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Systematic Synthesis of Organic Semiconductors with Variable Band Gaps

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SYSTEMATIC SYNTHESIS OF ORGANIC SEMICONDUCTORS WITH VARIABLE BAND GAPS

A Dissertation Presented by
CHRISTOPHER T. SCILLA

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

May 2012

Polymer Science and Engineering
SYSTEMATIC SYNTHESIS OF ORGANIC SEMICONDUCTORS WITH VARIABLE BAND GAPS

A Dissertation Presented
by
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ABSTRACT

SYSTEMATIC SYNTHESIS OF ORGANIC SEMICONDUCTORS WITH VARIABLE BAND GAPS

MAY 2012

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Directed by: Professor E. Bryan Coughlin

Polymeric materials are attractive candidates for the fabrication of low cost, large area photovoltaic devices. Controlling the band gap of the electroactive polymer is an essential factor in optimizing the resulting devices. In this dissertation, a methodology for the synthesis of well-defined semiconducting materials with tunable band gaps is described. First, the synthesis, characterization, and computational analysis of a variety of trimers consisting of two 3-hexylthiophene units flanking a central moiety consisting of thiophene, or one of the electron donating monomers isothianaphthene or thieno[3,4,b]thiophene will be described. From this analysis the influences of the electronic and steric structure of the materials will be investigated. Several of these trimers will then be used in the synthesis of well-defined, higher order, oligomers of thiophene and isothianaphthene in varying compositions. Polymerization of these oligomers yields polymers of known sequence allowing the band gap of the polymers to be systematically varied. Finally, preliminary investigations into the development of alternate oligomer core units will be described. The control over the band gap that this method affords will be useful in the optimization of polymeric semiconductor devices.
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<tr>
<td>A</td>
<td>Surface Area of the Solar Cell</td>
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<tr>
<td>CN-PPV</td>
<td>Cyano-polyphenylene Vinylene</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Band Gap</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>FF</td>
<td>Fill Factor</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel Permeation Chromatography</td>
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<tr>
<td>GRIM</td>
<td>Grignard Metathesis Polymerization</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>HT</td>
<td>Hexylthiophene</td>
</tr>
<tr>
<td>I, ITN</td>
<td>Isothianaphthene</td>
</tr>
<tr>
<td>$I_m$</td>
<td>Current at the Point of Maximum Power</td>
</tr>
<tr>
<td>$I_{sc}$</td>
<td>Short Circuit Current</td>
</tr>
<tr>
<td>LR</td>
<td>Lawesson’s Reagent</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td>Poly[2-methoxy, 5-(2-ethylhexoxy)-1,4-phenylene vinylene]</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Power Conversion Efficiency</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance Spectroscopy</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
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<tr>
<td>PCBM</td>
<td>[6,6]-Phenyl C61 Butyric Acid Methyl Ester</td>
</tr>
<tr>
<td>P&lt;sub&gt;i&lt;/sub&gt;</td>
<td>Incident Power</td>
</tr>
<tr>
<td>P&lt;sub&gt;in&lt;/sub&gt;</td>
<td>Power Input to the Solar Cell</td>
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<tr>
<td>pITN</td>
<td>Poly(isothianaphthene)</td>
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<tr>
<td>P&lt;sub&gt;m&lt;/sub&gt;</td>
<td>Point of Maximum Power</td>
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<td>P&lt;sub&gt;out&lt;/sub&gt;</td>
<td>Power Output of a Solar Cell</td>
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<td>P&lt;sub&gt;sun&lt;/sub&gt;</td>
<td>Power of the Sun Incident on a Solar Cell</td>
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<tr>
<td>Q&lt;sub&gt;s&lt;/sub&gt;</td>
<td>Generated Charge Density</td>
</tr>
<tr>
<td>T</td>
<td>Thiophene</td>
</tr>
<tr>
<td>TE</td>
<td>Transparent Electrode</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>V&lt;sub&gt;m&lt;/sub&gt;</td>
<td>Voltage at Point of Maximum Power</td>
</tr>
<tr>
<td>V&lt;sub&gt;oc&lt;/sub&gt;</td>
<td>Open Circuit Voltage</td>
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CHAPTER 1
INTRODUCTION AND MOTIVATION

1.1 World Energy Demand

The availability of abundant, inexpensive energy is vital to the social and economic development of mankind. Currently, the world uses about 13 terawatts (TW) of power per year, and the demand for energy is rapidly increasing. Growing populations and rapid economic development is expected to more than double the world’s energy demand in the next fifty years. The vast majority of the world’s power is generated through the burning of various fossil fuels. However, reserves of these fuels are dwindling, and they will soon be unable to continue to meet demand. In addition, the use of fossil fuels produces byproducts that are harmful to both humanity and to the environment at large.¹

1.2 Alternative Energy Sources

Given the economic, environmental, and political problems associated with the use of fossil fuels, it is clear that alternative power sources must be found. Various alternative energy sources are known, such as hydroelectric, wind, nuclear, and solar energy. Of these, solar energy holds the most promise to make a major impact in resolving the energy crisis.²

Hydroelectric power uses the power of moving water to generate electricity. Hydroelectric power is cheap, relatively easy to harness, and is carbon free after the initial installation of the power plant. Hydroelectricity currently accounts for about 300 GW of the power generated worldwide, making it one of the most widely used renewable energy sources. Unfortunately, the potential of hydroelectric power as a long term
solution to the energy crisis is limited, as there are only a limited number of additional sites available for the construction of hydroelectric power stations. It is estimated that hydroelectric power can provide a maximum of only about 1.5 TW of power globally.²

Similar problems plague the use of wind power. While wind power does have great potential in certain areas, such as the U.S. Great Plains and Northwestern China, the overall potential of wind power is severely limited. It is estimated that wind power could provide approximately 2 TW globally. Wind power is also limited by the fact that it is an intermittent power source, necessitating the development of both new power storage and distribution systems, increasing both the cost and environmental impact of this power source.²

Nuclear power avoids some of the problems plaguing hydroelectric and wind power. Nuclear plants are not dependent on proximity to a natural resource. Further, nuclear power plants produce about 1 GW of power, much more than a hydroelectric plant or wind farm. However, even with this level of output, it would still take 1,000 new power plants to produce 1 TW of electricity. Thus, in order to make a significant impact on the energy crisis, thousands of new nuclear plants would need to be built over the next several decades. Any such building program would inevitably tax supplies of nuclear fuel, and result in a large buildup of nuclear waste which would need to be disposed of safely.²

The sun is by far the largest source of energy available to mankind. The sun provides approximately 1 kW/m² of power to the surface of the Earth, resulting in more incident energy in one hour than global yearly energy demand. Thus, if even a small fraction of this solar energy could be harnessed, the world’s energy demands for the
foreseeable future could easily be met. The challenge is to find an efficient method for the capture, conversion, storage and distribution of the sun’s energy. However, even with these challenges, solar energy shows great potential to make a significant impact on the world’s energy crisis.¹

1.3 Photovoltaic Cells

One of the most promising methods for utilizing the sun’s energy is through the use of photovoltaic cells. These devices directly convert solar photons into electric current. Solar cells were first produced in 1954 by Chapin and Fuller using a semiconductor p-n junction consisting of doped silicon. This cell had an efficiency of about 6%.³ Research efforts toward improving the performance of solar cells were greatly increased in the aftermath of the oil crisis of the 1970’s, and succeeded in greatly increasing the efficiency of silicon solar cells. This flurry of research also gave rise to other solar cell designs (Figure 1). Currently, solar electricity accounts for less than 0.1% of the world’s generated electricity, well below solar power’s tremendous potential. Solar energy is so underutilized because, in part, it is too expensive to produce. Fossil fuel derived electricity costs about 1 to 8 cents per kilowatt hour, while electricity derived from solar power costs 25 to 50 cents per kilowatt hour. Thus, in order for solar electricity to become economically competitive with fossil fuels, the cost must be reduced by a factor of ten to twenty.²
The cost of solar electricity can be reduced in several ways. The most obvious method is to reduce the cost of production of the cells themselves. Monocrystalline silicon based solar panels with 10% efficiency cost approximately $350 per square meter to produce. The mounting systems and other non-energy producing parts that solar arrays require add another $250 to the price tag. Various methods have been used to lower the cost of solar cell production, such as fabricating devices from poly-crystalline or amorphous silicon, thin films of other semiconductors, or organic semiconductors. Each of these approaches, while lowering the price of production, results in lowered power output, reducing the overall economic benefit of the reduced production costs. The second way to lower the cost of solar electricity is to design higher efficiency photovoltaic cells. These cells will harvest a higher fraction of the incident energy, resulting in an increased economic payout over the lifetime of the cell. If higher
efficiency cells can be produced without a corresponding increase in the production costs, the final cost for solar derived electricity can be greatly reduced.\textsuperscript{1}

1.3.1 Organic Photovoltaic Cells

Organic semiconductors have great promise to allow for the inexpensive production of high volumes of photovoltaic cells. Organic semiconductors have many advantages over their inorganic counterparts. The use of organic materials allows for the use of rapid, inexpensive processing techniques such as inkjet printing and roll-to-roll processing in contrast to the stringent conditions which must be maintained in order to grow and process high quality single crystal silicon photovoltaic cells.\textsuperscript{4} Further, the use of organic materials allows for the production of light, flexible solar modules. The fabrication of cheap, light weight, and flexible solar modules will allow for the integration of solar cells into a variety of new applications as well as removing the need for expensive, non-power producing mounting equipment as mentioned previously. Further, organic semiconductors typically possess high absorption coefficients meaning that the majority of incident photons can be absorbed by films less than a micron thick, greatly reducing the amount of photoactive material needed for solar module production. Furthermore, the band gap of organic semiconductors can be tuned by modifying the chemical structure of the material, thereby allowing tuning of the absorption spectrum of the resulting cells, thus allowing the efficiency of the solar system to be optimized.

Unfortunately, organic semiconductors tend to have large band gaps (>1.4 eV) meaning that efficient harvesting of the low energy portion of the solar spectrum is difficult.\textsuperscript{5} Further, optical excitations in organic semiconductors tend to generate bound electron-hole pairs, called excitons. These tightly bound excitons are more prone to
recombination than the relatively free charges produced by the photoexcitation of inorganic semiconductors. This effect, coupled with the low charge mobilities and high abundance of charge traps typically present in organic semiconductors makes charge recombination a significant barrier to the production of high efficiency organic photovoltaic cells.

The simplest method to producing an organic photovoltaic cell is to sandwich a layer of semiconductor between two electrodes with dissimilar work functions. The difference in the work functions causes a distortion in the band structure of the semiconductor, yielding an internal electric field capable of driving photogenerated charges to the electrodes. Thus, the electrode materials play an important role in determining the overall photovoltaic response of the system. These cells typically exhibit low efficiencies. This low performance is primarily due to recombination of the majority of the excitons created throughout the film. Further, even when free charges are generated, the low charge mobility of the film forces the photogenerated charges to remain in the film for a long time promoting additional recombination, further lowering the efficiency.

An advance in organic photovoltaic devices was pioneered by C.W. Tang in 1985, when it was found that efficiency could be improved by building a device out of a bilayer of n- and p- type organic semiconductors. These cells limit exciton recombination by encouraging dissociation across the interface. An exciton created near the interface can undergo an energetically favorable transfer of charge across the junction, thus breaking the exciton into free charges. This process places the freed charges on opposite sides of the interface, limiting back electron transfer, and allowing for direct transport of the
Clash charges to the electrode. Unfortunately, excitons generated in organic semiconductors typically have a diffusion length of only 10-20 nm. This short exciton lifetime limits the efficiency of the cell as only excitations which are generated within this distance of the interface will produce free charges, thus wasting the majority of the excitons produced and limiting the number of free charges produced.8

In order to overcome this limitation, the idea of a bulk heterojunction solar cell was introduced by Hiramoto in 1992. The bulk heterojunction (Figure 2), which is comprised of a phase separated interpenetrating network of n-type and p-type semiconductors, applies the same principles as the bilayer solar cell on a microscopic scale.

![Figure 2: A) Schematic of a bulk heterojunction solar cell showing the mixture of donor and acceptor phases which comprises the active layer. B) Band diagram showing the charge creation and transport which occurs in these devices.](image)

The interpenetrating network is meant to ensure that any exciton produced in the mixed region is within the exciton diffusion length of an interface. It was found that these cells
yielded higher efficiency than bilayer devices. Several different classes of these devices have been fabricated including polymer-polymer heterojunctions, polymer-fullerene heterojunctions, and polymer-inorganic semiconductor heterojunctions.

Yu and Halls were the first to pioneer polymer-polymer bulk heterojunction solar cells in 1995. They independently fabricated cells with an active layer consisting of a mixture of poly[2-methoxy, 5-(2-ethylhexoxy)-1,4-phenylene vinylene] (MEH-PPV) and Cyano-Polyphenylene vinylene (CN-PPV) (Figure 3). These polymers phase separate upon spin-casting from solution, forming an interpenetrating network.

![Figure 3: Chemical structures for A) MEH-PPV and B) CN-PPV.](image)

It was found that efficient photoinduced charge transfer can occur between the two phases. Device efficiency remained low at ~0.9 %, but vast improvements in quantum efficiency were observed over corresponding bilayer devices. Device efficiency suffers because the high (~2 eV) band gap of the polymers means that the device is unable to capture a large portion of the solar spectrum. Further work has raised the energy conversion of this type of cell to 1.9 % and the quantum efficiency, a measure of the portion of incident photons which are converted to free charges, to 29 %.

