Design and Application of Organic Electronic Materials: Pendant Tuning in Polymeric and Molecular Systems

Jonathan S. Tinkham

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DESIGN AND APPLICATION OF ORGANIC ELECTRONIC MATERIALS:
PENDANT TUNING IN POLYMERIC AND MOLECULAR SYSTEMS

A Dissertation Presented

by

JONATHAN TINKHAM

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

DOCTOR OF PHILOSOPHY

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Department of Chemistry
DESIGN AND APPLICATION OF ORGANIC ELECTRONIC MATERIALS:
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To my bear
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It has been a long journey, and would not be possible without the people in my life. My family, friends, and of course my fiance.
Designing and synthesizing materials for use in organic electronic materials requires fine control over their optical and electronic properties. Variations through substitution can be used to tune solubility and electronic properties, but this can result in degradation of other properties. Substitution with orthogonal pendant groups in both molecular and polymeric systems has the potential for allowing tunability while decreasing the perturbation of other desirable properties of the parent system.

This idea was explored through experimental and computational work. Computational modeling was used to understand and predict the properties of molecular and polymeric systems to narrow the wide number of choices of possible materials. The ability to computationally predict not just molecular orbital energy levels, but other properties of the system such as UV-Vis transitions, unpaired spin-density, and changes in dipole moment is important not just for designing new materials, but in understanding how they work. This is accomplished in modeling a modular approach to tuning of frontier orbital energy levels. Newer strategies for predicting photovoltaic performance by analysis of the ground-to-excited state dipole moment change are also explored.

A series of low-bandgap polymers absorbing at a bandgap of 1.7 eV, near the “ideal” bandgap of 1.5 eV, were prepared by copolymerizing an electron-donating and electron-withdrawing unit to yield a low-bandgap “push-pull” copolymer. The donor unit was designed to study the effect of pendant phenyl substitution. The resulting copolymers were
oligomeric in nature, but devices prepared using these copolymers gave very promising photovoltaic power conversion efficiencies up to 5%. The influence of a pendant phenyl unit in the copolymers yielded a system with increased order in the solid state, and decent performance.

Design and synthesis of new materials through pendant tuning was shown to be a viable strategy for developing new organic electronic materials, and methods to explore this for new materials were established.
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CHAPTER 1
INTRODUCTION AND BACKGROUND

1.1 Introduction

With a few exceptions, almost all energy on earth’s surface can be traced back to solar irradiation. Most usable energy sources are a by-product of solar irradiation: either by thermal heating, such as hydroelectric and wind, or by photosynthetic behavior, such as biomass and fossil fuels. Photovoltaics allows the direct harvesting of sunlight as electricity, without using indirect processes. Harvesting at a modest 12% efficiency over just 2% of the Earth’s land surface would generate enough power to completely supply global projected energy demands for 2050.¹ Silicon solar cells are presently the dominant technology in photovoltaics. Monocrystalline silicon solar cells currently can provide the second highest efficiency for single-junction devices at 27.2%—very close to the theoretical limit of 30% (the Shockley-Quessier limit).¹ However, making monocrystalline devices is an expensive and energy-intensive process. Cheaper polycrystalline and amorphous silicon devices are now widely available, with performance ranging from 13-20%¹ (Figure 1.1). The past decade has seen a sharp increase in production of these devices that has dramatically driven down their cost and made them much more readily available.

However, one of the problems with these devices is their production requires the preparation and cutting of silicon wafers that, even with amorphous and polycrystalline materials, is a wasteful process, both in energy and silicon dust from the wafer preparation. The final silicon wafers are also very sensitive and brittle, and require heavy and rigid support scaffolding to protect them. These issues restrict a silicon-based photovoltaic device to be only truly useful as a static, planar array collection unit, usually in a large series of similar devices.
1.2 Organic Photovoltaics

Organic semiconductors are a large class of materials with greatly varied and fascinating optical and electronic properties. Semiconducting behavior in organic molecular and polymeric materials can be achieved by conjugation and delocalization of molecular orbitals, leading to band-like properties. Organic molecular band structure is largely a product of the “single-unit” electronic structure, but can also be influenced by other factors including (but not limited to): intrachain conformation, interchain interactions (such as pi-pi stacking), surface/interfacial interactions, and inter-unit complex formation (such as a charge-transfer complex). Nearly all of these can vary greatly by what morphology the molecules or polymer chains adopt. Designing new materials for photovoltaic applications therefore requires considering both the electronic structure and materials’ morphology.

Production of organic photovoltaics (OPVs) has the potential to achieve greatly increased scope for solar energy harvesting by allowing use of bulk preparation methods presently unsuited for solar cell production, such as roll-to-roll processing and vapor deposition. More importantly, OPV devices prepared on flexible substrates are lightweight plastic materials that can be bent, folded, and prepared in a wide variety of applications not feasible for
heavy and rigid silicon devices. Organic semiconductor deposition through spray-coating techniques has already resulted in OPV devices with comparable performance to traditional OPV devices. Further improvements in deposition techniques could one day give the ability to spray a photovoltaic “paint” on any exposed surface. These properties would allow greatly reduced production cost along with filling in niche applications and domains inaccessible by silicon devices.

1.2.1 Photovoltaic Principles of Operation

Figure 1.2: Schematic showing the overall operation of a photovoltaic cell. 1) absorption of light to generate exciton, 2) diffusion of exciton to interface, 3) charge-transfer of electron to acceptor material, and 4) charge-separation, and diffusion of free charge-carriers to be extracted by electrodes. Reproduced from Ref. [4] with permission from The Royal Society of Chemistry.

An interface between a p-type and n-type material can be used to produce a photovoltaic effect in organic electronic materials, analogously to the effect in inorganic systems, and shown schematically in Figure 1.2. Illumination leads to excitation of the active materials, moving an electron to an upper energy level. The electron and remaining hole vacancy are tightly bound and behave as a single unit, dubbed an exciton. The exciton can – at the cost of a surmounting some energy barrier – diffuse through the material, with the diffusion length controlled by the lifetime of the exciton before electron-hole recombination occurs. In organic materials, where the dielectric constant is low, the exciton lifetime is short and the diffusion length of typical materials is widely believed to be around 10 nm. If the exciton is able to diffuse to the p-n junction, the energetic offset between materials
results in charge-transfer from p- to n-type material. The exciton is thereby split, although the electron and hole are still coulombically bound, and require overcoming this barrier to undergo charge-separation and become free charge-carriers that are able to diffuse to the electrodes. At the electrodes, charge-extraction occurs and electrical work can be carried out. A state diagram of this process is shown in Figure 1.6 and discussed further below.

While the operating principles are well understood, overall it is a complicated process that still is under investigation. This description only highlights the importance of the electronics, and does not convey the importance of the morphology.

1.2.2 Electronic Properties and Performance Metrics in Photovoltaic Devices

![Image of a current-voltage (I-V) curve denoting open-circuit voltage (V\text{oc}), short-circuit current (J\text{sc}), and the maximum power point (M_{pp}). Reproduced from Ref. [8] with permission from the PCCP Owner Societies.](image)

\[ \text{FF} = \frac{V_m \times J_m}{V_{OC} \times J_{SC}} \]

**Figure 1.3:** Example of a current-voltage (I-V) curve denoting open-circuit voltage (V\text{oc}), short-circuit current (J\text{sc}), and the maximum power point (M_{pp}). Reproduced from Ref. [8] with permission from the PCCP Owner Societies.

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The foremost metric used to measure the performance of an OPV device is the conversion efficiency (\(\eta\), %). This is the percentage of incident photon power converted to electrical power, assuming a standard AM1.5G solar source. Since electrical power is the product of current and voltage (\(I \times V\)), the output characteristics of a cell can be determined by
analyzing its current-voltage \((I-V)\) curve (example shown in Figure 1.3), both with and without illumination. Measuring the current of a device under illumination while scanning an applied bias shows performance under varying loads and deviations from ideal behavior. The three performance metrics most commonly reported are open-circuit voltage \((V_{oc})\), short-circuit current \((J_{sc})\) and fill-factor (FF), which can be determined from an \(I-V\) curve (Figure 1.3).

\(J_{sc}\) is the maximum current generated and is related to successful extraction of charge carriers from photons. \(V_{oc}\) is the maximum operating potential, and is related to the energetic offset of the electron- and hole-transporting materials (shown in Figure 1.5b). Fill-factor is the ratio of maximum power output \((M_{pp})\) to the maximum theoretical power output \((V_{oc} \times J_{sc})\). The magnitude of fill-factor and the shape of the \(I-V\) curve relate to many different loss mechanisms in the final device and is a more complex, though useful, metric.

1.2.3 Bulk-Heterojunction Phase Morphologies

The low-dielectric constant of organic materials causes an exciton to be short-lived and tightly-bound, resulting in a short diffusion length of about 10 nm.\(^6,7\) Any excitons formed farther than this from an interface will recombine with resultant loss of photocurrent. Preparation of thin bilayers (such as in Figure 1.4b) enable all excitons to reach the interface, but these thinner films absorb less light and therefore yield less photocurrent. Thicker films are needed for typical organic materials to harvest enough light to be efficient. A nanosstructured material with domains on the order of the exciton diffusion length would be ideal (such as those in Figure 1.4c-d), but control of the morphology on this length scale without degrading other device parameters remains very difficult, and typically adhoc for each new material. By far, the most popular and effective method for generating the desired nanoscale morphology has been to exploit the solubility differences of the donor and acceptor materials to generate a bulk heterojunction (BHJ) through phase separation\(^9\) (Figure 1.4c). Dissolving the materials in solvent and casting the film will result in phase separation of the two materials upon solvent evaporation. Careful tuning of these conditions may result in highly branched, networked, phase-separated morphology with size features on the order of the exciton diffusion length. Once proper conditions are established, this is can be (but not
necessarily!) a relatively easy method to prepare high performing devices.

Figure 1.4: Examples of device architectures for organic photovoltaic devices. (a) single-layer PV cell, (b) bilayer PV cell, (c) disordered bulk heterojunction, (d) ordered bulk heterojunction. Reprinted with permission from [10]. Copyright 2015 American Chemical Society.

Annealing an “as-spin-coated” phase, either with solvent or heat, can increase phase separation and induce nanoscale crystallization as well. Increasing the crystallinity of the phases can increase charge-carrier mobility and thus ability of charge-carriers to reach the electrodes. The increased phase separation will also decrease the surface area of the interface. While a large surface area will increase the photocurrent, a smaller interfacial surface area will be decrease charge-recombination.\textsuperscript{11}

However, excessive phase separation will result in domains that are too large and result in recombination of the excitons before they reach a phase boundary. The phase separation is highly dependent on processing variables that differ from material to material (and in polymers, can differ from batch to batch). Device preparation from new materials needs to be optimized to find conditions that will generate an effective morphology, and there are no significant structure property relationships to predict these optimal conditions. The phase separation often cannot be confidently controlled and may or may not be stable over time.

The BHJ architecture also may form isolated domains that do not connect to any electrode. These isolated domains would function as charge-traps. Upon continued operation, these domains will accumulate charges that will cause increased series resistance in the device, decreased charge-separation and thus reduced photocurrent.\textsuperscript{11}
1.2.4 Design Considerations for Optimal Organic Photovoltaic Materials

Given common manufacturing techniques, it is thought that power conversion efficiencies over 10% would make OPVs economically competitive. Recent advances have come close to achieving this, with devices claimed by Heliatek to have exceeded the 10% mark. However, scaling from small test devices to large scale manufacturing is not a simple process. This is in part due to the batch to batch variations that typically occur in polymeric systems, giving variation in molecular weight, size dispersity and varying presence of defects, regioregular or otherwise. Molecular systems, as opposed to polymeric, do not suffer the same batch-to-batch variations since they have well-defined structures and are more easily purified into a single well-defined material. However, such well-defined structures and low molecular weight make these materials more crystalline solid than plastic and prove difficult for cheap and easy processing into effective device morphology. Proper molecular design and engineering is capable of overcoming these limitations and much progress has been made recently, but each new promising material requires a great deal of effort to optimize.

