, 133.62, 132.50, 130.63, 128.81, 128.51, 111.40, 35.98, 32.09, 31.57, 29.68, 29.62, 29.46, 22.88, 14.31. HRMS-DART: calc. 399.0227, found 399.0221.

In the air, a solution of SePhC8Br (1.81 g, 4.54 mmol), NIS (1.23 g, 5.43 mmol), CHCl$_3$ (45 mL), and CH$_3$COOH (15 mL) was prepared in a round bottom flask at 50 °C and stirred overnight. After cooling down to room temperature, the solution was diluted with CHCl$_3$ and washed with saturated Na$_2$S$_2$O$_3$ (aq), KOH (aq), and brine. The resulting CHCl$_3$ layer was dried over MgSO$_4$ and evaporated under reduced pressure. The crude product was purified using column chromatography with
hexanes as the eluent to afford the desired product (1.89 g, 79%). \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)):
7.47-7.45 (m, 1H), 7.39-7.35 (m, 2H), 7.25-7.20 (m, 2H), 2.26 (t, \(J = 7.54\) Hz, 2H), 1.63 (quin, \(J = 7.24\) Hz, 2H), 1.42-1.21 (m, 10H), 0.89 (t, \(J = 6.61\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\), \(\delta\)):
145.83, 142.85, 142.21, 135.18, 132.03, 128.49, 128.36, 114.73, 35.75, 31.87, 31.32, 29.46, 29.37, 29.24, 22.66, 14.10. HRMS-DART: calc. 524.9193, found 524.9198.
References


Appendices

Appendix 1: $^1$H and $^{13}$C Spectra from Chapter 2
Appendix 2: $^1$H and $^{13}$C Spectra from Chapter 3