Similar solar cells have also been constructed using a blend of semi-conducting polymers and fullerenes. It was found that these devices yielded better photovoltaic
properties than the polymer-polymer bulk heterojunction cells. The first of these cells were prepared with a blend of MEH-PPV/[6,6]-Phenyl C61 butyric acid methyl ester (PCBM) and yielded power conversion efficiencies above 2% and quantum efficiencies of ~30%. Further improvements to this design were realized by using poly(3-hexylthiophene) (P3HT) as the polymer semiconductor (Figure 4). The use of poly(3-hexylthiophene) is advantageous as the polymer has one of the highest hole mobilities reported for organic materials. Despite the relatively high band gap of P3HT (2 eV), cells fabricated using this polymer yield power conversion efficiencies of >3 % and quantum efficiencies of ~70 %. 

Figure 4: Chemical structures of A) P3HT and B) PCBM.

It is important to note that in order to achieve this high performance, a high loading of the non-photoactive fullerene (~80 % by weight) must be used to ensure the formation of continuous pathways for electron flow. Thus, much of the volume of the photoactive region does not take part in the generation of excitons, meaning that thicker layers must be used to effectively capture the solar spectrum. This creates a problem, as the higher residence time of the charges in the active layer, increase the incidence of back electron transfer.
1.3.2 Photovoltaic Conversion Process

In its simplest form, a solar cell consists of a layer of photoactive semiconductor (known as the active layer) sandwiched between a transparent electrode (T.E) and a metal back electrode. When light impinges upon the photoactive layer, electrons are promoted to the conduction band of the semiconductor, leaving a hole in the valence band. The charges are then funneled to the electrodes by an internal electric field, once the charges reach the electrodes they are able to move through an external circuit, thus generating electric current. The internal electric field is typically produced by either a p-n junction in the active layer, or by the variation in the work function of the electrodes (Figure 5).18

Figure 5: Charge separation and transport in A) a single layer device and B) a p-n junction.

1.3.3 Determination of Photovoltaic Efficiency

The efficiency of a solar cell is a measure of the ratio of the power produced by the cell to the power of the light incident upon its surface. The power output of the cell is determined by the current-voltage behavior of the cell (Figure 6). This curve is generated
by varying an opposing voltage, applied to the cell under illumination, and measuring the resulting current output. There are several important points on this curve.

Figure 6: General shape of the current/voltage response from an illuminated solar cell.\textsuperscript{17}

The short-circuit current ($I_{sc}$) is the current which is produced by the cell, when the opposing voltage is set to zero. The second important point is the open-circuit voltage ($V_{oc}$) which corresponds to the maximum voltage output of the cell. It corresponds to the point on the I-V curve where zero current is flowing, thus it occurs when the applied opposing voltage is equal to the voltage output of the cell. The third important point in the I-V curve is the point of maximum power ($P_m$). This occurs where the product of the current and voltage reaches a maximum and represents the point of peak efficiency.\textsuperscript{19}

From these three points, several important quantities can be calculated. The first of these is the fill factor. This is a measure of the “squareness” of the I-V curve. It is calculated by the following:

\[
FF = \frac{P_m \cdot V_m}{I_{sc} \cdot V_{oc}}
\]  

(1)
Where $I_m$ and $V_m$ are the current-voltage coordinates of the point $P_m$. The second quantity is the overall power conversion efficiency of the cell. This measures the fraction of the power incident on the cell that is converted into electrical power. It is given by the following:

$$\eta_p = \frac{P_m}{P_i} = \frac{FF \cdot I_{sc} \cdot V_{oc}}{P_i}$$

(2)

Where $P_i$ is the power of the light incident on the solar cell.

There are several factors which determine the overall efficiency of the solar cell. The most fundamental of these relates to the band gap of the semiconductor used in the manufacture of the cell. Since electrons can be promoted into the conduction band only by the absorption of photons with energies higher than the band gap, the low energy range of the solar spectrum is unused. Furthermore, an electron excited into a higher energy region of the conduction band, as occurs when a photon of energy higher than the band gap of the semiconductor is absorbed, quickly sheds energy as heat and decays to the conduction band edge (Figure 7). Even though this photon is still converted to an electron-hole pair, much of the energy imparted by the absorption of the photon is lost in this decay process.
Thus, the band gap of the semiconductor used for the photogeneration of excitons affects the efficiency of the cell in two ways. The band gap affects the short-circuit current as it determines the number of photons absorbed in the active layer and thus affects the number of charges generated. Further, the band structure of the semiconductor affects the open-circuit voltage in that it determines the energy with which the charges can be extracted from the active layer. In a heterojunction solar cell, the maximum open-circuit voltage is determined by the difference between the HOMO level of the p-type semiconductor and the LUMO level of the n-type semiconductor.

Shockley and Queisser calculated the theoretical upper limit of the efficiency of a simple p-n junction solar cell.\(^{20}\) This upper efficiency limit is a consequence of the workings of the atomic processes that generate electricity in the solar cell, and the second law of thermodynamics. They begin by assuming a solar cell consisting of a simple p-n
junction at zero Kelvin surrounded by a blackbody radiator. The solar cell possesses a band gap of $E_g$ and it is assumed that every photon with energy greater than this band gap results in the generation of a pair of free charges. The following expression can then be derived for the output power of a solar cell with surface area $A$:

$$ P_{out} = E_g A Q_s $$

(3)

Where $Q_s$ describes the number of charges generated in the cell per unit area and per unit time. The incident power on the cell is given by:

$$ P_{in} = P_{sun} A $$

(4)

Where $P_{sun}$ is the energy density of the sunlight falling on the solar cell per unit area and unit time. Combining these two equations yields an expression for the ultimate efficiency of the device of the following:

$$ \mu = \frac{E_g Q_s}{P_{sun}} $$

(5)

The authors show that this reduces to a function which depends only on the value of the cell’s band gap, which reaches a maximum of 44% efficiency for a silicon solar cell ($E_g = 1.1$ eV). The authors also considered a planar cell at 300 K, illuminated by sunlight incident at a limited solid angle. These alterations to the conditions complicate the analysis, as the cell itself becomes a blackbody radiator at a temperature above absolute zero. The energy lost by this radiation, combined with several other factors, reduce the maximum theoretical efficiency of the silicon solar cell to $\sim 30\%$.20
1.4 The Need For Band Gap Control

As previously mentioned, the maximum efficiency of a photovoltaic system is determined by the band gaps and band edge locations of the n- and p-type semiconductors making up the active layer of the cell. While many other factors can reduce the observed efficiency from this maximum value, there can be no hope for the production of high efficiency photovoltaic cells without the development of an optimized semiconductor system. One of the key difficulties in developing this optimized system is developing a low band gap material which maintains the proper band alignment with one of the relatively small number of organic n-type materials available.

1.4.1 Methods for Varying Band Gap In Semiconducting Polymers

There are many factors which influence the band gap of a semiconducting polymer. The band gap of the polymer varies with the conjugation length. The conjugation length in a semiconducting polymer refers to the length along the polymer backbone over which there is an uninterrupted cloud of delocalized electron density.\textsuperscript{21,22} The conjugation length effects the evolution of the band gap of the semiconducting polymer in a way analogous to the simple particle in a box problem in quantum mechanics. In this analogy, the delocalized $\pi$-electron region serves as the “box” in which charge resides and thus, as the conjugation length increases, the energy gap between successive energy levels decreases.

There are many handles that a synthetic chemist can use to tune the conjugation length of a polymer system. Among these are the sequence and electronic structure of the polymer backbone and the electronic and steric effects of any substituents attached to this backbone. The substituents affect the conjugation length electronically by either
Injecting or withdrawing electron density from the main chain. In a homopolymer, injecting electron density into the polymer backbone tends to increase the conjugation length. Further, if there are substantial steric interactions between substituents on successive monomer units, the aromatic units along the polymer backbone can be pushed out of planarity, weakening the overlap of the π-orbitals and decreasing the conjugation length of the polymer.

In a copolymer, the conjugation length can be increased by the incorporation of alternating electron rich and electron poor monomer units into the polymer structure. This alternating structure pulls electron density into the main chain of the polymer, stabilizing the quinoid structure of the backbone (Figure 8).22, 23 These factors have been applied to the synthesis of hundreds of semiconducting polymers with a wide range of band gaps.22, 24

![Aromatic Quinoid](image)

**Figure 8:** Resonance forms of poly(thiophene).

1.4.2 Low Band Gap Materials

The class of materials most relevant to this body of work are based on poly(thiophene). Due to the high charge mobility and high photovoltaic performance of poly(thiophene) derivates, there has been tremendous interest in modifying the structure of the thiophene based polymer to yield optical properties more appropriate for photovoltaic applications. The modifications typically performed on poly(thiophene) fall
broadly into two categories: modification of the thiophene monomer itself, and the synthesis of alternating copolymers of thiophene and an electron donating comonomer.

The most common modification of the structure of thiophene is the addition of a substituent in the 3 position of the aromatic ring. This substituent, typically an alkyl chain, serves to impart solubility and processibility to the otherwise intractable polymer, as well as to modify the optical properties of the polymer by the donation, or withdrawal, of electron density from the thiophene backbone. Many other types of side chains have been appended to the thiophene backbone to further tune the optical properties of the resulting polymer, while maintaining the solubility properties of alkyl thiophenes.25-29 Sterics also play an important role in how the addition of substituents onto the poly(thiophene) backbone affect the optical properties of the material. This can be readily seen in the most widely studied of the substituted poly(thiophene)s, poly(3-hexylthiophene). During the polymerization process, any 3-substituted thiophene can undergo head-to-head, head-to-tail, and tail-to-tail coupling (Figure 9). It has been shown that the optical and electronic properties of the polymer depend greatly on the percentage of these couplings present in the polymer.

![Figure 9: Possible configurations of 3-substituted poly(thiophenes).](image)
For example, the optical and electronic properties of the most studied of the 3-substituted poly(thiophene)s, poly(3-hexylthiophene), have been found to vary with the regioregularity of the polymer.\textsuperscript{30-32}

Another method which has been widely used in the modification of thiophene monomers is the incorporation of the thiophene moiety into a fused ring system. These fused ring monomers allow for more in-depth tuning of the electronic structure of the thiophene moiety compared to that seen in substituted thiophenes, as the fused ring system is in conjugation with the polymer backbone. Unfortunately, many of these fused ring systems require further modification to ensure that the resulting polymers remain soluble and processible so that they are appropriate for use in photovoltaic cells, or any other application. While these synthetic difficulties limit the utility of fused ring homopolymers, fused ring compounds have been extensively used as electron donating moieties in the synthesis of alternating donor-acceptor copolymers. This class of copolymers has received considerable interest in recent years for several reasons. The first is that the use of multiple monomer units allows for the chemist to assert a greater amount of control over the physical, chemical, optical, and electronic properties of the resulting materials. Further, the alternating electron donor-acceptor structure results in higher electron densities in the polymer backbone due to a synergistic effect between the two comonomers, resulting in a longer conjugation length and a lower band gap.\textsuperscript{22, 27, 33-40}

As previously discussed, the band gap of the semiconductors used in a photovoltaic cell plays an integral part in determining the maximum possible power conversion efficiency which can be extracted from the photovoltaic system. Given that lowering the band gap of the photoactive polymer typically results in the generation of
higher current densities and lower voltage output from the device, assuming the same n-type semiconductor is used, there should be an optimal band gap which gives the highest possible efficiency when the polymer is paired to a given n-type material. While there have been computational efforts aimed at discovering this optimal value as a function of the electronic properties of the n-type material (Figure 10), there has not yet been experimental confirmation of these results.\textsuperscript{41}

Given the tremendous number of semiconducting polymers that have been synthesized, characterized, and tested in photovoltaic cells, it may be possible to obtain experimental confirmation of these computational results through careful review of the literature. By constructing a plot of band gap vs. reported efficiency for a variety of literature results for polymers with a wide range of band gaps, a trend should make itself apparent.

![Figure 10: Calculated power conversion efficiency vs. the band gap and LUMO level of the semiconducting polymer when used in conjunction with PCBM in a bulk heterojunction photovoltaic cell. Taken from Ref. 41.](image-url)
However, when such a plot is constructed (Figure 11), no clearly defined trend appears. This lack of correlation is due to the fact that there are many factors, besides the band gap and band overlap of the semiconducting system, that influence overall photovoltaic cell efficiency. These factors range from the macroscopic, the conditions under which the photovoltaic cell is fabricated, to the microscopic, the physical and electronic structure of the various interfaces within the active layer and across the electrodes, to the molecular, the properties of the n- and p-type semiconductors. Thus, simply combing the literature will never elucidate a trend of band gap versus efficiency since polymers with differing chemical structure and physical properties will behave differently across the many length scales involved in the operation of an organic photovoltaic cell.

![Figure 11: Plot of selected literature results for polymer band gap vs. reported device efficiency.](image)

Therefore, in order to experimentally determine the relationship between band gap and photovoltaic cell efficiency, a method to synthesize a series of well-defined
semiconducting polymeric materials with similar chemical and physical properties, but having systematic variable band gaps must be found. In this dissertation the synthesis and characterization of a series of thiophene based semiconducting oligomers and copolymers that allow for systematic control over the band gap of the material will be described. Chapter 2 will discuss the synthesis, characterization, and computational analysis of a variety of ordered trimer structures. The trimers consist of a central unit flanked by two thiophenes. The structure of these trimers will be varied to determine the effects of the electronic structure of the central unit as well as the effects of steric interactions on the optical properties of the materials. In chapter 3, certain of the trimers studied in the previous chapter will be used as a core from which a series of well-ordered copolymers will be built. The band gap of these copolymers can be tuned via variation of comonomer concentration and the steric of the repeat unit. The penultimate chapter will detail synthetic efforts aimed at varying the basic core structure from of which these copolymers are built, allowing for the band gap to be fine tuned across a wider range. As a whole, this work details the development of a combined synthetic/computational methodology for the preparation of semiconducting copolymers with precise structures and sequences. The final chapter of this thesis will posit future directions in which this methodology can be applied for the development of new, high performance photovoltaic materials and systems.