Figure 1.5: Origin of photocurrent and $V_{oc}$ in organic photovoltaics. a) Chart of solar flux, and associated photocurrent of material as a function of bandgap ($E_g$). Generated using equation for $J_{sc}$. b) Energy level diagrams showing origin of maximum $V_{oc}$, with loss from exciton splitting ($\Delta LUMO$).

For single-junction devices, optimal active-layer materials share some basic characteristics. One of the biggest improvements in OPVs has been the development of low-bandgap materials. Photons of energy below the bandgap will not be absorbed, while most pho-
tons above the bandgap will be absorbed and excite the material to higher excited states.
Decreasing the bandgap would increase the range of photon energies able to be absorbed,
and increase coverage of the solar spectrum, which will increase the photocurrent of the final
device. This relationship is shown in Figure 1.5.

Lowering $E_{\text{LUMO}}^{\text{donor}}$ will increase photocurrent by decreasing the bandgap, but the
$E_{\text{LUMO}}^{\text{donor}}, E_{\text{LUMO}}^{\text{acceptor}}$ offset ($\Delta$LUMO in Figure 1.5b) must remain large enough to split the
exciton. For organic materials, where the exciton is tightly bound, this is typically
thought to be around 0.3 eV,\textsuperscript{15} but can be lower.\textsuperscript{18} Lowering the bandgap by raising $E_{\text{HOMO}}^{\text{donor}}$
will also increase photocurrent, but this has diminishing returns as it also decreases the
$E_{\text{HOMO}}^{\text{donor}}, E_{\text{LUMO}}^{\text{acceptor}}$ difference, which is proportional to the maximum $V_{oc}$. Any higher energy
photons that are absorbed will lose the excess potential energy by thermal relaxation to the
lower excited states, so this becomes an optimization problem. The point with the largest
power output is called the Shockley-Queisser limit, and in organic materials yields an “ideal”
bandgap around 1.5 ev.\textsuperscript{15}

The tunability of organic materials through synthetic modification gives them tremen-
dous potential. Aside from optimization of energy levels for single-junction cells, the wealth
of synthetic modifications that can tune optical and electronic properties also make organ-
ics ideal candidates for other reasons, such as color control (a result of bandgap control).
Color control is not only useful for aesthetics, but also makes them desirable to improve
existing solar cells, for example in tandem devices with silicon cells. Adding absorption
from an organic material, tuned with a larger bandgap, in a tandem setup would have the
ability to harness more energy of these short-wavelength photons and increase power out-
put when working in series, due to voltage addition.\textsuperscript{15,19} In organic tandem photovoltaics,
photoconversion efficiencies over 10% have already been achieved.\textsuperscript{20,21}

An important additional prospect from organic material tunability is to design materials
to reduce various losses seen in photovoltaic cells. For example, the loss in photocurrent
from exciton- and charge-recombination,\textsuperscript{22} and the loss in $V_{oc}$ from coulombic attraction
of separated charge carriers in the charge-transfer state.\textsuperscript{23–25} These loss-mechanisms are
typically described through the short and shunt resistance of the equivalent circuit, which
can also have various device and morphological origins.\textsuperscript{8}
Unbalanced charge-carrier mobility also harms performance. Ideally, an active layer with a very rapid charge-carrier mobility is desired; as electrons move out, the resulting holes are neutralized by electron in-flow to regenerate the ground state and allow absorption of the next photon, generating more photocurrent. However if one phase of the active layer has a different mobility than the other, the electron out-flow will not be properly balanced by the electron in-flow, and the result will be charge-buildup and performance degradation over time.\textsuperscript{26}

1.2.4.1 Interfaces, Charge-Separation and Hot-Carriers

![Figure 1.6: State diagram showing operation in organic photovoltaics. $G_D^*$: excitation of donor material. $D^*$: excited state of donor material. $k_{relax}$: charge-transfer from donor to acceptor, and CT: the resulting charge-transfer state. $k_{CS}$ (and $k^*_CS$): separation of electron and hole, and CS: the resulting charge-separation state. $k_r$: repopulation of CT state from CS state. Reproduced from Ref. [27] with permission\textsuperscript{a} from the Nature Publishing Group.]

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The interface between the donor and acceptor material has been the subject of much research interest, and identified as a large source of device losses. As understanding of the interface dynamics and mechanism has been elucidated, it has been proposed that the large internal quantum efficiency of polymer:fullerene devices is partly due to the behavior of hot excitons and hot carrier injection.\textsuperscript{5} Upon excitation with photons of energy larger than the bandgap, the exciton can undergo direct injection of the electron into the upper levels of the n-type material ($k^*_CS$ in Figure 1.6, before it undergoes thermal relaxation). By avoiding a
coulombically bound charge-transfer (CT) state, charge-recombination is decreased. However, while this has been observed spectroscopically,\textsuperscript{24,28,29} other studies have shown nearly all charge-carriers move through the CT state with minor contribution from hot carrier injection.\textsuperscript{27}

An interesting study postulated\textsuperscript{30} that exciton separation can be increased by increasing the polarization of the excited state. In particular there was an observed correlation between the efficiency of the final devices, the kinetics of exciton quenching, and the computed change in dipole moment upon excitation ($\Delta \mu_{ge}$). This was tied to earlier non-linear optics work, where the difference in excited state and ground state dipole moment ($\mu_e$ and $\mu_g$ respectively) relates linearly to the polarization of the excited state. This seems reasonable considering that greater charge-separation yields greater perturbation from the ground state, with a greater excited state dipole moment, an example is shown in Scheme 1.1.

\begin{equation}
V = \frac{e^2}{4\pi\epsilon_0\epsilon_r r}
\end{equation}

\textbf{Scheme 1.1:} Changing dipole moment with intramolecular charge transfer.

Other work\textsuperscript{31} quantified this intramolecular charge-separation in terms of charge-separation distance and amount of charge separated. The latter work breaks down the $\Delta \mu_{ge}$ relationship to be a product of the charge-separation distance vector and the amount of charge separated. Therefore, the more charges are separated in the excited state, the larger the resulting $\Delta \mu_{ge}$ will be. Given that coulombic exciton binding energy (Equation 1.1) is related to the square of charge, and inversely related to the distance, it follows that increasing the charge-separation distance, or decreasing the amount of charge-separation will decrease the exciton binding energy. As shown in Equation 1.1, where $e$ is the amount of charge, $\epsilon_0$ is permittivity of vacuum, $\epsilon_r$ is the dielectric constant of the material, and $r$ is the distance between charges.
Assuming the same magnitude of charge-separation occurs for any typical photoexcitation, the larger $\Delta \mu_{ge}$ implies the electron-hole pair to be farther apart, and not as tightly bound. This should increase the rate of charge-transfer ($k_{CT}$ in Figure 1.6). The original study implied$^{32}$ that a decrease in coulombic binding in the exciton also decreases the coulombic interaction in the charge-transfer state, such that the exciton should undergo charge-separation more rapidly, resulting in increased photocurrent due to less recombination, and less energy loss from coulombic interactions in the CT state. This assumes that all charge-carriers are generated by charge-transfer process. This type of analysis has been a predictive tool for evaluating charge-recombination potential in promising materials.$^{22,32–34}$

1.2.5 Summary of Dissertation Work

There are many ways to optimize the performance of a device solely based on processing conditions, however the focus in our group has been to design new materials to either improve performance, or to understand and study the influence of design choices on photovoltaic device performance. One of my goals was to develop low-bandgap polymers absorbing at the “ideal” bandgap (1.5 ev) discussed above and absorption covering the 500-900 nm region, where the solar spectrum is the strongest. I accomplished this by copolymerizing an electron-donating and electron-withdrawing unit to yield a low-bandgap “push-pull” copolymer.

An important consideration was to be able to vary substitution in a controllable way to tune solubility and/or electronic properties. My goal was to explore this tunability through orthogonal pendant positions in both molecular systems and in conjugated polymers, allowing tunability while avoiding backbone modifications. All these chapters cover either my computational or experimental work exploring these changes with different pendant substitution.

The active research for new non-fullerene n-type materials means that materials with optimal energetic alignment with fullerene derivatives may not align so well with these new materials, and will need to be tuned to work with the new acceptors, or new materials designed as replacements. Synthetic control will be needed, but the ability to predict promising candidates before investing significant effort in preparing new systems that have a chance
of not working is also of great importance.

I used computational modeling to understand and even predict the properties of fluorenone in 2, thienothiophene in 3, and dithienylpyrrole in 4. This made it possible to narrow the wide number of choices of possible materials. As the alignment of orbital energy levels between donor and acceptor will give the maximum possible theoretical performance in the final device, the ability to control, engineer, and most of predict these energy levels is of base importance when designing new materials. The ability to computationally predict not just molecular orbital energy levels, but other properties of the system such as UV-Vis transitions, unpaired spin-density, and changes in dipole moment is important not just for designing new materials, but in understanding how they work.

1.3 References


CHAPTER 2
COMPUTATIONAL DESIGN OF ORGANIC ELECTRONIC MOLECULAR MATERIALS

2.1 Introduction

Design and characterization of conjugated organic electronic materials can be an arduous process. Computational chemistry gives the ability to investigate properties of experimental systems through modeling their ground-state electronic structure and time-dependent phenomena such as absorption, but also to predict these properties in systems being considered for preparation. Using the results from systems already prepared as benchmarks for a particular computational procedure for prediction, synthesis, and further computational evaluation, an iterative cycle is established for the design of new materials.

This chapter presents the extensive computational work done to accompany experimental work performed by Dr. Paul Homnick to establish a modular approach to organic electronic materials through the use of fluorenone. This modular approach provides a complementary method to computational prediction of energy levels to allow one to tune the frontier orbital energy levels to ease the design and preparation of photovoltaic molecular materials with an “ideal” bandgap. Computational chemistry was a crucial, integrative part of the overall strategy to design and explain electronic and optical behavior. Computational modeling was particularly important to identify electronic transitions involved in Uv-Vis-NIR absorbance spectroscopy, and provided deeper understanding of the behavior of this class of systems as potential charge-carriers in organic materials.

2.2 Radical cations from diarylamino-substituted fluorenones


16
Conjugated aminium radical cations are of much interest as organic electronic materials. They can be spin-bearing building blocks in molecule based magnetic materials and polymers, and as charge carriers in organic batteries and conducting polymers. They also play important roles in photovoltaic charge pair generation, typically as donor materials. Simpler model triarylaminium radical cations thus are useful models for the behavior of more complex electro-active materials.

Triarylaminium cations tend to be very deeply colored, due in part to their strong conjugation. When structural connectivity allows direct π-resonance to the radical cation site, the resulting absorption bands can be energetically tuned. Adding triarylamine sites in direct π-resonance with a radical cation site can give inter-valence charge transfer (IVCT) that pushes the bandgap transition well into the near infrared (NIR) region. Comparison of the IVCT behavior gives insight about the ease of electron hopping through a π-conjugated linker or polymer, shows whether or not the radical cation and neutral triarylamine sites are strongly coupled, and shows how conjugative IVCT radical to amine coupling varies with linker types and lengths.

The following describes the absorption and electron paramagnetic resonance (EPR) spectra obtained by Paul Homnick of the Lahti group from oxidation of the diarylamine substituted fluorenones DAAFO, DPAFO, DAAFOPV, and BDAAFO (Figure 2.1). The latter two systems were investigated to test the effects of extending through-conjugation across the
fluorenone unit, with BDAAFO providing linkage for intervalence transfer behavior in the radical cation. Although electronic properties have been investigated for fluorenes linked to diarylamines,\textsuperscript{10,11} to our knowledge this has not been done for electron deficient fluorenones attached to diarylamines. This study shows that fluorenones yield highly persistent triarylaminium cations, and are effective IVCT linkers. My computational modeling of spin density distribution, molecular orbital distribution, and electronic spectral transitions provided key insight for the nature of the radical cations in the study.

### 2.2.1 Mono(diarylamino)fluorenone oxidations

DAAFO and DAAFOPV have lower oxidation potentials than DPAFO (Table 2.1), consistent with the decreased donor strength for diphenylamine versus dianisylamine. Added conjugation in DAAFOPV vs. DAAFO does not much change the oxidation potential. Density functional theory (DFT) computations at the B3LYP/6-31+G(d,p)//B3LYP/6-31G(d) level\textsuperscript{12–15} for the neutral amines give good agreement of computed HOMO energy levels with observed first oxidation potentials converted\textsuperscript{16–19} into HOMO energies (despite taking no computational account of solvent or counterion effects), where the redox potential to MO energy conversion follows the equation: $E_{MO} = -(E_{1/2} + 4.8)eV$.

Solution EPR spectroscopy that Homnick and Lahti obtained (from solution oxidation of the neutral monoamines or from dissolving precipitated solid radical cation salts) gives deeply-colored solutions showing triplet hyperfine coupling from one nitrogen (Figure 2.2, Table 2.1). The UV–vis-NIR spectra of oxidized DAAFO and DPAFO Homnick obtained (Figure 2.3, Table 2.1) exhibit intense long wavelength maxima at 777 and 823 nm, respectively, characteristic of triarylamine radical cations. The spectra from oxidation products are readily distinguished from those of the neutral reactants. The DAAFO$^+$ bands for DAAFO resemble those of the radical cations from p-(dianisylamino)benzoic acid (785 nm) and 5-(dianisylamino)isophthalic acid (777 nm),\textsuperscript{20} which also consist of an electron poor arene attached to a dianisylamine unit. DAAFOPV shows two vis-NIR bands at 747 and 1036 nm that increase proportionally together with titration of the oxidant, consistent with both arising from the same species.

Using UB3LYP\textsuperscript{12–15}/6-31G(d,p) time-dependent density functional theory (TDDFT),\textsuperscript{21}
I found the longest wavelength bands in the DAAFO, DPAFO, and DAAFOPV cations to have some singly occupied molecular orbital (MO) to lowest unoccupied π-MO (α-SOMO → α-LUMO) intramolecular charge transfer (ICT) character, but much stronger β-π-HOMO → β-π*-LUMO character. The computed band positions are in relatively good agreement with the experimental bands, even though the computations did not include counterion or solvent dielectric effects. The presence of two major bands in DAAFOPV is also supported by TDDFT, although the bandgap energy and higher energy band oscillator strength are underestimated. Computed band positions and relative strengths are shown in Figure 2.3. Despite the DAAFOPV longer wavelength band, TDDFT at the UB3LYP level also reproduces observed experimental bands for the cationic species, as shown in Figure 2.3. The agreement of computational modeling with experiment establishes a procedural baseline to understand the more complicated behavior in the diamino derivatives as shown below.
Table 2.1: Spectral and electrochemical characteristics of fluorenone radical cations and dications.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ox. absorption, (\text{nm} \ [\text{eV}] \ (\log_{10} \epsilon)^a)</th>
<th>Transition (\text{[eV]}) (oscillator str.)\textsuperscript{b}</th>
<th>(E_{1/2}) (mV)\textsuperscript{c}</th>
<th>(E_{HOMO}) (eV) \textsuperscript{d}</th>
<th>Ox. EPR hyperfine (g-value)\textsuperscript{e}</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAAFO</td>
<td>777 [1.60] (4.41)</td>
<td>[1.57] (f = 0.24)</td>
<td>320</td>
<td>-5.03 (-5.03)</td>
<td>8.6 gauss</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[1.77] (f = 0.22)</td>
<td></td>
<td></td>
<td>[1 N] (2.0033)</td>
</tr>
<tr>
<td>DPAFO</td>
<td>823 [1.51] (4.86)</td>
<td>[1.54] (f = 0.26)</td>
<td>460</td>
<td>-5.12 (-5.35)</td>
<td>5.8 gauss</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[1.66] (f = 0.03)</td>
<td></td>
<td></td>
<td>[1 N] (2.0028)\textsuperscript{f}</td>
</tr>
<tr>
<td>DAAFOPV</td>
<td>1036 [1.20] (4.02)</td>
<td>[0.77] (f = 0.65)</td>
<td>326</td>
<td>-4.98 (-4.95)</td>
<td>&lt;8 gauss</td>
</tr>
<tr>
<td></td>
<td>747 [1.66] (4.32)</td>
<td>[1.52] (f = 0.02)</td>
<td></td>
<td></td>
<td>[1 N] (2.0033)</td>
</tr>
<tr>
<td>BDAFO</td>
<td>1670 [0.74] (4.44)\textsuperscript{g}</td>
<td>[0.83] (f = 0.59)</td>
<td>220</td>
<td>-4.95 (-4.73)</td>
<td>4.7 gauss</td>
</tr>
<tr>
<td></td>
<td>873 [1.42] (4.88)\textsuperscript{h}</td>
<td>[1.21] (f = 1.38)</td>
<td>400</td>
<td></td>
<td>[2 N] (2.0032)</td>
</tr>
<tr>
<td></td>
<td>699 [1.77] (4.46)\textsuperscript{h}</td>
<td>[1.79] (f = 0.16)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[1.80] (f = 0.25)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Band maximum. \(\epsilon = M^{-1} \text{cm}^{-1}\).
\textsuperscript{b} B3LYP/6-31G(d,p) computed transition energy, oscillator strength for radical cations, and BDAFO singlet dication.
\textsuperscript{c} Cyclic voltammetric half-wave potential vs ferrocene/ferrocenium standard (acetonitrile).
\textsuperscript{d} \(E_{HOMO}\) from [16] using onset of first oxidation feature; computed \(E_{HOMO}\) from B3LYP/6-31+G(d,p)/B3LYP/6-31G(d) calculations in this work.
\textsuperscript{e} Solution X-band spectrum (\(\sim\)9.6 GHz) in dichloromethane.
\textsuperscript{f} Large linewidth spectrum (unresolved hfc?).
\textsuperscript{g} Monocation
\textsuperscript{h} Dication

2.2.2 Multiple oxidation steps in BDAFO

Homnick showed BDAFO to have overlapping reversible cyclic voltammetric oxidation peaks at about 220 and 400 mV, from mono- and di-oxidation, respectively. Solution oxidations with SbCl\textsubscript{5} or AgSbF\textsubscript{6} give similar pentet EPR spectra (Figure 2.2, Table 2.1). The spectra do not change significantly when cooled to -70°C. The pentet pattern is consistent with hyperfine coupling from two equivalent \(^{14}\text{N}\) nuclei, and indicates that BDAFO\(^+\) is a single, static, delocalized structure, or undergoes equilibrating intervalence charge transfer faster than the EPR time scale (Scheme 2.1).

Addition of more than 1 equiv of oxidant to BDAFO solutions gave somewhat decreased EPR spin counts. Frozen solution EPR spectra for samples oxidized with 4 equiv of SbCl\textsubscript{5} showed no dipolar interaction peaks or half-field transition from a possible triplet biradical
Figure 2.3: Normalized UV–vis-NIR spectra from solution protocol oxidation of DAAFO, DPAFO, and DAAFOPV with SbCl$_5$. Red bars show UB3LYP/6-31G(d,p) TDDFT predicted band positions and relative transition moments. b) Same data, plotted against energy.

dication state of BDAAFO$^{++}$. My UB3LYP/6-31G(d,p) computations showed a favored singlet state over the triplet biradical which is consistent, with an EPR silent dication. Optimized computational geometries for BDAAFO$^+$ and BDAAFO$^{++}$ (no counterions) show greater quinonoidal bond alternation in the dication, as shown in Scheme 2.1, but only by about 0.01 Å. The MeOPh groups are twisted out of the fluorenone plane, which reduces the tendency to form a highly semiquinonoidal/quinonoidal cation/dication structure.

Titration of BDAAFO with different oxidants in each case clearly shows initial growth of a NIR band at 1670 nm (Figure 2.4, Table 2.1), which grows to a maximum and thereafter decreases as new, visible region bands grow at 699 and 873 nm. Since the capability of U3BLYP TDDFT to predict band positions of cation radicals of these species was established in the previous work, I used the same computational procedure to confirm the NIR band as being an IVCT transition BDAAFO$^+$, and the visible bands at 700-900 nm in Figure 2.4 to come from BDAAFO$^{++}$. This allowed us to establish that the oxidized EPR spectrum of BDAAFO from one equivalent of oxidant was indeed a monocationic species with IVCT character (Figure 2.5). Of particular importance was the computational establishment of
Scheme 2.1: Oxidation sequence for BDAAFO.

Figure 2.4: UV–vis-NIR spectra for BDAAFO in MeCN oxidized with AgSbF$_6$. (A) 0 equiv, (B) 0.8 equiv, (C) 1.6 equiv, and (D) 4.0 equiv. Long wavelength solvent absorbance artifacts were digitally subtracted. Bars show B3LYP/6-31G(d,p) TDDFT predicted band positions and transition moment intensities for BDAAFO$^+$ (solid) and BDAAFO$^{++}$ (dashed).

A single state for the dication (explaining the decrease in EPR signal intensity for extra oxidant experiments with BDAAFO), and the assignment of the visible spectral bands to the dication, in accord with the experimental observation that this band grows with increasing amount of oxidant.

A small NIR absorption remains even at high oxidant concentrations, so Scheme 2.1 shows an equilibration of monocation and dication forms. The reaction of BDAAFO with AgSbF$_6$ shows a good isosbestic point at about 1100 nm, indicating no side reactions or decomposition over a few hours during the experiment. The band positions attributed to monocation and dication are completely consistent$^{8,9}$ with assignments of similar bands.
in oxidation of other through-conjugated diamines, as well as fitting the computed band-
assignments.

### 2.2.3 Conclusions

A test set of conjugated amines having one fluorenone substituent yields highly persistent
aminium radical cations upon solution oxidation. Solid powder samples of the radical cations
are very stable. UV–vis-NIR transitions for the radical cations are in reasonably good agree-
ment with hybrid functional TDDFT computational modeling. The through-conjugated di-
amine, BDAAFO, exhibits an intervalence charge transfer NIR band and EPR spectroscopy
consistent with swift electron transfer, or one static delocalized structure. The stabilities of
these radical cation species are promising for potential use as electronic materials.

The use of DFT and TDDFT for assigning transitions of different cationic species was
integral to the study, and also allowed the fairly accurate computational prediction of the
frontier molecular orbital levels. The computational procedures were used more extensively
in the following section as part of further developing effective linkage between theory and
experiment for modular design of conjugated organic molecules for electronic materials work.

2.3 Engineering Frontier Energy Levels in Donor-Acceptor Fluoren-9-ylidene Malononitriles versus Fluorenones


Donor-acceptor (D-A), or “push-pull”, systems have drawn much attention use as electronic materials for nonlinear optical, energy harvesting, and charge transport testing. Much work and molecular design strategy has aimed for specific optical transition energies (often taken as measures of bandgap) as well as specific highest occupied and lowest unoccupied molecular orbital (HOMO, LUMO) energy levels in donor-acceptor compounds because of their potential utility in electronic applications. Because of the high promise of molecular electronic devices, much effort continues in the design of new, synthetically simple donor-acceptor conjugated organic molecules and in the improvement of prediction of their spectral and electronic behaviors. The inexpensive, synthetically simple and readily functionalized fluorenone (FO) has been heavily studied for its electronic spectral behavior and for its role in green emission bands in fluorene-based organic LEDs. There have also been a number of studies of substitution effects on fluorenone spectroscopy. Recently, Homnick and Lahti described a study in which synthetically simple 2-fluorenonyl and 2,7-fluorenonediyi acceptor units can be linked in a modular fashion to diarylamine donor groups to give consistent LUMO levels from the fluorenone unit and tunable HOMO levels from the donors. In the present report, the initial design is extended to additional fluorenone systems and especially to the stronger electron acceptor fluoren-9-ylidene malononitrile (FM). FM-based systems have lower LUMO levels relative to their FO-based analogues, decreasing all optical transition energies because the donor-controlled HOMO levels remain the same, to a first approximation. The results described below show that the use of a modular
“building block” strategy produced FM-based D-A and D-A-D donor-acceptor compounds with molecular electronic properties that can be varied in a manner that is crucial for the development of new organic electronic materials. I carried out computational modeling as a key component of assigning and understanding the electronic natures and spectroscopy of these D-A molecules.