CHAPTER 2
EXPERIMENTAL AND COMPUTATIONAL STUDIES OF THIOPHENE-BASED TRIMERS

2.1 Introduction

The goal of this work is the development of a method for the synthesis of a series of materials with tunable band gaps having similar chemical and physical properties. As previously mentioned, we will approach this through the synthesis of a series of copolymers with varying comonomer concentrations. There are two approaches through which these copolymers can be produced. The first, and simplest, method for the creation of the desired copolymer series is through the random copolymerization of two monomers in varying ratios. While this is a facile method to access copolymers, it is unsuitable for the objectives of this dissertation. The polymers produced by random copolymerization, by definition, have random sequence, comonomer concentration, and regiochemistry. The inhomogeneity which will be present in any sample of a random copolymer leads to inhomogeneity in the measured properties. While aggregate averages of various chemical, physical, optical, and electronic properties can be measured, the random structure of the polymer precludes systematic study of structure-property relationships.

Therefore, in order for this study to be conducted, a method for the synthesis of well-ordered copolymers with precisely controlled molecular structures must be found. One method by which such materials can be prepared is through the polymerization of a series of well-defined oligomers with varying comonomer concentrations. The structure of these oligomers can be precisely controlled via small molecule synthetic organic
chemistry. This approach also allows for control of the steric interactions along the polymer chain. As mentioned in the previous chapter, steric interactions in semiconducting polymers can have profound effects on the optical properties of the material. In order to gain a better understanding on the effects the sterics and electronic structure of well-defined segments will have on the band structure of these materials, we start by conducting detailed studies on a series of ordered trimers (Figure 12). This series consists of 9 trimers with varying central units and varying levels of steric interaction, controlled by the presence and orientation of the alkyl chains on the flanking thiophene rings. The nomenclature of the trimers is based upon both the sequence of monomers which makes them up (thiophene (T), hexylthiophene (HT), Isothianaphthene (I), and octyl-thieno[3,4-b]thiophene (Tt8)) as well the orientation of flanking hexylthiophene moieties with respect to the central monomer, as indicated by a subscripted “in” or “out.

![Figure 12](image-url) Systems of well-defined trimers.
The study of this series of small molecules offers several advantages over the polymeric systems. Fundamentally, by studying small molecules the chemical system is ensured to be homogenous, with no variations in molecular weight or molecular structure. Also, the study of the small molecule systems allows for various computational methods to be applied to this analysis. These models allow for the computational determination of the both the lowest energy three dimensional configuration and the electronic band structure of the material. Studying the trimer series also offers advantages on a practical level. Specifically the greatest advantage is that the synthesis and purification of the small molecule materials is greatly simplified over the polymeric systems.

In order to conduct this study, the identity of the core electron-donating units had to be decided. The first core unit is simply a thiophene ring. This thiophene core series was chosen to highlight the role of steric effects in determining the band properties of the material, as there should be minimal variation in the electronic structure of the trimers across the series. The other two core units were chosen to be electron rich in order to lower the band gap of the trimers.\textsuperscript{1-3} Each of these core units have been studied as homopolymers and have demonstrated some of the lowest band gaps reported in the literature.

2.1.1 – Isothianaphthene as a Trimer Core Unit

The first electron donating unit which will be used in the synthesis of an ordered trimer series is isothianaphthene (ITN) (Figure 13). Homopolymers of ITN have a reported band gap of ~1 eV.\textsuperscript{4} Poly(isothianaphthene) (pITN) was first synthesized by Wudl and been prepared through chemical

\begin{figure}[h]
\centering
\includegraphics[width=0.2\textwidth]{figure13.png}
\caption{Chemical structure of ITN.}
\end{figure}
or electrochemical oxidative polymerization.\textsuperscript{5, 6} The homopolymer has also been prepared in greater quantities through the reaction of phthalic anhydride with phosphorous pentasulfide.\textsuperscript{7, 8} Unfortunately, regardless of polymerization technique, pITN is an intractable material. While soluble derivatives of ITN have been synthesized and polymerized, the route to these materials is difficult, and impractical for large scale production.\textsuperscript{9-14}

Isothianaphthene can be synthesized in three steps in high yield starting from $\alpha,\alpha'$-dibromo-$o$-xylene (Figure 14).\textsuperscript{15, 16} Functionalization of ITN allows for the incorporation of this moiety into a variety of copolymers.\textsuperscript{14}

![Figure 14: Synthesis of ITN from $\alpha,\alpha'$-dibromo-$o$-xylene.\textsuperscript{15}](image)

However, conducting functionalization chemistry on ITN is very difficult as the monomer is extremely unstable. If not used immediately, ITN, as well as some of the intermediate products, will undergo spontaneous autopolymerization to form insoluble polymers. Fortunately, flanking the ITN unit with thiophene moieties, as in the trimers series presented here, stabilizes the resulting material and allows for functionalization and incorporation of the trimer unit into copolymers.\textsuperscript{11, 13, 17-19} While such flanked ITN structures can be obtained through aromatic coupling reactions using functionalized ITN, it would be easier if the flanking thiophene units could be installed prior to the formation of the ITN ring. This strategy would remove the need to synthesize, purify, and functionalize the ITN monomer and directly yield the stable trimer. The formation of the
core ITN ring in a trimer system can be accomplished through the ring-closing reaction of Lawesson’s reagent (LR) with an ortho diketone (Figure 15).\textsuperscript{20}

Lawesson’s reagent is a mild thionating agent which has been widely used for the conversion of the carbonyl unit of ketones, esters, and amides into a thiocarbonyl under mild conditions in high yields. Lawesson’s reagent consists of a phosphorous pentasulfide-like core attached to two organic ligands (Figure 16).

![Figure 16: Chemical structure of Lawesson’s reagent.](image)

Upon heating, the core of the molecule fragments into two dithiophosphine ylides which proceed to react with the carbonyl through the formation and fragmentation of a four membered ring intermediate.\textsuperscript{21}

### 2.1.2 – Thieno[3,4-b]thiophene as a Trimer Core

The second core moiety which will be used in the synthesis of well-ordered trimers is thieno[3,4-b]thiophene which can be synthesized in moderate yield in a two step process (Figure 17).\textsuperscript{22} This monomer offers several advantages over the ITN core discussed previously. The first of these is that the upper thiophene ring of thieno[3,4-b]thiophene can be easily substituted with a variety of chemical groups through the use of the appropriate alkyne.\textsuperscript{22-25} This ease of substitution allows for the fine tuning of the monomer’s electronic structure and for the inclusion of solublizing groups such as alkyl
chains. The second advantage which thieno[3,4-b]thiophene offers is that the monomer has been reported to be stable under ambient conditions making functionalization chemistry much easier than on ITN.26

![Figure 17: Two step synthesis of thieno[3,4-b]thiophene moieties.](image)

The relative ease with which substituted thieno[3,4-b]thiophenes have been prepared has led to the synthesis of a wide range of materials. It has been shown that these substituents can have a profound impact on the electronic structure of the monomer, and thus have a profound impact on the optical and electronic properties of the resulting homopolymers.22, 23, 25, 27 For example, when the thieno[3,4-b]thiophene is substituted with a phenyl ring, the band gap of the resulting homopolymer was reported to be 0.85 eV.22 When the substituent on the upper thiophene ring is an alkyl chain the band gap increases to 1-1.5 eV. Further, work in our group has shown that the band gap of homopolymers of alkyl substituted thieno[3,4-b]thiophene changes with the length of the alkyl chain with an increase of ~0.5 eV as the length of the alkyl chain substituent is increased from 5 to 8 carbons.27 Because of the low band gap of the phenyl substituted monomer, it was the first monomer evaluated for inclusion into the trimer system.

Unfortunately, the synthesis of the phenyl substituted thieno[3,4-b]thiophene proved to be very difficult, proceeding only in very low yields. Also, selective functionalization of the aromatic system proved to be impossible as reactions on the phenyl substituent compete with the desired functionalization of the thiophene moiety.
Fortunately, these problems are avoided in the alkyl substituted material. The alkyl chains impart solubility to the resulting polymers, removing the need to incorporate the solublizing groups into the comonomers.

Trimers were built around a core of octyl substituted thieno[3,4-b]thiophene (Tt8) (Figure 18). The trimers were synthesized via the Suzuki or Stille coupling of appropriately functionalized 3-hexylthiophenes to a di-brominated Tt8 moiety. The utility of Stille and Suzuki couplings for the synthesis of the Tt8 core materials highlights the benefit of using a relatively stable central unit. It is important to note that the regiochemistry of the Tt8 incorporation cannot be controlled. While regiochemical concerns are not relevant for the study of the trimers, as they are symmetric materials, they may prove to be important in the synthesis of polymeric systems.

2.1.3 – Computational Methods For Studying Structure - Property Relationships

Computational methods were used to investigate the effects of sterics on the trimers, and the electronic structure of the core unit, in an effort to better understand the optical and electronic properties of these materials. These methods allow for the lowest energy structure of the trimers to be calculated. From this structure, the HOMO and LUMO levels of the materials were calculated. These values, along with the experimental results and computed structures, will yield important information on the effect that the electronic structure and sterics of the various trimers have on the optical and electronic properties of these trimers.
2.2 Experimental

General – Tetrahydrofuran was distilled over sodium/benzophenone, and chloroform was stored over molecular sieves prior to use. All other reagents were purchased from commercial sources and were used as received. All reactions were performed under an inert nitrogen atmosphere using degassed solvents. Di-brominated Tt8 and 3-hexylthiophene-5-boronic acid pinacol ester were prepared according to the published procedure. 27 2,2′:5′,2″-Terthiophene (T-T-T) was purchased from Sigma Aldrich and was used as received.

Instrumentation – 1H and 13C NMR spectra were recorded on an Advance DPX-300 spectrometer. Cyclic voltammograms of the trimers were obtained on a BASi-EC epsilon potentiostat against a Ag/Ag+ (0.1 M AgNO3 in acetonitrile) reference electrode using gold working electrodes at a scan rate of 100 mV/s. Samples were prepared as saturated solutions in 0.1 M LiClO4 in anhydrous, nitrogen saturated acetonitrile. All potentials are reported versus the ferrocene redox couple. Absorption spectra were obtained in hexane or chloroform, using a Perkin-Elmer Lambda 850 spectrometer. Band gaps were calculated from the onset of absorption. The HOMO levels of the materials were found from the onset of the oxidation wave obtained by cyclic voltammetry taking into account the ferrocene redox couple at -4.8 eV. In the samples where reduction waves were not observed, LUMO levels were calculated from the HOMO levels and the optical band gap.

Computational Studies – Computational studies were carried out using hybrid density functional theory using the B3LYP functional with the 631+G* basis set. Calculations were performed using Spartan ’10 for Linux (Wavefunction, Inc.). Each
molecule was geometrically optimized in multiple confirmations to find a global
minimum energy. UV-Visible absorbance peaks were computed using Spartan’s default
TDDFT method. Band gaps were determined from the onset of absorbance, which was
determined from Gaussian lineshape overlays for each of the calculated peaks. In order
to simplify the calculations, all of the alkyl groups for the trimer systems have been
calculated as ethyl groups to reduce the large number of spatial confirmations inherent
with longer hexyl or octyl chains.

**Activated phthaloyl chloride (1)** – To a 0 °C solution of 3-mercaptopyridine
(8.09 g, 72.9 mmol) in 100 mL dichloromethane was added phthaloyl chloride (7.31 g,
36.0 mmol). After stirring for 30 minutes, 7 mL pyridine was added and the resulting
mixture was allowed to warm to room temperature over 4.5 hours. An additional 50 mL
of dichloromethane was added, and the organic layer was washed with water and brine.
The organic layer was dried with magnesium sulfate. After evaporation and
crystallization from chloroform/diethyl ether, 9.64 g (76% yield) of the product was
obtained: MS (m/z) 352.0 (M++); 1H NMR (CDCl3) δ (ppm): 7.30 (m, 2H), 7.65 (dd,
2H), 7.78 (m, 4H), 7.88 (dd, 2H), 8.64 (m, 2H); 13C NMR (CDCl3) δ (ppm): 123.74,
128.63, 130.45, 132.02, 136.85, 137.29, 150.43, 151.39, 190.25.

**HT-I-HT** – To a mixture of iodine activated magnesium (0.95 g, 39.6 mmol) in
60 mL freshly distilled THF was added 2-bromo-3-hexylthiophene (4.47 g, 26.5 mmol).
After 3.5 hours, the resulting mixture was slowly added to a 0 °C solution of 1 (2.91 g,
8.27 mmol) in 50 mL THF. After 30 minutes, the reaction was quenched with 100 mL 10
% HCl(aq) and extracted with diethyl ether. The organic layer was successively washed
with 1 M NaHCO3, water, and brine. After drying with magnesium sulfate and
evaporation of the solvent, the residue was taken up in 100 mL dichloromethane and was reacted with Lawesson’s Reagent (4.01 g, 9.91 mmol) at 45 °C. After 30 minutes, the dichloromethane was evaporated and the residue was refluxed in ethanol for 30 minutes. The resulting solution was added to water and was extracted with diethyl ether. Afterward, the organic layer was washed with 10 % NaOH, water, and brine it was dried over MgSO₄ and the solvent was removed by evaporation. The crude product was purified via column chromatography (silica gel/hexane) yielding 3.43 g (89 % yield) of a yellow oil: MS (m/z) 466.2 (M⁺); ¹H NMR (CDCl₃) δ(ppm): 0.82 (t, 6H), 1.21 (m, 12H), 1.55 (t, 4H), 2.67 (t, 4H), 7.09 (m, 4H), 7.39 (d, 2H), 7.60 (dd, 2H); ¹³C NMR (CDCl₃) δ(ppm): 14.08, 22.57, 29.06, 29.09, 30.91, 31.61, 121.41, 124.04, 125.87, 126.08, 127.94, 129.33, 136.96, 142.34.