2.3.1 Computational Methods

All computations were carried out using Gaussian 09\textsuperscript{15} revision B.01 on a Linux computer running openSuSE. Molecular geometries were optimized at a B3LYP\textsuperscript{12–14} /6-31G(d,p) level, and these geometries were fixed to compute molecular properties at a B3LYP/6-31+G(d,p) level. Molecular orbital diagrams were generated from the final checkpoint files using GaussView\textsuperscript{59} version 5.0.9 with default parameter settings unless otherwise stated.

2.3.2 Results and Discussion

Subsequent discussions use the abbreviations shown in Scheme 2.2 for the structural modules used to make the donor-acceptor molecules of Scheme 2.3. As mentioned earlier, for analogous structures with the same donor units the LUMO level of an FO-based molecule will be lowered in the analogous FM-based system. The results described below show that this approach works well to give a range of absorption profiles and electronic HOMO and LUMO levels.

The spectroscopic behaviors of all of the donor-acceptor systems in this study are interpreted below in terms of interactions between the donor (D) and acceptor (A) modules that comprise the overall D-A and D-A-D molecules. These interpretations are, in turn, related to HOMO and LUMO levels estimated from the electrochemical measurements performed by Homnick. Table 2.2 lists the “building block” electrochemical potentials for use in subsequent discussions.

Homnick observed that the FOS long wavelength absorption band red shifts in polar solvents, a trend typically attributed to $\pi \rightarrow \pi^*$ transitions. Interestingly, the FMS long wavelength band exhibits a modest blue shift in acetonitrile versus less polar solvents, as do a number of the Scheme 2.3 FM-based derivatives described below. The latter behavior is
Scheme 2.2: General structural design units used in donor-acceptor fluoren-9-ylidene malononitrile (FM) and precursor fluorenone (FO) systems in this section.

However, I was able to show through computational modeling that the frontier orbitals of the Scheme 2.2 compounds are π-orbitals, without interspersed n-type orbitals. The long wavelength transitions in both FO- and FM-based systems are all computed to be π → π* type, from a π-HOMO that is delocalized throughout the full π-system to a LUMO that is largely localized on the FO or FM unit. Examples are shown in Figure 2.6 for both D-A and D-A-D systems.

Conformational differences in the AA donor-substituted systems give only small differences in computed MO energy levels (≤ 0.1 eV). As the electron donor strength of donor modules increases beyond AA due to more phenyl and anisyl substituents on the amine units, the HOMO and LUMO overlap less, with the HOMO primarily on the donor module and the LUMO primarily on the acceptor unit. This is conducive to intramolecular charge transfer (ICT) character in the lowest-energy photoexcitation. Negative solvatochromic shifts in polar, n-donor type solvents (like the acetonitrile used in this study) can be attributed to specific solvent-solute interactions in the ground state that are less favorable for the excited state, giving a net blue shift; this behavior can occur for both CT and n → π* transitions. For this reason, the blue shift seen in acetonitrile versus lower-polarity solvents for FMS and a number of other malononitrile derivatives in this study is reasonable for excited states.
Scheme 2.3: Donor-acceptor systems compared in this section.

having the significant ICT character indicated by my computations.

Experimentally, the FO systems all show solvatochromic red shifts of the lowest-energy transition in more polar solvents, consistent with $\pi \rightarrow \pi^*$ and ICT character for these transitions.\textsuperscript{61–66} The solvatochromic trends for the FM systems are not completely consistent but somewhat favor blue shifts in more polar solvents, like the case of the FMS versus FOS. As mentioned above, the blue shifts in some of these systems are presumably attributable\textsuperscript{60} to specific solvent-solute interactions in acetonitrile solvent.

Interestingly, the band onsets for the Cz-functionalized D-A systems are nearly the same as those for the trimethoxystyrene-functionalized systems. The pyrrole ring of Cz is less able to donate aromatic $\pi$-electrons than the other amine donors are able to donate nonaromatic lone pair electrons. This makes Cz a relatively poor donor, resulting in a relatively
Table 2.2: Optical and electrochemical properties of fluorenone molecules.  

aLowest-energy maxima; hexane solvent unless otherwise stated. All results obtained in acetonitrile, and referenced against ferrocene/ferrocenium oxidation in the same solvent.  
b$\epsilon = \log(L/(molcm))$.  
cLowest-energy maxima above 250 nm, acetonitrile solvent unless otherwise stated. All results obtained in acetonitrile, and referenced against ferrocene/ferrocenium oxidation in the same solvent.  
dNo resolvable feature.  
eOnset potentials in millivolts. All results obtained in acetonitrile, and referenced against ferrocene/ferrocenium oxidation in the same solvent.  
fCalculated using eqs 1 and 2.  
gComputed at the B3LYP/6-31+G(d,p)//B3LYP/6-31G(d,p) level of theory unless otherwise stated.  
hSpectrum obtained in dichloromethane because of hexane insolubility.  
iSpectrum obtained in diethyl ether because of hexane insolubility.  
jPotential of peak maximum in millivolts.  
kComputed at the B3LYP/6-31G(d,p)//B3LYP/6-31G(d) level.

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<th>compound</th>
<th>abs. $\lambda_{max}$ (nm)$^a$</th>
<th>(e)$^b$</th>
<th>abs. $\lambda_{max}$ (nm)$^c$</th>
<th>(e)$^b$</th>
<th>oxidation onset(s) (mV)$^c$</th>
<th>reduction onset(s) (mV)$^c$</th>
<th>$E_{HOMO}$ (eV)$^f$</th>
<th>$E_{LUMO}$ (eV)$^f$</th>
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<td></td>
<td></td>
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<td>expt. [comp.$^i$]</td>
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<td>d</td>
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<td>FMS</td>
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<td>539(2.84)</td>
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<td>-3.35 [-3.06]</td>
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<td>FODPA</td>
<td>479(3.19)</td>
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<td>635(2.76)</td>
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<td>$\ldots$</td>
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<td>$\ldots$</td>
<td></td>
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<td>155, 355, 949</td>
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<td>785(2.73)</td>
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<td>$\ldots$</td>
<td></td>
<td>-4.98 [-4.83]</td>
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<td>571(3.07)</td>
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<td>243, 543, 1160</td>
<td>$\ldots$</td>
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<td>-5.04 [-5.06]</td>
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<td>474(4.02)</td>
<td>290(424, 533)$^l$</td>
<td>$\ldots$</td>
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<td>597(3.64)</td>
<td>279 (437, 572)$^l$</td>
<td>$\ldots$</td>
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<td>140, 783, 1620</td>
<td>d</td>
<td>-4.94 [-4.92]</td>
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<td>FO</td>
<td></td>
<td>1550</td>
<td>-1820</td>
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<td>-2.98 [-2.63]</td>
<td></td>
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<tr>
<td>FM</td>
<td></td>
<td>1500</td>
<td>-1010, -1710</td>
<td>-6.36 [-6.87]</td>
<td>-3.79 [-3.55]</td>
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</table>
higher optical transition energy. Also, the relatively lower oxidation potential and higher computed HOMO energy of trimethoxystyrene (Table 2.2) indicate it to be a superior electron donor to Cz. For the stronger donor amines, the absorption onsets in Table 2.2 move to increasingly lower energy in the series FOCz > FODPA > FOAA > FODAA. The decreasing optical transition energies correlate with increasing $E_{HOMO}$ of Cz < DPA < AA < DAA, while $E_{LUMO}$ in the FO-series remains fixed at about -3.0 eV, as shown by both electrochemical measurements and computational modeling. The same trend is seen for the FM-functionalized analogues, but in each case the FM-analogue absorption is lower in energy by about 0.50 eV. The reduced optical transition energies in the FM-series occur because their HOMO levels are essentially defined by the same donor HOMO levels as in their FO analogues, but the FM-analogues all have lower $E_{LUMO}$ energies in the range of -3.4 to -3.7 eV (Table 2.2). My computations for all of the amine-functionalized D-A systems show an ICT character that is even stronger than that in the acceptor-only FOS or FMS, with the $\pi$-HOMO in each case favoring the side of the FO or FM ring that holds the amine and the

**Figure 2.6:** Example B3LYP/6-31+G(d,p) level frontier orbital plots for FMDAA and FMBDAA. FMBDAA (a) HOMO and (b) LUMO, FMBDAA (c) HOMO and (d) LUMO. Plotted using default parameters for GaussView version 5.0.9.
π*-LUMO being localized on the FO or FM module.

2.3.3 Modular Electronic Analysis of the Donor-Acceptor Molecules

The experimental electrochemical findings support two criteria for a modular scheme for understanding the electronic behavior of the donor-acceptor molecules in this study. First, the molecules exhibit reduction electrochemistry in very reasonable accord with voltammetry measured for the FO and FM acceptor modules; there are only minor variations with different attached donor groups. (The reduction half-wave potentials also compare well to the FM reduction potential of -1.00 V from Neckers and co-workers\textsuperscript{52}). Second, the oxidation potentials of donor components are well-retained in both FO- and FM-based systems. These trends encourage the notion that the donor and acceptor components can be considered interchangeable modules that can be used to design and understand the electronic properties of the overall D-A molecules. From a molecular engineering perspective, this is very desirable for designing new electronic materials. In addition, as Table 2.2 shows, the HOMO energy levels computed by density functional theory for the Scheme 2.3 donor-acceptor molecules are remarkably close to the experimentally estimated HOMO levels, on average about 0.1 ± 0.2 eV lower (uncertainty is standard deviation); the computed LUMO energy levels are 0.4 ± 0.3 eV higher than those obtained from voltammetry experiments.

![Scheme 2.4: Tuning of donor-acceptor system (D-A) frontier molecular orbitals derived from interaction of donors and acceptors.](image)

One can rationalize the behavior of related donor-acceptor systems composed of modular
units (like those in Scheme 2.2) by using computational and/or experimental frontier energy levels for the modular units. Scheme 2.4 shows how qualitative interactions between the frontier orbitals of donor and acceptor units decreases the optical transition energy of a donor-acceptor system, where donor strength $D_2 > D_1$ and/or acceptor strength $A_2 > A_1$. In the present study, the FO and FM acceptor unit HOMO energies are low enough not to interact strongly with the donor units. Similarly, the donor unit LUMOs are so high in energy relative to the acceptor LUMOs that the donor-acceptor system LUMOs are determined by the FO or FM units. Figure 2.7 shows quantitatively how the experimental donor-acceptor frontier energy levels track with the energies of their modular components. The B3LYP computational modeling reproduces these trends with similar orbital energies.

![Energy Levels Diagram](image)

**Figure 2.7:** Frontier molecular orbital energy levels for donor-acceptor molecules compared with orbital energies of constituent donor and acceptor modules. Data from Table 2.2.

The LUMO energy levels in the FM systems are lower by an average of 0.6 ± 0.1 eV in comparison to their FO-based analogues (uncertainty is standard deviation considering only the donor-acceptor systems, not the modular units). This correlates with the 0.8 eV LUMO energy decrease from FO to FM and with the optical transition energy decreases.
Table 2.2) in FM derivatives compared to FO derivatives. Therefore, the modular approach of Scheme 2.4 applied in Figure 2.7 is self-consistent in describing the electronic behaviors of the Scheme 2.3 donor-acceptor molecules.

### 2.3.4 Strengthening Absorption by a Connectivity Change

The success of the Figure 2.7 modular donor-acceptor design strategy is somewhat diluted by the decreased molar absorptivities of the desirably low optical transition energies in both FO and FM series. For photovoltaic and photoconversion applications, strong absorption bands are desirable to allow use of thinner layers of electroactive material.

![Scheme 2.5:](image)

Scheme 2.5: Neckers's push-pull FO- and FM-based systems with phenylethynylene-linked donors. Red arrows show dipole contributions in the 3,6-connectivity systems. Based on discussions from reference [67].