**T-I-T** To a mixture of iodine activated magnesium (1.01 g, 41.5 mmol) in 40 mL freshly distilled THF was added 2-bromothiophene (3.48 g, 21.4 mmol). The resulting mixture was heated to 55 °C for 3.5 hours after which the resulting solution was added to a 0 °C solution of 1 (2.98 g, 8.47 mmol) in 30 mL THF. After 30 minutes the reaction was quenched with 100 mL 10 % HCl(aq) and extracted with diethyl ether. The organic layer was successively washed with 1 M NaHCO₃, water, and brine. After drying with magnesium sulfate and evaporation of the solvent the residue was taken up in 100 mL dichloromethane and was reacted with Lawesson’s Reagent (3.35 g, 8.28 mmol) at 45 °C. After 30 minutes, the dichloromethane was evaporated and the residue was refluxed in ethanol for 30 minutes. The resulting solution was added to water and was extracted with diethyl ether. After the organic layer was washed with 10 % NaOH, water, and brine it was dried over MgSO₄ and the solvent was removed by evaporation. The crude product
was purified via column chromatography (silica gel/hexane) yielding 2.15 g (88 % yield) of a red powder: MS \((m/z)\) 298.0 (M\(^{++}\)); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) (ppm): 7.15 (m, 4H), 7.37 (m, 4H), 7.95(dd, 2H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) (ppm): 121.53, 124.81, 125.57, 125.61, 126.51, 127.90, 135.29, 135.61.

**HT-I-HT\textsubscript{out}** – To a mixture of 3-hexylthiophene (2.06 g, 12.3 mmol) and tetramethylethylenediamine (2.25 g, 19.4 mmol) in 30 mL THF at -78 °C was added 7.5 mL of a 2.5 M solution of n-butyl lithium in hexane. After 2 hours, the solution was added to a solution of phthaloyl chloride (1.09 g, 5.37 mmol) in 30 mL THF at -78 °C. The resulting mixture was stirred at this temperature for 5 hours and was then quenched in 10 % HCl\(_{aq}\). The mixture was extracted with diethyl ether and the organic layer was washed with 1 M NaHCO\(_3\), water, and brine. After drying with magnesium sulfate and evaporation of the solvent the residue was taken up in 75 mL dichloromethane and was reacted with Lawesson’s Reagent (2.20 g, 5.45 mmol) at 35 °C for 30 minutes. After 30 minutes, the dichloromethane was evaporated and the residue was refluxed in ethanol for 30 minutes. The resulting solution was added to water and was extracted with diethyl ether. After the organic layer was washed with 10 % NaOH, water, and brine it was dried over MgSO\(_4\) and the solvent was removed by evaporation. The crude product was purified via column chromatography (silica gel/hexane) yielding 0.11 g (5 % yield) of an orange red oil: MS \((m/z)\) 466.2 (M\(^{++}\)); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) (ppm): 0.90 (t, 6H), 1.35 (m, 12H), 1.68 (t, 4H), 2.65 (t, 4H), 6.96 (s, 2H), 7.12 (dd, 2H), 7.18 (s, 2H), 7.94 (dd, 2H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) (ppm): 13.59, 22.10, 28.52, 29.89, 31.16, 33.46, 118.70, 119.60, 121.08, 122.04, 123.61, 124.05, 125.45, 126.25
**HT-T-HT**<sub>in</sub> - A mixture of 2,5-dibromothiophene (0.42 g, 1.74 mmol), 3-hexylthiophene-2-boronic acid pinacol ester (1.76 g, 5.98 mmol), potassium fluoride (1.01 g, 17.4 mmol), and [1,1′-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (64.5 mg, 0.09 mmol) was absorbed onto 3 g of neutral alimuna in a 10 mL microwave vial. The mixture was homogenized by the addition and removal under reduced pressure of methanol. The mixture was heated to 100 °C for 15 minutes using microwave heating. The resulting mixture was removed from the microwave tube, and was washed thoroughly with hexane. The solvent was evaporated under reduced pressure, and the residue was purified via column chromatography (silica gel/hexane) yielding 0.24 g (34 % yield) of a pale yellow oil: MS (m/z) 416.2 (M⁺); <sup>1</sup>H NMR (CDCl₃) δ (ppm): 0.89 (t, 6H), 1.33 (m, 12H), 1.65 (t, 4H), 2.78 (t, 4H), 6.94 (d, 2H), 7.02 (d, 2H), 7.13 (d, 2H), 7.18 (d, 2H); <sup>13</sup>C NMR (CDCl₃) δ (ppm): 14.12, 22.66, 29.27, 29.31, 30.75, 31.71, 123.76, 126.07, 130.08, 130.41, 136.06, 139.72.

**HT-T-HT**<sub>out</sub> - A mixture of 2,5-dibromothiophene (0.44 g, 1.81 mmol), 3-hexylthiophene-5-boronic acid pinacol ester (1.57 g, 5.34 mmol), potassium fluoride (1.14 g, 19.6 mmol), and [1,1′-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (131 mg, 0.18 mmol) was absorbed onto 3.3 g of neutral alimuna in a 10 mL microwave vial. The mixture was homogenized by the addition and removal under reduced pressure of methanol. The mixture was heated to 100 °C for 15 minutes using microwave heating. The resulting mixture was removed from the microwave tube, and was washed thoroughly with hexane. The solvent was evaporated under reduced pressure, and the residue was purified via column chromatography (silica gel/hexane) yielding 0.36 g (47 %) of a pale yellow oil: MS (m/z) 417.4 (M⁺⁺); <sup>1</sup>H NMR (CDCl₃) δ (ppm): 0.90 (t, 6H),
HT-Tt8-HT in – To a solution of Br₂Tt8 (0.410 g, 1.0 mmol) in 60 mL 1:1:1 toluene:ethanol:water (v/v/v) was sequentially added 3-hexylthiophene-2-boronic acid pinacol ester (0.647 g, 2.2 mmol), sodium carbonate (Na₂CO₃) (0.848 g, 8.0 mmol) and tetrakis(triphenylphosphine) palladium(0) (57.75 mg, 0.05 mmol). The resulting mixture was stirred at 105 °C for 20 hours after which the mixture was poured into water. After extraction with dichloromethane, the organic layer was washed with NaHCO₃, water and brine, and was then dried over MgSO₄. After evaporation of the solvent under reduced pressure, the product was further purified by column chromatography (silica gel/hexane) yielding 0.51 g (87 %) of a viscous light yellow oil: MS (m/z) 584.3 (M⁺); ¹H NMR (CDCl₃) δ(ppm): 7.25 (d, 2H), 6.90 (d, 2H), 6.74 (s, 1H), 2.70 (m, 6H), 1.60 (m, 6H), 1.31 (m, 22H), 0.87 (t, 9H); ¹³C NMR (CDCl₃) δ(ppm): 14.15, 22.66, 22.69, 29.05, 29.17, 29.23, 29.36, 29.64, 30.41, 30.48, 30.55, 31.72, 31.89, 32.16, 114.07, 119.09, 120.99, 124.62, 134.94, 136.32, 140.10, 143.09, 144.33, 154.13.

T-Tt8-T – To a solution of Br₂Tt8 (0.410 g, 1.0 mmol) and 2-(Tributylstanny1) thiophene (0.748 g, 2.0 mmol) in 50 mL 1,2-dichlorobenzene was added bis(triphenylphosphine) palladium(II) dichloride (35 mg, 0.050 mmol). After the reaction mixture was stirred at 130 °C for 48 h, the solvent was evaporated under reduced pressure. The residue was poured into water and was extracted with dichloromethane. The organic layer was washed with NaHCO₃, water and brine, and was dried over MgSO₄. After evaporation of the solvent under reduced pressure, the product was further
purified by column chromatography (silica gel/hexane:ethylacetate (95:5)) yielding 0.15 g (35%) of a viscous light-red oil: MS (m/z) 416.1 (M+) : $^1$H NMR (CDCl$_3$) $\delta$(ppm):
7.27 (dd, 2H), 7.22 (t, 2H), 7.10 (dd, 2H), 6.92 (s, 1H), 2.75 (m, 2H), 1.65 (m, 2H), 1.31 (m, 10H), 0.87 (t, 3H) : $^{13}$C NMR (CDCl$_3$) $\delta$(ppm): 14.17, 21.23, 22.71, 29.17, 29.57, 30.44, 32.16, 34.25, 114.18, 120.81, 123.75, 124.31, 127.86, 128.82, 135.25, 136.66, 143.35, 154.38.

HT-Tt8-HT out - To a solution of Br$_2$Tt8 (0.410 g, 1.0 mmol) in 60 mL 1:1:1 toluene : ethanol : water (v/v/v) was sequentially added 3-hexylthiophene-5-boronic acid pinacol ester (0.647 g, 2.2 mmol), sodium carbonate (0.848 g, 8.0 mmol), and tetrakis(triphenylphosphine) palladium(0) (57.75 mg, 0.05 mmol). The resulting mixture was reacted at 105 °C for 20 hours after which the mixture was poured into water and was extracted with dichloromethane. The organic layer was washed with NaHCO$_3$, water, and brine, and was then dried over MgSO$_4$. After evaporation of the solvent under reduced pressure, the product was further purified by column chromatography (silica gel/hexane), yielding a 0.40 g (65 %) of a viscous light yellow oil: MS (m/z) 584.3 (M++) : $^1$H NMR (CDCl$_3$) $\delta$(ppm): 7.08 (s, 2H), 6.87 (s, 2H), 6.83 (s, 1H), 2.78 (t, 2H), 2.59 (t, 4H), 1.67 (m, 6H), 1.32 (m, 22H), 0.87 (t, 9H) : $^{13}$C NMR (CDCl$_3$) $\delta$(ppm): 14.16, 14.17, 22.21, 22.63, 22.72, 27.82, 28.90, 29.20, 30.34, 30.56, 31.64, 31.74, 31.91, 32.17, 114.26, 119.08, 121.01, 125.00, 134.95, 135.94, 143.09, 144.43, 151.25, 154.12.

2.3 Results and Discussion

2.3.1 Synthesis

The eight trimers have been synthesized through a variety of methods. The ITN core trimers were synthesized in a two step process involving the reaction of phthaloyl
chloride, or a 2-mercaptopyridine activated derivative of phthaloyl chloride, with a lithiated thiophene or the Grignard reagent derived from 2-bromothiophene or 2-bromo-3-hexylthiophene (Figure 19). The substituted ortho di-ketones were allowed to react with Lawesson’s reagent to close the central thiophene ring, and synthesize the ITN moiety. This approach allows for the direct synthesis of the timers without the need to synthesize and functionalize ITN directly. This chemistry proceeds in excellent yields for the HT-I-HT\textsubscript{in} and T-I-T trimers, while the HT-I-HT\textsubscript{out} trimer was only obtained in low yield. The low yield of HT-I-HT\textsubscript{out} is likely due to non-specific lithiation of the thiophene ring. While 3-hexylthiophene is typically lithiated at the 5 position at -78 °C, the lithium readily transfers to the 2 position at higher temperatures. While the reaction is kept at -78 °C, the solution of the lithiated thiophene warms during the transfer between reaction flasks, generating a mixture of trimers with mixed regiochemistry.

Figure 19: Synthesis of the ITN core trimers.
The thiophene and Tt8 core trimers were synthesized via Suzuki or Stille coupling between di-brominated core moieties and either hexylthiophene boronic acid pinacol esters or stanylated hexylthiophenes (Figure 20). The Tt8 series was synthesized using standard solution techniques\(^\text{28, 29}\) while the thiophene core trimers were synthesized using a solvent free microwave method.\(^\text{30}\) The solution method typically gave higher yields than the microwave method. Despite this, the solvent-free microwave technique does have advantages, namely the much shorter reaction times and less stringent reaction conditions, over the solution based method. The yield of the microwave technique could likely be improved through better homogenization of the reaction mixture on the alumina support.

### 2.3.2 Optical Properties of the Trimers

The absorption spectra of the trimers (Figure 21) show several important trends which highlight the effects of the electronic and steric structures of the trimers. There are two trends which can be examined in these materials. The first deals with the effect of the central monomer unit in the trimer on the optical properties of the material. From examination of the absorption spectra, the electron donating ability of the ITN and Tt8 moieties becomes apparent due to the dramatic red shift from the thiophene core timers and the ITN and Tt8 core trimer systems. Further, it can be seen that the two electron donating moieties have similar effects on the optical properties of the trimer systems.
Figure 20: Synthesis of thiophene and Tt8 trimers.
The second trend which can be examined using these spectra is the effects of the steric interactions of the trimers on the optical absorption. The regiochemistry of the thiophene core trimers has very little effect on the optical properties of the materials. The absorption onset is virtually identical in all three of the thiophene core trimers, and the location of the absorbance maximum only shifts 25 nm between the three trimers. The ITN and Tt8 trimer systems show much more variation between the three regiochemistries with total shifts in the absorbance maximum of between 65 and 75 nm respectively. The location of the absorption onset in these systems shows much greater variation with shifts of about 100 nm in both systems. These trends indicate that the effects which alter the optical properties of the materials are steric interactions between the alkyl chains on the flanking

Figure 21: Normalized absorption spectra of the trimers.
thiophene units and the large central ITN or Tt8 moiety rather than interactions between the alkyl chains on the two flanking thiophene units. Further, it is interesting to note that, while the hexyl-in trimers are the bluest shifted in all three trimer systems, the hexyl-out trimers are the most red shifted in the thiophene and Tt8 core trimers, while the non-hexyl trimer is the most red shifted ITN core material.

2.3.3 Electrochemical Properties of the Trimers

The electronic structures of the trimers have been successfully measured through cyclic voltammetry (Table 1). The HOMO levels of the trimers were determined from the oxidation onset of the trimers, while the LUMO levels were determined either from the onset of reduction, or from the HOMO level and the optical band gap, in the cases where no reduction wave was observed. Interestingly, reduction waves were only observed in the Tt8 core trimers. From the HOMO and LUMO levels we can examine the trends observed in the optical absorption spectra in more detail. From these results, it can be seen that the HOMO level is largely independent of the regiochemistry of the trimer. Further, the identity of the core monomer has little effect on the HOMO level, especially between the ITN and thiophene core trimer systems which have almost identical HOMO levels around -5.2 eV. The Tt8 core trimers have HOMO levels which lie slight lower than the other trimer systems, but the shift is fairly small at ~0.3 eV.
Table 1: Optical and electrochemical properties of the trimers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$E_g^{\text{(opt)}}$ (eV)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-T-T</td>
<td>349</td>
<td>3.06</td>
<td>-5.3</td>
<td>-2.2</td>
</tr>
<tr>
<td>HT-T-HT (in)</td>
<td>331</td>
<td>3.08</td>
<td>-5.3</td>
<td>-2.2</td>
</tr>
<tr>
<td>HT-T-HT (out)</td>
<td>356</td>
<td>3.06</td>
<td>-5.2</td>
<td>-2.1</td>
</tr>
<tr>
<td>T-I-T</td>
<td>450</td>
<td>2.21</td>
<td>-5.1</td>
<td>-2.9</td>
</tr>
<tr>
<td>HT-I-HT (in)</td>
<td>386</td>
<td>2.62</td>
<td>-5.1</td>
<td>-2.5</td>
</tr>
<tr>
<td>HT-I-HT (out)</td>
<td>433</td>
<td>2.38</td>
<td>-4.9</td>
<td>-2.5</td>
</tr>
<tr>
<td>T-Tt8-T</td>
<td>409</td>
<td>2.68</td>
<td>-5.4</td>
<td>-2.8</td>
</tr>
<tr>
<td>HT-Tt8-HT (in)</td>
<td>382</td>
<td>2.78</td>
<td>-5.5</td>
<td>-2.8</td>
</tr>
<tr>
<td>HT-Tt8-HT (out)</td>
<td>458</td>
<td>2.34</td>
<td>-5.6</td>
<td>-3.0</td>
</tr>
</tbody>
</table>

The effects of steric interactions and electronic effects are more evident in the LUMO levels of the trimers where significant shifts are seen between trimer series with differing core moieties, with the ITN and Tt8 core trimer systems having significantly lower lying LUMO levels than their thiophene core trimer counterparts. Within each series, the LUMO levels largely echo the results seen in the optical absorption spectra, as would be expected from the ITN and thiophene core systems, as the LUMO levels were calculated using the optical band gaps. However, in the Tt8 core system, where the LUMO levels were calculated directly from the reduction wave of the cyclic voltammograms, there is very little variation in the LUMO levels of the three trimers. The electrochemical band gaps of these materials match closely to the optical results for the HT-Tt8-HT$_{\text{in}}$ and T-Tt8-T trimers, but show a significant difference for the HT-Tt8-HT$_{\text{out}}$ trimer. The electrochemical band gap of the HT-Tt8-HT$_{\text{out}}$ trimer is virtually identical to the band gaps of the other two Tt8 trimers, and does not agree with the large
red shift exhibited by the absorption spectrum of this trimer. This discrepancy between the optical and electrochemical results is most likely due to the polarity of the acetonitrile used as a solvent in the electrochemical studies, which should cause the alkyl chains on the HT-Tt8-HT\textsubscript{out} trimer to assume a more globule conformation, resulting in higher steric interactions, thus pushing the trimer out of planarity.

### 2.3.4 Computational Studies of the Trimers

The computational studies of the trimers have focused on calculating both the lowest energy conformation and the HOMO/LUMO levels of the trimers. These calculations were accomplished using hybrid density functional theory. From the calculated lowest energy structure of the trimers (Figure 22), the effect of the regiochemistry of the trimers becomes clear. As surmised from the absorption spectra, there are steric interactions in the HT-I-HT\textsubscript{in} and HT-Tt8-HT\textsubscript{in} trimers which cause the thiophene rings to be pushed out of plane with the central moiety of the trimer. While none of the structures are perfectly planar, the non-hexyl and hexyl out trimers display significantly less structural distortion across the three trimer systems. As in the optical absorption results, the structure of the thiophene core trimers exhibit very little variation regardless of the regiochemistry of the trimer, indicating that the flanking hexylthiophenes are pushed out of planarity primarily by steric interactions between the hexyl chains and the bulky central unit, while steric interactions between the alkyl chains on the flanking thiophene units have comparatively little effect.

The HOMO and LUMO levels of the optimized structures have been successfully calculated (Table 2). The calculated HOMO levels and “optical” band gaps are generally in good agreement with the experimental values, especially in the thiophene and ITN core
trimer series. The calculated and experimental HOMO levels of the thiophene core trimers only vary by 0.1 eV, while the ITN core series shows a bit more variation with differences of about 0.2 – 0.3 eV. The computational results for the Tt8 core trimers show mixed results, with excellent agreement between the experimental and computational values for the HT-Tt8-HT in trimer, while the values for the HT-Tt8-HT out trimer vary by over 0.5 eV. The calculated band gaps match very well with the experimental results, with all of the values falling within 0.2 eV of each other.

Table 2: Comparison of experimental and computational results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental Results</th>
<th></th>
<th>Computational Results</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_g$(opt) (eV)</td>
<td>HOMO (eV)</td>
<td>LUMO (eV)</td>
<td>$E_g$ (eV)</td>
</tr>
<tr>
<td>T-T-T</td>
<td>3.06</td>
<td>-5.3</td>
<td>-2.2</td>
<td>3.02</td>
</tr>
<tr>
<td>HT-T-HT in</td>
<td>3.08</td>
<td>-5.3</td>
<td>-2.2</td>
<td>3.20</td>
</tr>
<tr>
<td>HT-T-HT out</td>
<td>3.06</td>
<td>-5.2</td>
<td>-2.1</td>
<td>3.00</td>
</tr>
<tr>
<td>T-I-T</td>
<td>2.21</td>
<td>-5.1</td>
<td>-2.9</td>
<td>2.43</td>
</tr>
<tr>
<td>HT-I-HT in</td>
<td>2.62</td>
<td>-5.1</td>
<td>-2.5</td>
<td>2.65</td>
</tr>
<tr>
<td>HT-I-HT out</td>
<td>2.38</td>
<td>-4.9</td>
<td>-2.5</td>
<td>2.39</td>
</tr>
<tr>
<td>T-Tt8-T</td>
<td>2.68</td>
<td>-5.4</td>
<td>-2.8</td>
<td>2.51</td>
</tr>
<tr>
<td>HT-Tt8-HT in</td>
<td>2.78</td>
<td>-5.5</td>
<td>-2.8</td>
<td>2.82</td>
</tr>
<tr>
<td>HT-Tt8-HT out</td>
<td>2.34</td>
<td>-5.6</td>
<td>-3.0</td>
<td>2.47</td>
</tr>
</tbody>
</table>
Figure 22: Lowest energy structure of the trimers.
The calculated LUMO levels show poor agreement with the experimental values. The poor agreement in the LUMO values spans all three sets of trimers, but is particularly pronounced in the ITN and Tt8 core trimer systems. The variation in the experimental and computational values for the LUMO level of the trimers can be partially attributed to the use of the onset of absorption for the calculation of optical band gaps (and thus the calculation of the LUMO levels in the ITN and thiophene core trimer systems). While this method of band gap measurement is the most relevant for solar cell applications, the calculated HOMO/LUMO values consider the molecule in a fixed conformation and without solvent effects. The vibrational structure of the trimers and the interactions between solvent and the trimers can allow for the molecules to undergo lower energy transitions, resulting in measured band gaps which are lower than the difference between the calculated HOMO and LUMO levels of the molecule. Further, substitution of the long alkyl chains for ethyl groups may explain some of the variation between the experimental and computational LUMO levels as the strength of the steric interactions should depend on the alkyl chain length. This effect would explain why the variation is especially pronounced in the ITN and Tt8 core trimer systems as these are the sets of trimers which exhibit significant steric interactions.

2.4 Conclusions

As a first step toward the synthesis of polymers with a systematically tunable band gap, a series of well-ordered trimers have been synthesized. The trimers consist of two thiophene moieties flanking a central unit. This central unit is either thiophene, or one of two strongly electron donating units: ITN or Tt8. A set of three trimers have been synthesized for each core unit to study the effects of steric interactions on the
development of the optical and electronic properties of the materials. Characterization of the trimers shows that the electronic properties of the central unit have a profound impact on the optical absorption of the trimers with the inclusion of electron donating moieties resulting in pronounced red shifts from the all thiophene system. The optical and electrochemical measurements also highlight the importance of steric interactions between alkyl chains on the flanking thiophene units and the bulky ITN or Tt8 central units in the determination of the properties of the material.

Computational studies have been undertaken to determine the lowest energy structures of the trimers. These structures support the trends seen in the optical and electrochemical measurements, and further demonstrate the ability of steric interactions to push the flanking thiophene units out of planarity with the central core. The HOMO and LUMO levels of the trimers were also calculated in the hopes that good correlation with the experimental results would be found. While the calculated and experimental HOMO levels and optical band gaps showed excellent agreement across most of the trimers studied, the calculated LUMO levels varied widely from the experimental results. This poor agreement in the LUMO levels is likely due to a variety of factors including underestimation of the steric effects of the hexyl chains on the flanking thiophene units and the inability for the computational technique to account for the effect of the vibrational modes on the structure of the trimers and the corresponding influence on band locations.

Through this study, we have gained a better understanding on the effects that the electronic structure and steric effects play in the development of the properties of highly conjugated small molecules. This study could only be conducted because of the ability to
synthesize trimers with well-defined structures. In the next chapter of this thesis, this methodology will be extended to the synthesis of a series of copolymers with a well-defined sequence and regiochemistry. By controlling the level of incorporation of the comonomers, the sequence of the polymer chain, and the regiochemistry of the repeat unit we will demonstrate systematic control over the band gap of the resulting materials.


CHAPTER 3
TUNABLE BAND GAP POLYMERS FROM THIOPHENE –
ISOTHIANAPHTHANENE COPOLYMERS

3.1 Introduction

As previously mentioned, the synthesis of a series of variable band gap polymeric semiconductors is of great interest for the optimization of bulk heterojunction photovoltaic cell power conversion efficiency. The previous chapter presented detailed investigations on a variety of well-ordered trimer structures into the effects of the electronic structure of the core unit and the steric of the flanking units on the evolution of the optical and electronic properties of the material. These results demonstrate, on the small molecule scale, the ability to vary the optical and electronic properties of the materials by the variation of the material’s chemical structure.

![Figure 23: Well ordered polymers based on the ITN core trimers described previously.](image)

In this chapter, several of the trimers presented previously will be used as the foundation for the synthesis and characterization of a series of optically active polymers with tunable band gap (Figure 23). These materials will be obtained through the
polymerization of a series of well-ordered oligomers which have been built from the trimer cores through the successive coupling of 3-hexylthiophene units to the ends of the trimer unit using Suzuki coupling. Through this chemistry, the molar incorporation of the central electron donating moiety can be controlled, and varied, while maintaining the well-ordered molecular structure which was obtained through the synthetic methods previously described.

The trimer units which were chosen as the core from which the well-ordered oligomers will be built are T-I-T and HT-I-HT_{in}. These trimer units were chosen because the ITN core unit was previously shown in the trimer systems to have the greatest impact on the electronic band structure of the three core moieties studied. Also, this set of trimers can be obtained in the highest yield with the fewest synthetic steps compared to the Tt8 core. By using these core units, the steric effects discussed previously can be harnessed as a method to further tune the band gap of the material beyond what is possible through the variation of the comonomer incorporation.

3.2 Experimental

**General** – N-bromosuccinimide was recrystallized from water; chloroform was stored over molecular sieves prior to use. All other reagents were purchased from commercial sources and were used as received. All reactions were carried out under an inert nitrogen atmosphere using degassed solvents. The two starting trimers HT-I-HT_{in} and T-I-T were synthesized as described in the previous chapter.

**Instrumentation** – $^1$H and $^{13}$C NMR spectra were recorded on an Advance DPX-300 spectrometer. Molecular weights were measured against polystyrene standards using gel permeation chromatography (GPC) using a THF mobile phase and a refractive index
Cyclic voltammograms of the oligomers were obtained on a BASi-EC epsilon potentiostat against a Ag/Ag\(^+\) (0.1 M AgNO\(_3\) in acetonitrile) reference electrode using gold working electrodes at a scan rate of 100 mV/s. Samples were prepared as saturated solutions in 0.1 M LiClO\(_4\) in anhydrous, nitrogen saturated acetonitrile. Voltammograms of the polymers were measured, using similar conditions, on films drop cast on glassy carbon electrodes from solutions of the polymer in 0.1 M LiClO\(_4\) in anhydrous THF. All potentials are reported versus the ferrocene redox couple. Absorption spectra were obtained using a Perkin-Elmer Lambda 850 spectrometer. Absorption spectra of the oligomers were obtained in hexane while the spectra of the polymers were obtained in chloroform. Band gaps were calculated from the onset of absorption. The HOMO levels of the materials were found from the onset of the oxidation wave obtained by cyclic voltammetry taking into account the ferrocene redox couple at -4.8 eV. Since reduction waves were not observed for any of these materials, LUMO levels were determined from the HOMO levels and the optical band gap.