Therefore, the results in Figure 2.7, were extended to follow work by Neckers and co-workers\textsuperscript{51,52,67} that tested the effect of connectivity in the FO- and FM-based push-pull
molecules shown in Scheme 2.5. They found that the absorption spectral blue shift from deconjugating the donor substituents in the 3,6-FO/FM systems (FOPE36, etc.) by comparison to the through-conjugated 2,7-FO/FM systems (FOPE27, etc.) was accompanied by a substantially increased molar absorptivity. In the 2,7-connectivity systems, excited-state dipole shift effects through the phenylethynyl groups cannot interact directly with the C=O or C=C(CN)_2 dipoles. In the 3,6-connectivity systems, the donor substituents are no longer through-conjugated with one another, but they are linked to the C=O or C=C(CN)_2 units. This gives higher optical transition energies, but reinforces excited-state dipole moment changes for donor Cz groups interacting with C=O or C=C(CN)_2 dipoles.

### Table 2.3: TDDFT computational predictions of long wavelength absorption bands for 2,7- versus 3,6- connectivity systems. Performed at B3LYP/6-31G(d,p).

<table>
<thead>
<tr>
<th>Name</th>
<th>Transition Energy</th>
<th>Oscillator Strength</th>
<th>Expt. abs. λ_max (eV) (ε)</th>
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<td>FOBDAW</td>
<td>1.98 eV</td>
<td>f = 0.090</td>
<td>2.12 (3.24)</td>
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<tr>
<td>FMBDAW</td>
<td>1.19 eV</td>
<td>f = 0.035</td>
<td>1.58 (2.73)</td>
</tr>
<tr>
<td>FOBDAW36</td>
<td>2.53 eV</td>
<td>f = 0.228</td>
<td>2.62 (4.02)</td>
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<td>FMBDAW36</td>
<td>2.01 eV</td>
<td>f = 0.244</td>
<td>2.08 (3.64)</td>
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</table>

I tested the qualitative expectation of an analogous dipole enhancement using the modules from Scheme 2.2. Computational modeling of FOBDAW and FMBDAW with time-dependent density functional (TDDFT\(^{21}\)) at the B3LYP/6-31G(d,p) level gave long wavelength bands at 625 and 1042 nm, with oscillator strengths of 0.09 and 0.04, respectively (Table 2.3). The predicted band positions are good matches to the observed band onsets (Table 2.2), and the computed decrease in oscillator strength from the FO- to the FM-based system agrees with experiment. By comparison, the isomeric FOBDAW36 and FMBDAW36 were predicted to have long wavelength bands at 490 and 616 nm, with oscillator strengths of 0.23 and 0.24, respectively. Save for different orbital energies due to different connectivities, the 2,7-and 3,6-systems both have similar push-pull separation in HOMO versus LUMO (Figure 2.9), indicating ICT (or at least strongly dipolar) character to be expected for transitions in both systems. These computations supported the use of Neckers’s connectivity change strategy to increase absorptivity and indicated that FMBDAW36 would absorb
well into the visible spectrum despite deconjugation of the donor groups from one another (which causes the HOMO energies to be raised significantly in the 3,6-isomers, Table 2.2).

Figure 2.8: Lowest-energy absorption spectral regions in acetonitrile comparing FOBDAA, FMBDAA, FOBDAA36, and FMBDAA36.

Figure 2.8 shows that the absorption band energies increase in the 3,6- versus the 2,7-connectivity systems, as expected. The observed absorption onsets in acetonitrile are at $0.3 \pm 0.1 \text{ eV}$ (standard deviation) higher energy than the TDDFT modeling predictions (Table 2.3), but the predicted and observed spectra both show the desired strong increases in molar absorptivity for both the FO- and FM-based systems. Overall, the combination of LUMO lowering by use of the FM unit plus increased dipole coupling in the 3,6-connectivity makes FMBDAA36 absorb 8-fold more strongly (molar absorptivity $4500 \text{ M}^{-1}\text{cm}^{-1}$) than any of the 2,7-connectivity systems. Also, FMBDAA36 still absorbs well into the 400-700 nm region that is important for organic photovoltaics. Recent work has shown other FO or FM derivatives to have promise for hole-transport or ambipolar charge transport, where morphological considerations do not curtail solid-state charge-transport behavior. This turns out to be the case for FMBDAA36, which was the only variant among these to be moved forward for solar cell fabrication development that led to a 4.2% power conversion device by a relatively simple fabrication procedure. Therefore, the iterative modular development strategy yielded an effective candidate as desired.
2.3.5 Conclusions

The absorption spectroscopy and electrochemistry of strong electron acceptor fluorenylidene malononitriles (FMs) bearing common 2- or 2,7- electron donor substituents were compared to the results for less electron withdrawing fluorenone (FO) analogues. The FM and FO units are structurally simple and synthetically accessible acceptor (A) units that interact with donor (D) substituents to give donor-acceptor electronic behavior, including longer wavelength optical transition energies associated with intramolecular charge transfer (ICT) behavior.

This modular electronic engineering approach provides a rational path for tuning $E_{HOMO}$, $E_{LUMO}$, optical transition energy, and absorptivity strength. Starting from FO-based systems bearing moderate donors such as trimethoxystyrene connected in a 2,7-fashion to maximize conjugation, stronger donor diarylamine substituents were used to raise HOMO levels, increasing ICT character and lowering the optical transition energy. Changing to a
3,6-connectivity strengthened molar absorptivity considerably, at a cost of increasing the optical transition energy by about 0.50 eV. As described above, the overall approach gave a successful candidate for organic molecular material solar cell development, with quite good power conversion.

2.4 References


(23) Prasad, P. N.; Williams, D. J., Introduction to nonlinear optical effects in molecules and polymers; Wiley New York etc.: 1991.


CHAPTER 3
ELECTRONIC PUSH-PULL THIENO[3,4-B]THIOPHENE COPOLYMERS WITH PENDANT VARIATION


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This chapter presents the computational work done to accompany the synthetic and experimental work performed by Patrick Homyak of the Coughlin group to study the effects of pendant fluorination of push-pull thieno[3,4-b]thiophene copolymers. Initial interest was to confirm the fluorination would have the desired effect on the frontier orbital energy levels in order to encourage the synthesis of the PTB series. Homyak also hypothesized the pendant fluorination would result in increased charge-transfer in the excited state, and lead to an effect previously reported\(^2\)\(^3\) that related the change in dipole moment upon excitation (\(\Delta \mu_{ge}\)) to the final device performance. The application and expansion of this method to Homyak’s systems revealed interesting length dependence of the models used on the final computed outcome.

### 3.1 Introduction

Design, preparation, and characterization of new conjugated polymers has received increased attention over the past two decades due to their potential to serve as semiconducting materials for relatively low-cost, thin, flexible organic electronics such as organic photovoltaics (OPVs), organic field-effect transistors (OFETs), and organic light-emitting diodes (OLEDs).\(^4\)\(^-\)\(^11\) This concentrated research effort has led to significant improvements in the understanding and design of conjugated systems, which in the case of OPVs has resulted in
vastly improved device efficiencies. Specifically, single junction OPVs have been reported to have power conversion efficiencies (PCEs) consistently around 6-8% and tandem junction devices with PCEs approaching and now exceeding 10%.

The design of polymers with appropriate electrochemical and structural properties to improve OPV efficiencies has been a central research focus of numerous research groups. Low-bandgap polymers have been engineered to have appropriately aligned $E_{HOMO} / E_{LUMO}$ electronic levels relative to PCBM, optimized side chains to enhance solubility while enabling good interchain interactions, good crystallinity/planarity through the backbone to promote high charge mobility, and low bandgaps ($E_g$) to increase the harvested range of the solar spectrum.

Recent developments have focused on incorporating fluorine atoms onto the acceptor unit in the backbone of donor-acceptor (D-A) alternating copolymers. It has been demonstrated that the incorporation of a single fluorine atom can have drastic effects not only on the electrochemical properties of the polymer but also on chain packing and orientation as well as interpolymer interactions and miscibility with PCBM. These effects have been shown to give significant absolute increases in the PCE ranging from 1% to 2%. Several reports of polymers with mono- or difluorinated acceptor units have yielded similar observations.

While it has been shown that fluorinated polymers are quite advantageous for various uses due to superior performance and enhanced stability, it is not entirely clear what fundamental changes arise from fluorine substitution to create these favorable properties.

Several observations have been made regarding both the electrical and morphological changes induced upon incorporation of fluorine on the acceptor unit in a D-A conjugated polymer backbone. First, both $E_{HOMO}$ and $E_{LUMO}$ are lowered, leading to enhanced open-circuit voltage ($V_{oc}$) due to the increased $E_{HOMO}^\text{polymer} / E_{LUMO}^\text{PCBM}$ energy offset. Second, the ground-to-excited state dipole change ($\Delta \mu_{ge}$) is increased, decreasing geminate recombination by allowing more efficient charge separation and increasing both the external quantum efficiency (EQE) and internal quantum efficiency (IQE) for harvesting charges. Studies have suggested a strong correlation between computational values for $\Delta \mu_{ge}$ and observed PCE.

Studies of conjugated polymers with fluorine substitution are necessary to elucidate how
Patrick Homyak developed the design, synthesis, and preliminary characterization of a new series of alternating thieno[3,4-b]thiophene dithienyl-substituted benzodithiophene polymers which utilize the D-A alternating copolymer approach for achieving low-bandgap materials. In order to study the effects of fluorination, thienothiophene monomers were synthesized with octyl (T8), phenyl (TP), perfluorooctyl (TF8), and perfluorophenyl (TFP) substituents, as shown in Figure 3.1. Polymerization of these monomers with benzodithiophene by direct arylation polymerization yielded the corresponding PT8B, PTPB, PTF8B, and PTFPB alternating D-A copolymers (Figure 3.2).

3.2 Results and Discussion

3.2.1 Molecular Orbital and Ground-to-Excited State Dipole Change Calculations

Excited- and ground-state DFT computations, with the polymers modeled as oligomers, were performed at the hybrid density functional level B3LYP/6-31G(d,p) in Gaussian09. Ground-state geometries were optimized at the same level, and first excited state computations carried out by time-dependent density functional theory (TDDFT) at the ground-state geometry.
Figure 3.2: Poly(thieno[3,4-b]thiophene-alt-dithienylbenzodithiophene) (PTB) series.

Figure 3.3: Molecular orbitals for D-A polymer dimer models (n = 2).

As seen in the molecular orbital diagrams of Figure 3.3, the polymer dyads HOMOs are delocalized over the entire backbone in each case, while the LUMOs have more electron density localized upon the thienothiophene unit, particularly in the cases with the perfluorinated groups, PTF8B and PTFPB. Additionally, for PTPB and PTFPB, the phenyl group is nearly planar with the thienothiophene unit, giving further delocalization of electron density and leading to relatively lower bandgaps. The effect of this extended conjugation is observable in the LUMO density maps by the nonzero contributions of the pendant phenyl groups. This is also reflected in the computed energy levels, where the effect of the extended conjugation into the aryl group is small, but observable, leading to slightly reduced bandgaps by 0.05-0.12 eV. The computations also show a significant electron withdrawing
effect of perfluorinated groups, with lowering of both the $E_{HOMO}$ and $E_{LUMO}$.

Table 3.1: Computational modeling of $E_{HOMO}$, $E_{LUMO}$, and $\Delta \mu_{ge}$, compared to experimental optical and electrochemical data.