**Br\(_2\)HT-I-HT** – To a 0 °C solution of HT-I-HT\(_{in}\) (4.84 g, 10.4 mmol) in 100 mL chloroform/acetic acid (1:1 v:v) was added N-bromosuccinimide (3.91 g, 22.0 mmol). The resulting mixture was stirred for 2 hours at 0 °C before being added to 100 mL H\(_2\)O. After extraction with hexane, the organic layer was successively washed with 1 M NaHCO\(_3\), H\(_2\)O, and Brine. The organic layer was then dried over MgSO\(_4\), and the solvent was removed under reduced pressure. The resulting crude product was purified via column chromatography (silica gel/hexane) yielding 6.31 g (98 %) of an orange oil:

**MS** (m/z) (M\(^{++}\)) 624.0, Calculated: 624.6; \(^1\)H NMR (CDCl\(_3\)) \(\delta\) (ppm): 0.83 (m, 6H), 1.21 (m, 12H), 1.57 (t, 4H), 2.60 (t, 4H), 7.04 (s, 2H), 7.11 (dd, 2H), 7.58 (dd, 2H); \(^{13}\)C NMR
HT₂-I-HT₂ – To a solution of Br₂HT-I-HT (1.71 g, 2.74 mmol) and 3-hexylthiophene-2-boronic acid pinacol ester (1.70 g, 5.78 mmol) in 60 mL 1 : 1 : 1 toluene : ethanol : water (v/v/v) was added Tetrakis(triphenylphosphine)palladium(0) (0.66 g, 0.57 mmol) and sodium carbonate (0.62 g, 5.1 mmol). The mixture was refluxed overnight after which the organic layer was evaporated off with a flow of nitrogen. The remainder of the mixture was added to 100 mL of water and was extracted with hexane. The organic layer was dried over MgSO₄ and was evaporated under reduced pressure. The product was purified by column chromatography (silica gel/hexane) yielding 1.87 g (86%) of a red oil: MS (m/z) (M⁺) 799.3, Calculated: 799.3; ¹H NMR (CDCl₃) δ(ppm): 0.85 (m, 12H), 1.30 (m, 24H), 1.64 (m, 8H), 2.69 (t, 4H), 2.82 (t, 4H), 6.96 (d, 2H), 7.09 (s, 1H), 7.12 (dd, 2H), 7.19 (d, 2H), 7.71 (dd, 2H); ¹³C NMR (CDCl₃) δ(ppm): 14.08, 14.12, 22.59, 22.66, 29.09, 29.27, 29.38, 30.74, 30.87, 31.62, 31.70, 121.52, 123.69, 124.21, 125.90, 127.80, 128.02, 130.17, 130.57, 136.48, 136.95, 139.71, 142.48.

Br₂HT₂-I-HT₂ – To a 0 °C solution of HT₂-I-HT (0.50 g, 0.63 mmol) in 40 mL 3 : 1 chloroform : acetic acid (v/v) was added N-bromosuccinimide (0.26 g, 1.5 mmol). After stirring for 2 hours at 0 °C, the mixture was poured into 100 mL water. The combined mixture was extracted with hexane and the organic layer was successively washed with 1 M sodium carbonate, water and brine. After drying over MgSO₄ and evaporation of the solvent, the product was purified via column chromatography (silica gel/hexane) yielding 0.318 g (53%) of a viscous red oil: MS (m/z) (M⁺⁺) 956.5, Calculated: 957.1; ¹H NMR (CDCl₃) δ(ppm): 0.85 (m, 12H), 1.26 (m, 24H), 1.61 (m,
8H), 2.70 (m, 8H), 6.91 (s, 2H), 7.02 (s, 2H), 7.12 (dd, 2H), 7.67 (dd, 2H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) (ppm): 14.07, 14.11, 22.56, 22.62, 29.05, 29.14, 29.17, 29.30, 30.58, 30.82, 31.59, 31.63, 110.43, 121.44, 124.36, 125.74, 128.28, 128.36, 132.05, 132.78, 135.14, 136.99, 140.28, 142.58.

**HT\(_2\)-I-HT\(_3\)** – To a solution of Br\(_2\)HT\(_2\)-I-HT\(_2\) (0.80 g, 0.84 mmol) and 3-hexylthiophene-2-boronic acid pinacol ester (0.55 g, 1.9 mmol) in 30 mL 1:1:1 toluene : ethanol : water (v/v/v) was added tetrakis(triphenylphosphine)palladium(0) (0.21 g, 0.18 mmol) and sodium carbonate (0.19 g, 1.6 mmol). The mixture was refluxed overnight after which the organic layer was evaporated off with a flow of nitrogen. The remainder of the mixture was added to 100 mL of water and was extracted with hexane. The organic layer was dried over MgSO\(_4\) and was evaporated under reduced pressure. The product was purified by column chromatography (silica gel/hexane) yielding 0.81 g (86 %) of a dark red oil: MS (\(m/z\)) (M-H)+ 1131, Calculated: 1132; \(^1\)H NMR (CDCl\(_3\)) \(\delta\) (ppm): 0.88 (m, 18H), 1.32 (m, 36H), 1.67 (m, 12H), 2.70 (t, 4H), 2.18 (m, 8H), 6.95 (m, 4H), 7.14 (m, 6H), 7.72 (dd, 2H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) (ppm): 14.12, 22.58, 22.65, 29.09, 29.24, 29.28, 29.51, 30.59, 30.67, 30.87, 31.62, 31.70, 121.55, 123.63, 124.25, 125.90, 127.84, 128.83, 130.13, 130.39, 130.53, 134.18, 136.16, 136.95, 139.68, 139.88, 142.53.

**Br\(_2\)T-I-T** – To a 0 °C solution of T-I-T (0.50 g, 1.7 mmol) in 40 mL DMF was added drop-wise a solution of N-bromosuccinimide (0.73 g, 4.1 mmol) in 10 mL DMF. The combined solution was stirred at 0 °C for 2 hours after which the solution was added to 200 mL H\(_2\)O. The resulting orange solid was collected, and purified via recrystallization in chloroform/hexane to yield 0.37 g (49 %) of a red powder: MS (\(m/z\)) (M\(^{+}\)) 455.8, Calculated: 456.2; \(^1\)H NMR (CDCl\(_3\)) \(\delta\) (ppm): 7.10 (m, 4H), 7.18 (m, 2H),
7.87 (m, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$(ppm): 121.08, 121.56, 125.15, 125.40, 126.33, 130.80, 133.56, 134.68.

**HT-T-I-T-HT** – To a solution of Br$_2$T-I-T (0.62 g, 1.4 mmol) and 3-hexylthiophene-2-boronic acid pinacol ester (0.91 g, 3.1 mmol) in 30 mL 1:1:1 toluene : ethanol : water (v/v/v) was added tetrakis(triphenylphosphine)palladium(0) (0.35 g, 0.30 mmol) and sodium carbonate (0.32 g, 2.6 mmol). The mixture was refluxed overnight after which the organic layer was evaporated with a flow of nitrogen. The remainder of the mixture was added to 100 mL of water and extracted with hexane. The organic layer was dried over MgSO$_4$ and was evaporated under reduced pressure. The product was purified by column chromatography (silica gel/hexane) yielding 89 mg (11 %) of a dark red oil: MS (m/z) (M-H)$^+$ 630.2, Calculated:631.0; $^1$H NMR (CDCl$_3$) $\delta$(ppm): 0.89 (t, 6H), 1.34 (m, 12H), 1.69 (t, 4H), 2.83 (t, 4H), 6.97 (d, 2H), 7.16 (m, 6H), 7.31 (d, 2H), 7.96 (dd, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$(ppm): 14.14, 22.66, 29.27, 29.39, 30.71, 31.70, 121.71, 123.98, 124.98, 125.70, 126.44, 126.51, 130.20, 130.28, 135.27, 135.35, 139.97.

**General Procedure for the Oxidative Polymerization of the Oligomers** - All of the hexylthiophene containing oligomers were polymerized using the same general method. A solution of the oligomer in chlorobenzene was added drop wise to an approximately four fold excess of iron (III) chloride dispersed in chlorobenzene (final oligomer concentration ~0.03 M). The resulting mixture was stirred at elevated temperatures under a slow nitrogen flow for several days. The resulting mixture was poured into methanol, and the solid was collected. The resulting polymer was de-doped via stirring in aqueous ammonium hydroxide overnight and was purified via successive
Sohxlet extractions with methanol, hexane, and chloroform. Pure polymer was obtained from the chloroform soluble fraction.

\[ p(\text{HT-I-HT}_n) \] – HT-I-HT\(_n\) (0.81, 1.74 mmol) was allowed to react with iron (III) chloride (1.23 g, 7.59 mmol) at 65 °C for 40 hours according to the general procedure yielding 0.32 g of polymer (39 %) as a brown powder.

\[ p(\text{HT}_2\text{-I-HT}_2) \] – HT\(_2\)-I-HT\(_2\) (0.69 g, 0.86 mmol) was polymerized according to the general procedure with iron (III) chloride (0.62 g, 3.7 mmol) at 60 °C for 72 hrs yielding 44.1 mg (12 %) of the polymer as a brown powder.

\[ p(\text{HT}_3\text{-I-HT}_3) \] – HT\(_3\)-I-HT\(_3\) (0.70 g, 0.62 mmol) was allowed to react with iron (III) chloride (0.42 g, 2.5 mmol) at 60 °C for 70 hours according to the general procedure to yield 36 mg (5 %) of the polymer as a brown powder.

\[ p(\text{HT-T-I-T-HT}) \] – HT-T-I-T-HT (40.0 mg, 0.065 mmol) was allowed to react with iron (III) chloride (42.0 mg, 0.25 mmol) at 45 °C for 48 hours according to the general polymerization procedure yielding 44.8 mg of the polymer as a dark purple viscous oil. The excessive yield indicates that some residual iron, or other impurity, remained behind after ammonium hydroxide treatment.

\[ p(\text{T-I-T}) \] – T-I-T was electrochemically polymerized from a saturated solution of the trimer in 0.1 M LiClO\(_4\) in anhydrous acetonitrile. The polymerization was performed under galvanostatic conditions at -1.5 mA of current for 40 minutes. The oxidized polymer was deposited onto an ITO coated glass slide. After the polymerization was complete, the product was dedoped by holding the polymer film at a potential of -600 mV (vs. the Ag/Ag\(^+\) redox couple) until the flow of current stopped. The resulting film was
thoroughly washed in acetonitrile and THF resulting in an insoluble blue film on the surface of the ITO electrode.

3.3 Results and Discussion

3.3.1 Synthesis

Using the T-I-T and HT-I-HT trimers as core moieties, a series of higher order oligomers have been successfully synthesized by successive bromination and Suzuki coupling steps (Figure 24). In general, it was found that the synthesis of the HT-I-HT core materials proceed in much higher yields than those materials built from the T-I-T core. This is due primarily to the difficulty in isolating di-brominated T-I-T.

![Chemical structures and reactions](image)

Figure 24: Synthesis of well-ordered oligomers through successive Suzuki coupling. Due to the lack of substituents and the increased aromaticity of the un-substituted trimer, the bromination tends to proceed in an uncontrolled manner. Because the various
brominated products are chemically similar, it has proven extremely difficult to obtain pure material through any chemical purification technique. This difficulty also affects the synthesis of the higher order T-I-T core oligomers, and has prevented us from obtaining HT₂-T-I-T-HT₂.

The polymerization of these materials leads to a series of well-ordered materials with precisely controlled comonomer incorporation and molecular structure. These materials were polymerized via oxidative polymerization (Figure 25).² ³ For the oligomers containing hexylthiophene groups the polymerization was performed using chemical oxidative polymerization using iron (III) chloride as an oxidant. However, since the polymerization of T-I-T is expected to yield an intractable polymer, it was polymerized directly onto an ITO coated glass slide using galvanostatic electrochemical oxidation.

![Oxidative polymerization of well-ordered oligomers.](image)

Figure 25: Oxidative polymerization of well-ordered oligomers.

The chemical oxidative polymerizations proceed to moderate molecular weights and broad dispersities (Table 3). While oxidative polymerization is suitable for the polymerization of a wide variety of aromatic monomers, there are many drawbacks to its use as a method to synthesize materials for photovoltaics.
Table 3: Molecular weight of the polymers obtained from oxidative polymerization of the oligomers.

<table>
<thead>
<tr>
<th></th>
<th>$M_n$ (g/mol)</th>
<th>$D^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>p(HT-I-HT)</td>
<td>12,400</td>
<td>2.05</td>
</tr>
<tr>
<td>p(HT$_2$I-HT$_2$)</td>
<td>12,500</td>
<td>2.10</td>
</tr>
<tr>
<td>p(HT-T-I-T-HT)</td>
<td>2,300</td>
<td>1.21</td>
</tr>
<tr>
<td>p(HT$_3$I-HT$_3$)</td>
<td>26,200</td>
<td>1.57</td>
</tr>
</tbody>
</table>

* Measured against polystyrene standards using THF GPC

The most obvious of these drawbacks is the difficulty in removing the spent oxidant from the isolated polymer product. This is especially critical to the performance of these materials in electronic devices as the residual iron in the material can create charge traps and otherwise alter the material’s electronic behavior. Thus, care must be taken to fully remove iron contamination from the isolated polymer. Further, as seen with the polymerization of the trimers and oligomers, obtaining high molecular weight polymer from oxidative polymerization can be challenging. Polymerization occurs through the step-growth coupling of radical cations generated by the oxidation of monomer species. The step-growth nature of the polymerization means that high molecular weight polymer can only be obtained at high monomer conversion, but since the growing polymer chains are highly oxidized, in many cases they will lose solubility and precipitate from the reaction mixture before high molecular weight can be achieved. Polymerizations can be pushed toward higher molecular weight products through a variety of methods including performing the reactions under a gentle flow of nitrogen to sweep away the hydrochloric acid generated from the oxidation of the monomer, using more potent oxidants such as antimony (V) chloride, or performing the polymerization at elevated temperature.$^4$ However, care must be taken when attempting these methods to
avoid the formation of a large insoluble fraction in the final product. This insoluble fraction is most likely due to the formation of highly branched or crosslinked polymer chains. The branching is caused by oxidation and radical coupling of the monomer at positions other than the terminal positions, a process which is promoted by elevated temperatures, larger oligomer systems, and increasing oxidant amount and strength. Thus, there is a constant balancing act between maximizing molecular weight while limiting the formation of insoluble material in choosing conditions for these types of polymerizations.

Due to the drawbacks of the oxidative techniques, finding another method of polymerization would be advantageous. One of the most widely used methods for the polymerization of thiophene based materials is Grignard metathesis polymerization (GRIM) (Figure 26). Grignard metathesis polymerization addresses many of the problems inherent to oxidative polymerizations.

**Figure 26:** GRIM polymerization of 3-hexylthiophene.

GRIM uses only a catalytic amount of transition metals (the magnesium salts produced by the reactions of the Grignard reagent being very easy to remove after polymerization) compared to the many-fold excesses of iron needed in oxidative polymerization, removing the need for lengthy purification of the polymer. Further, as GRIM polymerization does not oxidize the monomer, it allows the growing polymer chain to remain in solution throughout the polymerization process and removes the need for de-
doping the final product. Finally, GRIM polymerization has living character which allows materials to be produced with a targeted molecular weight and the easier production of high molecular weight material. The living character of this polymerization technique also allows for more versatility, as a variety of end-functionalization, or block copolymerization chemistries can be employed allowing for the fabrication of well-controlled, complex molecular architectures.5-7

Unfortunately, when the polymerization of the oligomers was attempted through the GRIM mechanism, only low molecular weight products were obtained. Gel permeation chromatography analysis indicated that the GRIM polymerization of HT-I-HT resulted in the coupling of only two or three trimer units. The poor performance of GRIM polymerization for these oligomers can be explained by one of two factors, either the failure in the formation of the Grignard reagent or problems with the nickel catalyzed coupling. This question was studied through proton NMR analysis of a quenched sample from the Grignard exchange reaction prior to the addition of the transition metal catalyst. It was found that the conversion of di-brominated HT-I-HT to the Grignard reagent through an exchange reaction with isopropyl magnesium chloride proceeded to approximately 50%. The high level of residual di-brominated trimer present in the polymerization mixture serves as a chain capping agent, limiting the molecular weight of the final product. The low yields of the Grignard reagent of the trimer persisted regardless of the conditions used. These observations echo findings in the literature where the GRIM method has proven problematic for use with highly conjugated monomers.10
Recently, it has been found that the addition of lithium chloride to the Grignard reagent boosts its reactivity toward Grignard exchange. The increased reactivity of the Grignard reagent in the presence of lithium chloride has been attributed to the breakup of aggregates of the Grignard reagent by the addition of the salt. This method for increasing the efficiency of Grignard exchange reactions has been successfully applied to the GRIM polymerization (a process which has come to be known as Turbo GRIM) of a variety of highly conjugated monomers which have proved unsuitable for conventional GRIM polymerization techniques. Unfortunately, when applied to the polymerization of the HT-I-HT trimer, the same results as with conventional GRIM were obtained.

### 3.3.2 Optical Properties of the Materials

The optical and electronic properties of the oligomers tend to proceed as one would expect. The UV-visible absorption spectra of the oligomers show a pronounced red shift as the size of the oligomers increases (Figure 27). This is simply due to the higher order oligomers allowing for a more conjugated system. A second trend can be seen in the optical properties of the oligomers. It was found that the T-I-T trimer and the T-I-T core pentamer each have significantly lower band gaps than their all hexylthiophene counterparts (Table 4). This finding echoes the results from the trimer systems reported in the previous chapter, and is due to the increased steric interactions in the all hexyl-substituted systems twisting the aromatic system out of planarity.
Table 4: Optical properties of the well-ordered oligomers.

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$E_{g, \text{opt}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT-I-HT_{in}</td>
<td>386</td>
<td>2.6</td>
</tr>
<tr>
<td>T-I-T</td>
<td>450</td>
<td>2.2</td>
</tr>
<tr>
<td>HT$_2$-I-HT$_2$</td>
<td>415</td>
<td>2.3</td>
</tr>
<tr>
<td>HT-T-I-T-HT</td>
<td>460</td>
<td>2.1</td>
</tr>
<tr>
<td>HT$_3$-I-HT$_3$</td>
<td>420</td>
<td>2.2</td>
</tr>
</tbody>
</table>

The UV-visible absorption spectra of the polymers highlight the role that steric and ITN incorporation play in determining the optical properties of the polymer (Figure 28). In the polymeric systems, the effects of oligomer length are removed, and the only influence on the optical properties is the molecular structure of the repeat unit. From the optical properties of the polymers (Table 5), it is clear that the steric of the repeat unit play the most significant role in modulating the band gap, while the ITN content of the material has a relatively minor impact. In fact, all of the polymers based upon the sterically hindered HT-I-HT$_{in}$ trimer display band gaps higher than regioregular poly(3-hexylthiophene) even at the highest level of ITN incorporation. Taken as a series however, we have demonstrated the ability to tune the band gap of semiconducting polymers across a wide range through modulation of the molecular structure of the material.
Figure 27: Normalized absorption spectra of the well-ordered oligomers.
3.3.3 Electronic Properties of the Oligomers and Polymers

The HOMO levels of the oligomers (Table 6) exhibit the expected trend with respect to oligomer length. The decrease in the onset of oxidation with increasing oligomer length is due to the increased conjugation length of the higher order oligomers, the same effect that caused the red shift in the optical absorption spectra. However, in contrast to the optical absorption results, the onset of oxidation seems to be only weakly
influenced by the steric of the oligomer. This result suggests that the steric of the molecule influence the energy of LUMO level almost exclusively.

Table 6: Electrochemical properties of the well-ordered oligomers.

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>Onset of Oxidation (mV)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_{g, \text{opt}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT-I-HT$_{in}$</td>
<td>470</td>
<td>-5.1</td>
<td>-2.5</td>
<td>2.6</td>
</tr>
<tr>
<td>T-I-T</td>
<td>480</td>
<td>-5.1</td>
<td>-2.9</td>
<td>2.2</td>
</tr>
<tr>
<td>HT$_2$-I-HT$_2$</td>
<td>324</td>
<td>-5.0</td>
<td>-2.7</td>
<td>2.3</td>
</tr>
<tr>
<td>HT-T-I-T-HT</td>
<td>290</td>
<td>-5.0</td>
<td>-2.9</td>
<td>2.1</td>
</tr>
<tr>
<td>HT$_3$-I-HT$_3$</td>
<td>332</td>
<td>-5.0</td>
<td>-2.8</td>
<td>2.2</td>
</tr>
</tbody>
</table>

The electrochemical properties of the polymers (Table 7), show the effect that ITN incorporation has on the energy levels of the materials. The effect of ITN incorporation is more prevalent in the systems containing all hexyl functionalized thiophenes where there is significant variation in the location of the energy levels of $p$(HT-I-HT$_{in}$), $p$(HT$_2$-I-HT$_2$), and $p$(HT$_3$-I-HT$_3$). In the T-I-T based polymers however, the HOMO level is unaffected by the decrease in ITN content between $p$(T-I-T) and $p$(HT-T-I-T-HT), possibly showing that the electron density in the HOMO levels of the T-I-T based polymers is primarily located around the central trimer unit.

Table 7: Electrochemical properties of the polymers.

<table>
<thead>
<tr>
<th>ITN Content</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_{g, \text{opt}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$(T-I-T)</td>
<td>33 mol %</td>
<td>-4.97</td>
<td>-3.25</td>
</tr>
<tr>
<td>$p$(HT-T-I-T-HT)</td>
<td>20 mol %</td>
<td>-4.98</td>
<td>-3.15</td>
</tr>
<tr>
<td>$p$(HT-I-HT$_{in}$)</td>
<td>33 mol %</td>
<td>-4.92</td>
<td>-2.80</td>
</tr>
<tr>
<td>$p$((HT)$_2$-I-(HT)$_2$)</td>
<td>20 mol %</td>
<td>-5.35</td>
<td>-3.15</td>
</tr>
<tr>
<td>$p$((HT)$_3$-I-(HT)$_3$)</td>
<td>14 mol %</td>
<td>-5.28</td>
<td>-3.05</td>
</tr>
</tbody>
</table>
Unfortunately, the low molecular weights obtained through the oxidative polymerization of the oligomers made it impossible to obtain good, defect free, thin films of the polymers. Thus, we were unable to fabricate photovoltaic devices with these materials. However, their performance in a photovoltaic cell can be estimated using the optical and electrochemical properties of the polymers (Figure 29). In a photovoltaic system with PCBM as the n-type semiconductor, these materials are expected to yield energy conversion efficiencies between 2 % and 4 %. The low expected efficiencies are due to the high LUMO levels found in these materials. If the LUMO level of these materials could be lowered, which could be accomplished by increasing the conjugation across the polymer backbone, while leaving the band gap unaffected higher efficiencies would be expected.

Figure 129: Estimated photovoltaic efficiency of the polymers (adapted from Ref. 13).
3.4 Conclusions

This chapter describes the synthesis and characterization of a sequence of well-defined oligomers and copolymers based on the HT-I-HT
 and T-I-T trimers studied in the previous chapter. The oligomers were successfully synthesized through successive bromination and transition metal catalyzed aromatic coupling, overcoming the difficulties with the purification of the T-I-T based products. While the oligomers proved resistant to several polymerization techniques, polymers were obtained through oxidative polymerization using ferric chloride. The absorption spectra of the polymers obtained through the oxidative polymerization of the oligomers span a large portion of the visible spectrum and demonstrates systematic tuning of the band gap across ~0.5 eV. Unfortunately the materials produced through this method were unsuited to the production of photovoltaic cells due to their low molecular weight and poor film formation properties. Based on the optical and electrochemical properties of the materials their photovoltaic performance can be estimated to be between 2 % to 4 % power conversion efficiency when paired with PCBM. In order to reach higher device efficiencies, the LUMO level of the p-type material must be shifted to lower energy while keeping the band gap of the polymer low. Such shifts in the LUMO level can be affected by the synthesis of polymeric structures with increased conjugation along the backbone. Preliminary efforts into the synthesis and characterization of ITN based materials meeting these criteria are described in the next chapter.


CHAPTER 4
SYNTHESIS AND CHARACTERIZATION OF ISOTHIANAPHTHENE DYAD
CONTAINNING MATERIALS

4.1 Introduction

Throughout the course of this dissertation all of the materials studied have been, or have been based upon trimers. These trimers all consist of a central unit, either thiophene or one of two electron donating moieties (Tt8 or ITN), flanked by two thiophene or hexylthiophene rings. While these systems allow for the synthesis of well-defined polymeric structures with tunable band gaps, there are several disadvantages inherent in this geometry. The first of these disadvantages is simply that it imposes an upper limit of 33 % on the molar incorporation of the central low band gap moiety. While the molar incorporation of the electron donating unit can be easily diluted through appending hexylthiophene units to the ends of the trimers, there is no simple method by which additional units of the central moiety can be included in the material. The second limitation of the use of trimers as the basis for the materials is that the resulting materials are locked into an alternating morphology. The polymers alternate between the electron donating moiety and thiophene lengths of one to three units.

The simplest method to overcome these limitations is to change the structure of the central building block unit. In this chapter, preliminary efforts to develop materials based on tetramers consisting of an ITN dyad core flanked by two hexylthiophene moieties (Figure 30). This oligomer has an ITN incorporation of 50 % and the two adjacent electron donating units should work synergistically to increase the conjugation across the oligomer and depress the LUMO level of the resulting materials. As seen in
the previous chapter, lowering the LUMO level of the polymer should yield higher photovoltaic efficiencies.

![Chemical structure of the ITN dyad containing tetramer.](image)

**Figure 30:** Chemical structure of the ITN dyad containing tetramer.

Because of the instability of the ITN monomer, the tetramers will be synthesized through a similar method used in the synthesis of the ITN core trimers. The first synthetic route which was attempted mimics exactly the synthesis of the HT-I-HT$_{in}$ trimer (Figure 31). While the di-phthalic acid could be easily obtained in moderate yield, the di-acid chloride could not be readily obtained. In order to avoid the need to proceed through the acid chloride route, the direct reaction of the Grignard reagent of 3-hexylthiophene with 3,3’-diphthalide was used to generate the intermediate needed for the ring closing via Lawesson’s reagent (Figure 32). In this way, the desired ITN dyad structure can be obtained without the need to synthesize, isolate, and functionalize ITN.
4.2 Experimental

**General**—Tetrahydrofuran was distilled over sodium/benzophenone. All other reagents were purchased from commercial sources and were used as received. All reactions were carried out under an inert nitrogen atmosphere using degassed solvents.
**Instrumentation** – $^1$H and $^{13}$C NMR spectra were recorded on an Advance DPX-300 spectrometer. Cyclic voltammograms of the oligomer were obtained on a BASi-EC epsilon potentiostat against an Ag/Ag$^+$ (0.1 M AgNO$_3$ in acetonitrile) reference electrode using gold working electrodes at a scan rate of 100 mV/s. Samples were prepared as saturated solutions in 0.1 M LiClO$_4$ in anhydrous, nitrogen saturated acetonitrile. All potentials are reported versus the ferrocene redox couple. Absorption spectra were obtained in hexane or chloroform using a Perkin-Elmer Lambda 850 spectrometer. Band gaps were calculated from the onset of absorption. The HOMO levels of the materials were found from the onset of the oxidation wave obtained by cyclic voltammetry taking into account the ferrocene redox couple at -4.8 eV. LUMO levels were calculated from the HOMO levels and the optical band gap since reduction waves were not observed.