<table>
<thead>
<tr>
<th>polymer</th>
<th>$E_{HOMO}$ (eV)</th>
<th>$E_{LUMO}$ (eV)</th>
<th>$E_g$ (eV)</th>
<th>$\Delta \mu_{ge}$ (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CV$^a$</td>
<td>UPS$^b$</td>
<td>DFT$^c$</td>
<td>DFT$^{DFT}_LUMO$ $^c$</td>
</tr>
<tr>
<td>PT8B</td>
<td>-5.13</td>
<td>-4.75</td>
<td>-4.60</td>
<td>-2.10</td>
</tr>
<tr>
<td>PTPB</td>
<td>-5.10</td>
<td>-4.76</td>
<td>-4.66</td>
<td>-2.21</td>
</tr>
<tr>
<td>PTF8B</td>
<td>-5.35</td>
<td>-5.09</td>
<td>-4.95</td>
<td>-2.48</td>
</tr>
<tr>
<td>PTFPB</td>
<td>-5.24</td>
<td>-4.99</td>
<td>-4.81</td>
<td>-2.43</td>
</tr>
</tbody>
</table>

$^a$Versus Fc/Fc$^+$ external reference.
$^b$Measured on ITO-coated substrate.
$^c$Computed with B3LYP/6-31G(d,p) using dimer structure (n = 2).
$^d$Calculated using polymer film absorbance onset.
$^e$Taken as $E^{DFT}_{LUMO} - E^{DFT}_{HOMO}$
$^f$Computed with B3LYP/6-31G(d,p) using monomer structure (n = 1).

Previously, Yu et al. noted a positive correlation between increased PCE and larger computed values of $\Delta \mu_{ge}$, which were calculated by the semiempirical AM1 method.\(^{2,3}\) Semiempirical methods for conjugated D-A molecules have been shown to underestimate $\Delta \mu_{ge}$.\(^{29}\) My own independent DFT calculations confirm this underestimation for AM1 by comparison to the same reported set of diphenylacetylene donor-acceptor small molecules (Figure 3.4).\(^{29}\) However, DFT calculations using B3LYP/6-31G(d,p) for the benchmark molecules were shown to overestimate $\Delta \mu_{ge}$ compared to experimental results\(^{30}\) (Table 3.2). The computed ground state dipole moments and excited state dipole moments were taken from ground state SCF density and the excited state TDDFT CI density, respectively. The ground-to-excited state dipole changes were calculated from the previously reported relationship $\Delta \mu_{ge} = \sqrt{(\mu_{gx} - \mu_{ex})^2 + (\mu_{gy} - \mu_{ey})^2 + (\mu_{gz} - \mu_{ez})^2}$.\(^{2,3,27}\) Both AM1 and DFT methods agree fairly well when calculating the ground state dipole moment, so the difference is attributed to excited state dipole moment calculations. This comparative evaluation is listed in Table 3.2.

In order to understand how $\Delta \mu_{ge}$ changes with structural variations in this study, the ground and excited state dipole moments were calculated using B3LYP/6-31G(d,p), and
\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{\(\equiv\)} & \quad \text{\(\equiv\)} & \quad \text{\(\equiv\)} & \quad \text{\(\equiv\)} & \quad \text{\(\equiv\)} \\
\text{H}_2\text{N} & \quad \text{\(\equiv\)} & \quad \text{\(\equiv\)} & \quad \text{\(\equiv\)} & \quad \text{\(\equiv\)} & \quad \text{\(\equiv\)} \\
\end{align*}
\]

**Figure 3.4:** D-A diphenylacetylene test system.

**Table 3.2:** Establishing DFT baseline test system results.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>(\Delta \mu_{ge}^{DFT}) (D)\textsuperscript{a}</th>
<th>(\Delta \mu_{ge}^{AM1}) (D)\textsuperscript{b}</th>
<th>(\Delta \mu_{ge}^{INDO}) (D)\textsuperscript{c}</th>
<th>(\Delta \mu_{ge}^{expt}) (D)\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 1</td>
<td>15.58</td>
<td>4.35</td>
<td>5.79</td>
<td>9.5</td>
</tr>
<tr>
<td>n = 2</td>
<td>18.68</td>
<td>4.16</td>
<td>5.07</td>
<td>8.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molecule</th>
<th>((\mu_g, \mu_e)^{DFT}) (D)\textsuperscript{a}</th>
<th>((\mu_g, \mu_e)^{AM1}) (D)\textsuperscript{b}</th>
<th>(\mu_g^{expt}) (D)\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 1</td>
<td>10.06, 25.64</td>
<td>9.23, 13.58</td>
<td>5.5</td>
</tr>
<tr>
<td>n = 2</td>
<td>10.85, 29.54</td>
<td>9.70, 13.86</td>
<td>6.3</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Calculated as described in main text using B3LYP/6-31G(d,p).

\textsuperscript{b}Calculated as described in main text using AM1.

\textsuperscript{c}INDO calculations reported by Brédas \textit{et al.}\textsuperscript{29}

\textsuperscript{d}Experimental numbers reported by Perry \textit{et al.}\textsuperscript{30}

\(\Delta \mu_{ge}\) was calculated for the model systems (with \(n = 1\)) using the method described above (Table 3.1). The fluorinated pendants were found to greatly increase \(\Delta \mu_{ge}\) by approximately 10 D compared to the nonfluorinated analogues. The \(\Delta \mu_{ge}\) was also increased by 5-6 D by extending the conjugation away from the polymer backbone with the incorporation of phenyl pendants in the cases of PTPB and PTFPB (structures in Figure 3.2). The \(\Delta \mu_{ge}\) was the highest, 18.15 D, for PTFPB where the fluorine atoms are directly bonded to the conjugated system. For comparison, \(\Delta \mu_{ge}\) was calculated for a series of experimentally known polymers prepared by Yu \textit{et al.}, and shown in Figure 3.5, using the B3LYP/6-31G(d,p) method.\textsuperscript{2,31}

The calculated \(\Delta \mu_{ge}\) values for the reported materials PBB3, PTBF2, PTB2 and PTB7 are given in Table 3.3. The new PTB series studied have \(\Delta \mu_{ge}\) values that span an even wider range overall, from 2.34 to 18.15 D. This PTB series provides an opportunity to evaluate the correlation of \(\Delta \mu_{ge}\) and PCE in a new set of materials and determine if \(\Delta \mu_{ge}\) is a critical factor for improving device efficiencies. If this trend applies to these materials, \(\Delta \mu_{ge}\) could potentially be used in future research as an easily computable value for designing and screening new conjugated materials.
Figure 3.5: Structures of reported polymers used for comparison.\textsuperscript{2,31}

Table 3.3: Calculation of $\Delta \mu_{ge}$ and comparison to reported values.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\Delta \mu_{ge}^{DFT}$ (D)\textsuperscript{a}</th>
<th>$\Delta \mu_{ge}^{AM1/Lit}$ (D)\textsuperscript{b}</th>
<th>PCE\textsubscript{Lit} (%)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBB3</td>
<td>4.12</td>
<td>0.47</td>
<td>2.04</td>
</tr>
<tr>
<td>PTBF2</td>
<td>13.5</td>
<td>2.41</td>
<td>3.2</td>
</tr>
<tr>
<td>PTB2</td>
<td>15.7</td>
<td>2.96</td>
<td>5.1</td>
</tr>
<tr>
<td>PTB7</td>
<td>14.83</td>
<td>3.92</td>
<td>7.4</td>
</tr>
</tbody>
</table>

\textsuperscript{a}B3LYP/6-31G(d,p) calculations as described in main text. 
\textsuperscript{b}AM1 Computations and PCE reported by Yu, L. \textit{et al.}\textsuperscript{2,31}

It is interesting to speculate about the nature of $\Delta \mu_{ge}$ and the structural features of a polymer that may increase or decrease ground and excited state dipoles, and also how $\Delta \mu_{ge}$ changes in computations with greater chain lengths that better model polymers. Most computations of $\Delta \mu_{ge}$ have been performed using a monomeric model system. In one single repeat unit the possibility of dipole cancellation created by other acceptor units is avoided. At chain lengths greater than $n = 1$ this effect could be significant, especially since the polymers mentioned have off-axis pendant functionality which could cancel or offset many moment contributions. To investigate this, computations were performed with $n = 2$ and $n = 2.5$ unit model oligomers. The $n = 2.5$ systems – in contrast to the $n = 2$ and $n = 1$ systems – are electronically symmetrical in order to place each electron acceptor in the same chemical environment (resulting in a D-A-D-A-D arrangement). In cases with $n = 2$ and $n$
2.5 the magnitude of $\Delta \mu_{ge}$ decreases significantly, yet the main trends are preserved by comparison to the $n = 1$ models (Table 3.4). Further investigation of $\Delta \mu_{ge}$ as a function of $n$ could provide more of an understanding of the effects of $\Delta \mu_{ge}$ on polymeric systems when compared with experimental data, or at least could suggest using $\Delta \mu_{ge}$ with caution if there are qualitative differences between trends using different $n$.

Table 3.4: Comparison of $\Delta \mu_G$ vs. $n$.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$n = 1$</th>
<th>$n = 2$</th>
<th>$n = 2.5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PT8B</td>
<td>2.34</td>
<td>1.57</td>
<td>3.45</td>
</tr>
<tr>
<td>PTPB</td>
<td>8.24</td>
<td>1.58</td>
<td>3.27</td>
</tr>
<tr>
<td>PTF8B</td>
<td>11.18</td>
<td>6.54</td>
<td>5.60</td>
</tr>
<tr>
<td>PTFPB</td>
<td>18.15</td>
<td>4.59</td>
<td>4.85</td>
</tr>
</tbody>
</table>

$^a$Calculated as described in main text using B3LYP/6-31G(d,p) on model systems in straight chain conformation.

3.2.2 Optical and Electrochemical Properties of the Polymers.

The optical absorption and electrochemical analyses demonstrate significant changes in the electron density as a result of changing from octyl to phenyl and from adding the fluorinated pendant groups along the backbone. The electron withdrawing nature of the different thienothiophene units were examined using cyclic voltammetry (CV) as shown in Figure 5. The measured $E_{HOMO}$ levels for PT8B, PTPB, PTF8B, and PTFPB are -5.13, -5.10, -5.35, and -5.24 eV, respectively. These results were supported by both density functional theory calculations (Table 3.1) and ultraviolet photoelectron spectroscopy (UPS) measurements (Table 3.1). Both experimental and computational results show that the perfluorinated units TF8 and TFP have lower $E_{HOMO}$ levels due to the strong electron withdrawing nature of the fluorine atoms. The thienothiophene units display the following trend for the least to most electron withdrawing: $T8 \approx TP < TFP < TF8$. The reduction of the $E_{HOMO}$ level due to fluorine substitution has been well documented, and our results are consistent with previous literature reports.$^{2,3,20-27}$ Directly comparing the polymers with nonfluori-
nated and perfluorinated side groups, the TF8 unit reduces the $E_{HOMO}$ by 0.22 eV versus the T8 unit, while the TFP unit reduces the $E_{HOMO}$ by 0.14 eV relative to the TP unit.

From the experimental absorption onsets and oxidation potential onsets of the polymer films, the $E_{LUMO}$ were calculated and the bandgaps were determined for each of the polymers. Each of the polymers has a low-lying $E_{HOMO}$ which resides mainly on the dithienyl-substituted benzodithiophene donor unit. Addition of the flanking thiophene units has been shown to lower the $E_{HOMO}$, creating polymers with higher $V_{oc}$ and greater oxidative stability.\textsuperscript{32} Changing from alkyl to aryl substituents on the thienothiophene unit slightly lowers the bandgap (by 0.08 to 0.11 eV) which can be attributed either to the extended conjugation or the different electron withdrawing nature of the pendant groups. Replacement of the alkyl pendant groups with perfluorinated pendant groups induces a significant lowering of both the $E_{HOMO}$ (0.14-0.22 eV) and $E_{LUMO}$ (0.22-0.26 eV). Additionally, in comparison, the experimental voltammetric orbital energies agree very well with B3LYP/6-31G(d,p) computational orbital energies of the dimeric (n = 2) models, after applying an empirical correction factor of -0.45±0.06 eV for the $E_{HOMO}$ levels and -1.26±0.05 eV for the $E_{LUMO}$ levels (uncertainties are standard deviations in the tested data set, Table 3.1).

The “ideal” low-bandgap polymer energy levels are based on the following requirements: (1) high $E_{HOMO}^{polymer} / E_{LUMO}^{PCBM}$ level offset to promote high $V_{oc}$, (2) low-bandgap for good absorption of the solar spectrum with a high $J_{sc}$, and (3) appropriate $E_{LUMO}^{polymer} / E_{LUMO}^{PCBM}$ level offset (>0.3 eV) for donor-acceptor charge transfer. The PTB polymers compare well to these ideal energy levels and have potential to function well in an OPV device. Relative to a recent high performing low-bandgap polymer, PTB7,\textsuperscript{33} it can be seen that the PTB polymer series displays similar or slightly lower $E_{HOMO}$ levels and lower bandgaps.

### 3.3 Summary of Published Work

The work reported the design, synthesis, and characterization of a new series of thienothiophenebenzodithiophene alternating copolymers with octyl (PT8B), phenyl (PTPB), perfluoroctyl (PTF8B), or perfluorophenyl (PTFPB) side groups on the thienothiophene unit. The phenyl units were found to increase the conjugation area, leading to relatively lower...
bandgaps. The perfluorinated groups increased the electron withdrawing nature of the thienothiophene acceptor unit, decreasing the $E_{HOMO}$ and $E_{LUMO}$ levels and enhancing the calculated $\Delta \mu_{ge}$. The PTB series have good absorption over the visible/near-IR spectrum, strong absorption coefficients, and appropriately aligned energy levels compared to “ideal” polymer energy levels, which should translate to strongly performing electronic materials. Further studies to investigate the effect of perfluorinated groups on the morphology, mobility, and device performance are currently in progress and will be reported upon completion.

### 3.4 Recent Additional Progress

Range-separated hybrid (RSH) functionals attempt to compensate the inaccurate asymptotic exchange behavior in DFT with hybrid functionals. While the models used are not large enough for the DFT inadequacies to influence greatly the predicted properties in the ground-state, the use of RSH functionals in the excited state were found to give good improvement in excited-state computations of ICT behavior, both here (Table 3.5) and elsewhere. The results of using different RSH functionals to model the benchmark systems shown in Figure 3.4 are presented in Table 3.5. While CAM-B3LYP properly reproduces the experimental length dependent trend seen in the DFT benchmark cases (Table 3.5), it still overestimates relative to the experiment numbers. $\omega$B97xD gave numbers much closer to the experimental values, but at significantly increased computational cost. Application of CAM-B3LYP to the PTB series did not have an impact on the relative $\Delta \mu_{ge}$ trend already observed (Table 3.6).

While extending the monomeric models did not have an impact on the trend of $\Delta \mu_{ge}$ in the PTB series (Table 3.4), I found the same did not hold true in comparison to other systems reported in the literature (shown in Figure 3.5). Notably, extending these systems to $n = 2.5$ models resulted in a complete reversal of the reported $\Delta \mu_{ge}$ trend, with the lowest PCEs having the largest computed $\Delta \mu_{ge}$ (Table 3.6). This was found for both non-RSH and RSH functionals (B3LYP and CAM-B3LYP).

The reasoning given in the literature that increased $\Delta \mu_{ge}$ results in decreased germi-
Table 3.5: Establishing DFT baseline with range-separated hybrid functionals on test system. (Figure 3.4).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\Delta \mu_{ge}^{B3LYP}$ (D)$^a$</th>
<th>$\Delta \mu_{ge}^{CAM}$ (D)$^b$</th>
<th>$\Delta \mu_{ge}^{\omega B97xD}$ (D)$^c$</th>
<th>$\Delta \mu_{ge}^{expt}$ (D)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 1</td>
<td>15.58</td>
<td>15.60</td>
<td>11.86</td>
<td>9.5</td>
</tr>
<tr>
<td>n = 2</td>
<td>18.68</td>
<td>11.04</td>
<td>10.80</td>
<td>8.5</td>
</tr>
</tbody>
</table>

$^a$Calculated as described in main text using B3LYP/6-31G(d,p).
$^b$Calculated as described in main text using CAM-B3LYP/6-31G(d,p).
$^c$Calculated as described in main text using $\omega$B97xD/6-31G(d,p).
$^d$Experimental numbers reported by Perry et al.$^{30}$

![Graph](image)

(a) Effect of extension to n = 2.5  
(b) $J_{sc}$ trend for literature series with n = 2.5 $\Delta \mu_{ge}$ numbers

Figure 3.6: Results for range-separated hybrid functional methods with n = 2.5 models of literature series. Data from Table 3.6 and $J_{sc}$ from [2].

Nate recombination was only supported by a relationship to $J_{sc}$ in final devices, and transient absorption spectroscopy showing that PBB3 had long lived exciton states, and short-lived charge-separated states.$^{2}$ Instead, the larger $\Delta \mu_{ge}$ may not be a sign of more well-separated electron and hole that are less likely to recombine, but rather a stabilization of the exciton- and/or charge-transfer state, and/or a destabilization of the charge-separated state (CT and CS respectively in Figure 3.7.

The more stable charge-transfer state will result in a decreased rate of charge-separation, and a likely quicker population of the charge-transfer state from the charge-separation state, which would account for the quicker decay kinetics of the charge-separated state. The longer lived excitonic state could arise from stabilization of the first excited state relative to the
Table 3.6: Comparison of $\Delta \mu_{ge}$ vs. $n$ for literature series [2, 3], and of range-separated hybrid functional use for PTB and literature series.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\Delta \mu_{ge}^{DFT} (D)^a$</th>
<th>$\Delta \mu_{ge}^{CAM} (D)^b$</th>
<th>$J_{sc} (mA/cm^2)$</th>
<th>PCE (%)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBB3</td>
<td>4.12</td>
<td>1.59</td>
<td>6.37</td>
<td>2.04</td>
</tr>
<tr>
<td>PTBF2</td>
<td>13.50</td>
<td>2.58</td>
<td>11.10</td>
<td>3.20</td>
</tr>
<tr>
<td>PTB2</td>
<td>15.70</td>
<td>3.89</td>
<td>14.10</td>
<td>5.10</td>
</tr>
<tr>
<td>PTB7</td>
<td>14.83</td>
<td>3.62</td>
<td>14.50</td>
<td>7.40</td>
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<tr>
<td>PT8B</td>
<td>3.45</td>
<td>0.69</td>
<td>11.5$^d$</td>
<td>3.20$^d$</td>
</tr>
<tr>
<td>PTPB</td>
<td>3.27</td>
<td>0.78</td>
<td>11.0$^d$</td>
<td>2.37$^d$</td>
</tr>
<tr>
<td>PTF8B</td>
<td>5.60</td>
<td>0.97</td>
<td>5.5$^d$</td>
<td>2.35$^d$</td>
</tr>
<tr>
<td>PTFPB</td>
<td>4.85</td>
<td>1.02</td>
<td>12.8$^d$</td>
<td>3.16$^d$</td>
</tr>
</tbody>
</table>

$^a$Calculated as described in main text using B3LYP/6-31G(d,p) on model systems in straight chain conformation.

$^b$Calculated as described in main text using CAM-B3LYP/6-31G(d,p) on model systems in straight chain conformation.

$^c$PCE and $J_{sc}$ reported by Yu et al.$^2$

$^d$PCE and $J_{sc}$ reported by Homyak et al.$^{36}$

charge-transfer state, due to increased intramolecular charge-transfer (ICT) implied by a larger computed $\Delta \mu_{ge}$. Further TDDFT studies might help to support these hypotheses.

Early work in this area argues that $\Delta \mu_{ge}$ of monomeric systems helps show the monomeric behavior of charge-separation.$^2$ However, this does not follow the actual dynamics of conjugated polymers, which do not function as isolated chromophores but as single electronic systems (up to a given persistence length). This inconsistency shows a need for either proof that the approximations made in a monomeric model have a physical justification, or a need for larger models that more accurately describes the actual physics.

Patrick Homyak has recently reported the successful preparation and characterization of optimized photovoltaic devices based on his PTB series.$^{36}$ The devices showed good PCEs over 3%, but the structural variation in the series was the dominant factor in performance differences, and a correlation to $\Delta \mu_{ge}$ could not be gleaned.
Figure 3.7: State diagram showing operation in organic photovoltaics. $G_D^*$: excitation of donor material. D*: excited state of donor material. $k_{\text{relax}}$: charge-transfer from donor to acceptor, and CT: the resulting charge-transfer state. $k_{CS}$ (and $k_{CS}^*$): separation of electron and hole, and CS: the resulting charge-separation state. $k_r$: repopulation of CT state from CS state. Reproduced from Ref. [37] with permission from the Nature Publishing Group.

3.5 References


4.1 Introduction

Increasing photocurrent by decreasing the bandgap in order to absorb more of the solar spectrum has been one of the major advances in organic photovoltaics (OPVs), and the literature has seen a wealth of low-bandgap systems prepared. By far the most accessible and popular method of preparation of low-bandgap systems has been the use of alternating copolymers of an electron-donating push unit, and an electron-withdrawing pull unit. This strategy has resulted in some of the highest efficiency single-junction polymer OPV devices published. This push-pull configuration results in a low-bandgap system in the same way as described previously in Chapter 2, where the final HOMO and LUMO orbital energy levels are predominately contributed from the donor and acceptor respectively. Using a donor with a high $E_{HOMO}$ and an acceptor with a deep $E_{LUMO}$ will result in a low-bandgap system close to this difference between orbital energies of the component modules. This low-bandgap absorbance can provide increased coverage of the solar spectrum and increased photocurrent (see Section 1.2.4 and Figure 1.5).

One other strategy to improve photovoltaic performance that has gained popularity involves adding pendant conjugated units to a donor core. The pendant conjugated units can influence single-chain frontier energy levels, alter $\pi-\pi$ stacking distance, and induce greater order and/or local crystallinity on the overall morphology. The increased amount of order can yield higher charge-carrier mobilities, but tend to have little effect on short-circuit current.

I focused most of my effort on variations with a donor unit that seems surprisingly under-utilized in the OPV literature, 2,5-di(2-thienyl)pyrrole (DTP). The central nitrogen allows one to attach a variety of pendant units, while retaining a symmetrical structure between...
the attachment points on the backbone portion. This eliminates concerns about controlling side-chain regioregularity in a polymer, a major factor in systems such as P3HT.\textsuperscript{15} The need to carefully craft a catalytic system to ensure regioselective polymerization can add much time, effort, and cost to a material’s design, and even can be detrimental to overall yield and degree of polymerization.\textsuperscript{16} Removing regioregularity as a concern lessens the need for complex synthetic strategies, and allows more straightforward methodologies, such as electrochemical polymerization.

The dispersity of the final polymer product is also important, as a larger dispersity tends to lead to a more morphologically disordered sample with lower charge-carrier mobility.\textsuperscript{17} Products with narrow dispersities and well-defined chain-lengths can be achieved through the use of methods such as chain-growth polymerizations. Quasi-living polymerization techniques exist for P3HT, and have been used to prepare well-defined samples.\textsuperscript{16} It is also possible to adapt the synthesis of alternating copolymers to a chain-growth type mechanism,\textsuperscript{18,19} but this approach seems to be rarely used. A more tedious possibility for achieving narrow polymer dispersity, typically only useful on a small laboratory scale, is to fractionate the polymer using preparative GPC, previously reported to achieve various fractions of P3HT with narrow dispersity,\textsuperscript{17} or to exploit changes in solubility with molecular weight–using more marginal solvents to remove lower molecular weight fractions.\textsuperscript{20}

DTP has previously been utilized for novel pendant attachment in fields other than photovoltaics.\textsuperscript{21} Of particular interest was a previous report of DTP with a pendant stable radical, where the radical spin was shown to ferromagnetically couple with spin-bearing radical cations in the main chain if oxidized.\textsuperscript{22} The positive coupling of stable radicals to mobile charge-carriers was envisioned to enable the preparation of spin-polarizing polymers. But, other than this example and some work cited later in this chapter, DTP has not been much utilized. Possibilities for using DTP include relocation of the electron-withdrawing
unit in a push-pull polymer from the backbone to a pendant position on the donor unit. This should prevent the extent of conjugation along the backbone from being interrupted, while still resulting in a low-bandgap system. Such expanded applications of DTP all involve the inclusion of a simpler pendant aromatic unit being attached to the $N$-position. Before evaluation of the influence of these electronically interesting pendants, the effect of a simple pendant aromatic ring containing DTP unit had on morphology and optical/electronic properties needed to be determined. The starting hypothesis was, much like in previous studies on different systems, a pendant phenyl group would impart increased $\pi$-$\pi$ interactions, leading to an increase in charge-carrier mobility and increased probability of formation for charge-carrier pathways to the electrode. This would allow better charge-extraction in OPVs, giving a better fill factor, and hopefully better performing systems overall.