**3,3' Diphthalide** – Phthalic anhydride (15.02 g, 101.4 mmol) was slowly added to a stirred mixture of anhydrous calcium chloride (11.51 g, 103.7 mmol) and zinc powder (4.59 g, 70.2 mmol) dispersed in 100 mL of 1:1 THF/water. The resulting mixture was stirred for two hours at room temperature resulting in the formation of a white precipitate. The bulk of the precipitate was dissolved by the addition of 2 M aqueous hydrochloric acid and the remaining solid was removed by filtration. Additional hydrochloric acid was added to the resulting solution to precipitate 10.29 g (72 %) of the product as a white solid.³

Sodium borohydride (1.76 g, 46.5 mmol) was slowly added to a mixture of this product (3.14 g, 11.1 mmol) in 50 mL of 2:5 THF/EtOH (v:v) at 0 °C. After the addition of the sodium borohydride, the mixture was heated to reflux and was stirred overnight. The resulting orange solution was poured into 300 mL of ice water which was then
acidified to pH 2 by the addition of 10 % hydrochloric acid. The acidified solution was stirred for 30 minutes and the resulting solid was collected via filtration. Recrystallization from acetic acid yielded 0.54 g (18 % yield) of the product as a pale yellow powder: MS (m/z) (M+•) 266.0, Calculated: 266.3; 1H NMR (CD3COOD) δ (ppm): 5.92 (s, 2H), 6.13 (s, 2H), 7.11 (d, 2H), 7.45 (m, 2H), 7.59 (m, 8H), 7.75 (d, 2H), 7.86 (d, 2H); 13C NMR (CD3COOD) δ (ppm): 67.33, 80.29, 122.2, 122.69, 125.84, 126.33, 129.96, 145.27.

HT-I-I-HT – To a mixture of iodine activated magnesium (0.25 g, 10.4 mmol) in 50 mL freshly distilled THF was added 2-bromo-3-hexylthiophene (1.20 g, 4.8 mmol). The resulting mixture was stirred at room temperature for 2.5 hours after which a mixture of 3,3’ diphthalide (0.50 g, 1.9 mmol) in 10 mL THF was slowly added. The reaction was quenched in 0.1 M aqueous ammonium chloride after 30 minutes. The resulting solution was extracted with dichloromethane. The organic layer was reacted with Lawesson’s reagent (0.81 g, 2.0 mmol) at room temperature overnight. The solvent was removed and the residue was refluxed in ethanol for 30 minutes. The ethanol solution was poured into 100 mL water and the mixture was extracted with diethyl ether. The organic layer was washed with 1 M sodium bicarbonate, water, brine and was dried with magnesium sulfate. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel/hexane) yielding 18 mg (1.6 % yield) of the product as a red oil: MS (m/z) (M+•) 598.1, Calculated: 598.9; 1H NMR (CDCl3) δ (ppm): 0.80 (t, 6H), 1.22 (m, 12H), 1.61 (t, 4H), 2.70 (t, 4H), 7.12 (m, 6H), 7.44 (d, 2H), 7.62 (m, 2H), 7.87 (m, 2H); 13C NMR (CDCl3) δ (ppm): 14.08, 22.57, 29.06, 29.15, 30.92, 31.59, 121.57, 121.69, 124.46, 124.56, 126.09, 129.39, 136.07, 137.59, 142.55.
4.3 Results and Discussion

4.3.1 Synthesis

HT-I-I-HT was successfully synthesized, albeit in low yield, through the reaction of Lawesson’s reagent with the product from the ring-opening of 3,3’ diphthalide with the Grignard reagent derived from 2-bromo-3-hexylthiophene. The low yield of this reaction is likely due to impurities in the 3,3’ diphthalide starting material. This starting material proved to be very difficult to synthesize and purify. A variety of synthetic techniques were attempted including radical coupling of phthalide, and the radical coupling and ring closure of phthalaldehyde before a successful synthetic route was found. 3,3’ Diphthalide was synthesized in good yield through a two step process starting from phthalic anhydride. Unfortunately, since the compound is insoluble in most common organic solvents, the only suitable purification technique was recrystallization in acetic acid. The low solubility also makes analysis of the product difficult, possibly allowing for impurities to be carried along to the reaction with the Grignard reagent.

The low yield of HT-I-I-HT made it impossible to obtain enough material to perform chemical oxidative polymerization. Further, the tetramer proved unsuitable for electrochemical polymerization since the oxidized material did not deposit on the working electrode. Thus, the polymer could not be obtained. In order for polymer to be obtained, a new synthetic method must be developed.

There are several possible avenues toward a new method for the synthesis of HT-I-I-HT. First, 3,3’ diphthalide can be synthesized from the reaction of lithiated hydrobenzoin with carbon dioxide. This reaction has been reported to proceed in
relatively high yield and with no special purification difficulties. Further investigations into the various radical coupling routes to diphthalide may yield a cleaner product, if an appropriate radical source can be found. Also, it may be possible to reach the desired oligomer through activation of di-phthalic acid with the proper reagent. Finally, if none of these methods bear fruit, direct synthesis, functionalization, and coupling of ITN could be used yield the desired structure.

4.3.2 Characterization of the Oligomer

The optical absorption spectrum of the oligomer shows a dramatic red shift from the HT-I-HT$_{in}$ trimer (Figure 33). The optical band gap of the tetramer is 2.21 eV which is 0.41 eV lower than HT-I-HT$_{in}$. While some of this red shift is simply due to the lengthening of the oligomer from a trimer to a tetramer, the fact that HT-I-I-HT tetramer has a lower band gap and higher absorption maximum than the longer HT$_2$-I-HT$_2$ pentamer demonstrates that the incorporation of the ITN dyad is effective at increasing the conjugation across the oligomer and lowering the band gap.

Figure 33: Optical absorption spectrum of HT-I-I-HT.
The HOMO level of the ITN dyad containing tetramer was determined from the electrochemical onset of oxidation to be at an energy level of -4.9 eV. Since no reduction wave was observed, the LUMO level was calculated from the HOMO level and the optical band gap of the material to be at an energy of -2.7 eV. Comparing these values to those obtained from the HT-I-HT_in trimer shows that the HOMO level increases in energy while the LUMO level decreases (Figure 34). These results are consistent with the increased conjugation caused by the incorporation of the ITN dyad and the lengthening of the oligomer.

![Graph showing energy levels of HT-I-I-HT and HT-I-HT_in oligomers](image)

Figure 34: Comparison of the HOMO/LUMO levels of the HT-I-I-HT and HT-I-HT_in oligomers.

### 4.4 Conclusions

While the study of the trimers and the trimer based materials has given insight into the effects various factors play in determining the optical and electronic properties of organic semiconducting materials, the trimer architecture has several drawbacks. In an effort to engineer materials which avoid these drawbacks, a tetramer containing an ITN dyad flanked by two hexylthiophene units was synthesized. The synthesis was
accomplished through great difficulty and in very low yield. Because of the difficulty in the synthesis of the tetramer, the polymerization of the oligomer could not be performed. The optical and electrochemical characterization of the tetramer shows a decrease in the band gap and shifts in the HOMO and LUMO levels relative to the trimer based materials previously studied consistent with the increased conjugation afforded by the ITN dyad structure. While these structures show promise for use in photovoltaic devices, a new synthetic strategy must be found in order to generate useable quantities of material.


CHAPTER 5
SUMMARY AND FUTURE WORK

5.1 Summary

Solar derived electricity has great potential as a large scale source of alternative energy. Unfortunately, while silicon based photovoltaic cells have made great strides in increasing power conversion efficiency over the past several decades, solar derived power is still too expensive to compete with traditional power generation techniques.\(^1\) Solar cells fabricated using organic materials show promise for widespread use as they have the potential for low cost, high area fabrication through processing techniques such as roll-to-roll processing and inkjet printing. While many materials have been studied in organic photovoltaics, the efficiency of these devices remains low. In order to optimize the performance of these devices, a wide range of factors across many length scales need to be optimized. Through the synthesis of a series of materials with a tunable band gap, but similar chemical structure and physical properties, the effect of altering the electronic structure of the p-type semiconductor on the efficiency of a photovoltaic device can be isolated from the other factors influencing the efficiency of the device. In this way, the electronic structure of the semiconducting polymer can be optimized, opening the door to the development of higher efficiency organic photovoltaic cells. This work details the development of a methodology for the synthesis of this class of well-defined materials.

In order to better understand the factors which affect the optical and electronic properties of semiconducting polymers, a series of well-defined trimers were synthesized and characterized (both experimentally and computationally). The central unit of the trimers was varied between thiophene and one of two electron donating moieties, ITN or
This unit was sandwiched between two thiophene units which were varied between unsubstituted thiophene and hexylthiophene with the hexyl groups orientated toward, or away from, the central unit. In this way, three sets of three oligomers were designed in order to give insight into the role that the electronic and steric structure of the molecule has on the material’s optical and electronic properties. From this, several trends became evident, namely that the incorporation of an electron donating unit into the trimer does cause dramatic lowering of the band gap and that steric interactions between the bulky central units (ITN and Tt8) and the hexyl chains on the flanking thiophene units play a large role in determining the final properties of the material. These trends are also seen in the computational results, where the structures of HT-I-HT_{in} and HT-Tt8-HT_{in} trimers show higher distortions from planarity than what is calculated for the other trimers. Further, the computed band gaps and HOMO levels of the trimers match closely with the experimental results. This close agreement between experimental and computational results illustrates a powerful synergy between experimental and computational chemistry which can be leveraged as a means for the rapid evaluation of proposed materials for use in photovoltaic cells.

Using the insights into the factors which affect the optical and electronic structure of semiconducting polymers gained in the evaluation of the trimers, a series of well-defined copolymers with tunable band gaps were synthesized. These polymers were synthesized through the polymerization of a series of oligomers built from the HT-I-HT_{in} and T-I-T trimers. The trimers were successively built into pentamers and heptamers by the successive bromination and Suzuki coupling reactions to append hexylthiophene units to the end of the preceding oligomer generation. The optical properties of the oligomers
show expected red shifts with increasing oligomer length and in the trimer and pentamer derived from T-I-T. Oxidative polymerization of the oligomers yielded low molecular weight materials which proved unsuitable for testing in a photovoltaic cell due to their poor film forming ability. The optical and electronic properties of the materials show that the band gap can be tuned over a range of ~0.5 eV, and once again demonstrates the importance that steric interactions have on the properties of the material, as the polymers derived from the T-I-T trimer have significantly lower band gaps than the HT-I-HT\textsubscript{in} based materials. While the materials proved to be unsuitable for testing in a photovoltaic device, their performance can be estimated from the optical band gap and the results of the electrochemical characterization. From these results, the polymers should yield device efficiencies of less than 4 % due, in large part, to their high LUMO levels.

In order to obtain materials with lower LUMO levels and in order to gain access to polymer structures other than alternating copolymers, oligomers containing an ITN dyad were synthesized. Unfortunately, the synthetic route to this oligomer is very difficult, proceeding in only very low yield. Due to these difficulties, the oligomer could not be obtained in sufficient quantities to allow for polymerization. The tetramer exhibited a lower band gap and LUMO level than HT-I-HT\textsubscript{in}, indicating that ITN dyad containing materials may be excellent candidates for photovoltaic materials.

5.2 Future Work

This work has focused on the development of a methodology for the optimization of the electronic structure of the p-type semiconductor in a photovoltaic cell. In the short term, the work can be pushed forward in a variety of ways. The nine trimers studied in the first portion of the work can be polymerized and the polymers characterized.
Through this, the effects of sterics and electronic structure on the properties of the polymeric material can be further studied as can the shift in properties which occurs during the polymerization process. Further, the computational studies can be extended to these polymeric systems to develop a computational methodology which can provide accurate predictions of the properties of the polymer. Better polymerization methods must be found for the oligomers. Oxidative polymerization through the use of iron (III) chloride, while sufficient for the generation of materials for characterization, has been insufficient at yielding materials suitable for use in photovoltaic devices. Once materials of higher molecular weight have been obtained, their performance in photovoltaic devices can be determined. Finally, a better synthesis of the ITN dyad containing tetramer should be found, allowing for the polymer to be obtained. Once the polymer has been synthesized, this promising material can be tested in photovoltaic devices.

In the long term, this methodology can be extended in a variety of ways. The synthesis of well-defined oligomers and polymers can be applied to any number of monomers, allowing for materials with a wide range of optical and electronic properties to be obtained. Also, the oligomers can be further copolymerized with other electron donating or withdrawing moieties to fine tune the electronic properties of the materials. Through this, the electronic structure of the semiconducting polymer can be optimized. Once the optimal p-type material has been found, the other factors which influence the efficiency of a photovoltaic device can be studied and optimized in turn allowing for the eventual production of high efficiency organic photovoltaic devices.
APPENDIX

ANALYSIS OF CYCLIC VOLTAMMOGRAMS

Figure 35: Cyclic voltammograms of the series of thiophene core trimers.

Figure 36: Cyclic voltammograms of selected ITN core well-defined polymers.
Cyclic voltammograms of the oligomer were obtained on a BASi-EC epsilon potentiostat against an Ag/Ag\(^+\) (0.1 M AgNO\(_3\) in acetonitrile) reference electrode using gold working electrodes at a scan rate of 100 mV/s. Samples were prepared as saturated solutions in 0.1 M LiClO\(_4\) in anhydrous, nitrogen saturated acetonitrile. All of the potentials and cyclic voltammograms are reported versus the ferrocene redox couple. Oxidation onsets were determined from the intersection of two best-fit lines. One of these lines was drawn through several points along the baseline of the voltammograms and the other was drawn through several points along the initial portion of the oxidation wave. The HOMO levels were calculated from the oxidation onset potentials by comparison to the ferrocene redox level of -4.8 eV.


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