![Scheme 4.1: DTP-benzothiadiazole donor-acceptor copolymer targets for work in this dissertation.](image)

This chapter presents the synthesis and characterization of a series of DTP based donor-acceptor alternating-copolymers to investigate the effect of pendant phenyl attachment through characterization of the morphology and the electronic and optical properties. These are all supplemented with computational modeling of the electronic structure of model oligomers and periodic chains. The systems prepared (Scheme 4.1) include both an $N$-alkyl DTP copolymer with benzothiadiazole (pDT12PocB), and the related $N$-phenyl derivative (pDTP12PcoB). The donor-acceptor nature results in a low-bandgap system that is ideal for single-junction OPV devices (Section 1.2.4). An additional benefit of the phenyl-bearing pendant group is the ease of varying side-chain functionalization.
4.2 Results and Discussion

4.2.1 Synthesis

Monomer DTP synthesis is depicted in Scheme 4.2. All DTP monomers were prepared through variations of Paal-Knorr condensations of dithienylbutane-1,4-dione, which itself was prepared by a modification of Stetter’s original procedure.\textsuperscript{23} Stetter’s method has a lower overall yield than a classic Friedel-Crafts acylation, but is an easier procedure that can be consistently scaled up, and gives products that are more easily purified. \textit{N}-Alkyl DTP monomers were prepared by condensation of the diketone with ammonium acetate to make the dithienylpyrrole, followed by \textit{N}-alkylation with bromoalkanes. Monomers bearing \textit{N}-aryl pendants were prepared by Paal-Knorr condensation with the corresponding aniline.

### Scheme 4.2: Synthetic routes to target DTP monomers.

Paal-Knorr condensations with longer, non-polar alkyl substituted amines and anilines can be challenging due to solubility issues. This condensation also grows more difficult for electron rich thiophenes, perhaps because they reduce the electrophilicity of the 1,4-diketones. For these reasons, Paal-Knorr condensations need a fairly strong electrophilic catalyst to assist them—most literature procedures use a full equivalent of \textit{p}-toluenesulfonic acid (pTSA). While I found this to work well for shorter alkyl chains, such as tolyl and hexyloxyphenyl derivatives, the yields when moving to dodecyloxyphenyl derivatives decreased significantly. The decrease in yield with increased alkyl chain length has been seen previously in the

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The Paal-Knorr condensation requires the removal of water due to the equilibrium nature of the intermediate steps prior to final aromatization. This is typically achieved through either the use of a Dean-Stark apparatus or a hygroscopic solvent such as acetic acid. The longer, non-polar alkyl chains are not soluble in acetic acid and require the addition of toluene to fully solubilize the reactants. Pivalic acid, which has a bulkier and more non-polar substituent, was attempted to remedy the solubility problem while maintaining the hygroscopic behavior of acetic acid, but this variation did not show improved yields. Microwave procedures served only to reduce the reaction time, with no increase in yield. Both classic and microwave procedures yielded a mix of spots on thin-layer chromatography (TLC) and a deep green crude reaction mixture. The deep green color is due to a TLC baseline byproduct that needed to be removed by column chromatography. Other Lewis-acidic catalysts such as various Cu(II) salts and iodine were also tested to increase yield and reduce side-product formation, but were unsuccessful. Cu(II) salts gave no increase in yield relative to using pTSA alone, and iodine only yielded insoluble, TLC baseline products. Possibly, the iodine oxidized any product formed, causing it to polymerize, react, or decompose. In any case, no usable product was recovered.

Serendipitously, I found that adding a full equivalent of PPh₃ not only increased yield, but vastly reduced side-product formation. Attempts to use other nucleophilic catalysts, such as pyridine, did not have the same effect. At least a full equivalent of PPh₃ was needed to produce the best results: catalytic amounts of PPh₃ gave results that closely mirrored those without PPh₃. PPh₃ is also fully consumed, even when using stoichiometric amounts. This set of results suggest occurrence of an oxaphilic condensation, with triphenylphosphine oxide formation as an excellent driving force for the removal of oxygen during condensation. Triphenylphosphine oxide does not move along a silica gel TLC plate and is easily removed by column chromatography. This finding is similar to previous reports of using triphenylphosphinoanhydride salts for the room-temperature condensation of oxadiazoles.²⁵,²⁶

<table>
<thead>
<tr>
<th>Aniline Used</th>
<th>PPh₃</th>
<th>pTSA</th>
<th>Solvent</th>
<th>Method</th>
<th>Notes</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>1 eq</td>
<td>1 eq</td>
<td>Tol:AcOH (10:1)</td>
<td>Dean-Stark</td>
<td></td>
<td>97%</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1 eq</td>
<td>Xylenes</td>
<td>Dean-Stark</td>
<td>extra spots</td>
<td>30%</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>cat. pyridineᵃ</td>
<td>AcOH</td>
<td>MW</td>
<td>garbage</td>
<td>none</td>
</tr>
<tr>
<td>H₃C—O—C₆H₄—NH₂</td>
<td>1 eq</td>
<td>1 eq</td>
<td>Tol:AcOH (10:1)</td>
<td>Dean-Stark</td>
<td>very clean</td>
<td>64%</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>catalyticᵇ</td>
<td>Tol:AcOH(1:1)</td>
<td>MW</td>
<td>extra spots</td>
<td>low</td>
</tr>
<tr>
<td>H₃C—OC₆H₄</td>
<td>1 eq</td>
<td>1 eq</td>
<td>PivOH</td>
<td>MW</td>
<td>clean</td>
<td>48%</td>
</tr>
<tr>
<td>-</td>
<td>1 eq</td>
<td>1 eq</td>
<td>Tol:AcOH(1:1)</td>
<td>MW</td>
<td>clean</td>
<td>50%</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1 eq</td>
<td>Tol</td>
<td>Dean-Stark</td>
<td>extra spots</td>
<td>25%</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1 eq</td>
<td>PivOH</td>
<td>MW</td>
<td>extra spots</td>
<td>17%</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>AcOH</td>
<td>MW</td>
<td>extra spots</td>
<td>20%</td>
</tr>
<tr>
<td>H₃C—OC₆H₄</td>
<td>-</td>
<td>-</td>
<td>AcOH</td>
<td>MW</td>
<td></td>
<td>33%</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1 eq</td>
<td>Xylenes</td>
<td>Dean-Stark</td>
<td>extra spots</td>
<td>12%</td>
</tr>
</tbody>
</table>

ᵃCatalytic amount (3 mol%) of pyridine added.
ᵇPPh₃ existed as contaminant in starting material.
ᶜCatalytic amount (3 mol%) of PPh₃ added.

4.2.1.2 DTP Donor-Acceptor Copolymer Synthesis

My initial goal was to copolymerize DTP monomers with a commercially available electron withdrawing monomer, using a simple straightforward route to copolymers. This would give the ability to easily interchange different DTP monomers or different withdrawing units for the preparation of further copolymers variations. Benzothiadiazole was chosen for its popularity in the literature,²⁷,²⁸ and its interesting electronic properties. The phenyl portion of benzothiadiazole cannot adopt a benzenoid configuration without breaking the aromaticity of the thiadiazole ring. This causes more quinoidal character in the phenyl ring system²⁹ which is responsible for the low-bandgap behavior. The resulting polymers and
Typically, palladium catalyzed cross-coupling favors halides on the electron-withdrawing unit, which increases the rate of the initial oxidative insertion. However, the preparation of stannane and boronic acid derivatives of N-phenyl DTP proved to be difficult. Preparation directly from N-phenyl DTP did not work, due to inability to lithiate N-phenyl DTP with n-butyl lithium (n-BuLi). The preparation of dibrominated DTP was possible under carefully controlled conditions (0°C with very slow addition in THF), and with good purification. The availability of benzothiadiazole-4,7-bis(boronic acid) made Suzuki polymerizations possible. Initially, the dibrominated N-hexyl DTP derivatives and benzothiadiazole diboronic acid were used in polymerizations to prepare DT6PcoB and DTP6PcoB. While this route was feasible, it suffered from multiple problems. The careful dibromination conditions for DTP proved difficult to upscale, benzothiadiazole-4,7-bis(boronic acid) was expensive even in smaller amounts, and the favored polarity of groups for Suzuki coupling is reversed in this approach.

These issues were addressed, and the synthetic route improved, by the adoption of direct-arylation cross-coupling methods. This allowed elimination of one or more synthetic steps, improved atom economy, and the use of commercially cheaper 4-7-dibromobenzothiadiazole.

Direct-arylation is a cross-coupling reaction between catalytically activated aryl C–H
bonds and aryl bromides. The methodology makes use of catalytic cycles shown in Scheme 4.4, and has been much improved in recent work, as described elsewhere.\textsuperscript{30} Thiophenes are particularly amenable to these conditions, especially at the 2,5 positions.\textsuperscript{30} DTP, bearing two flanking thiophenes with available 5-positions, proved very apt for direct arylation polymerization: my work appears to be the first case of using DTP in direct-arylation coupling. This method proved to be extremely convenient and applicable to the preparation of various oligomeric and polymeric species.

A potential problem with direct-arylation is the possibility of activating other aryl C—H bonds, resulting in cross-linked chains and other defects. Typically, the rates of reaction differ between C—H bond sites, so this problem typically will only occur with long reaction times or with very active catalysts.\textsuperscript{30} A cross-linked network would interfere with linear conjugated polymers being able to adopt flat linear conformations and would result in blue-shifts in their UV-Vis spectral onsets, increased morphological disorder detectable by X-ray scattering techniques, and broadened endotherms.\textsuperscript{31} More practically, cross-linking would generate material that is insoluble (or very poorly soluble), so the presence of insoluble material is often taken as evidence of cross-linking.

The behavior of the direct arylation catalysis systems is solvent dependent. It has been
previously reported that more non-polar solvents such as tetrahydrofuran (THF) and toluene worked best with a Pd$_2$dba$_3$/P(o–MeOPh)$_3$/Cs$_2$CO$_3$ system, for which polar solvents like N,N-dimethylformamide (DMF) gave no reaction.\textsuperscript{32} I found this activation system in THF to give very dependable results. More polar solvents such as DMF and N-Methyl-2-pyrrolidone (NMP) seem to work best with a Pd(OAc)$_2$/K$_2$CO$_3$ catalytic system.\textsuperscript{30,33}

Table 4.2: Yields of Soxhlet extraction fractions in polymerization of pDTP12PcoB. conv.: conventional. MW: microwave. nr: no reaction. cont.: contaminated (see end of Section 4.2.1.2). n-Bu$_2$O: n-dibutylether. DCB: 1,2-dichlorobenzene

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Cat.</th>
<th>Method</th>
<th>THF yield</th>
<th>CHCl$_3$ yield</th>
<th>Insoluble</th>
<th>$M_w$ (Da)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>A$^b$</td>
<td>conv.</td>
<td>7%</td>
<td>8%</td>
<td>4%</td>
<td>3500</td>
</tr>
<tr>
<td>THF</td>
<td>A$^a$</td>
<td>MW</td>
<td>19%</td>
<td>11%</td>
<td>5%</td>
<td>3400</td>
</tr>
<tr>
<td>DCB/NMP (2:1)</td>
<td>A$^a$</td>
<td>conv.</td>
<td>nr</td>
<td>nr</td>
<td>nr</td>
<td>-</td>
</tr>
<tr>
<td>n-Bu$_2$O</td>
<td>A$^a$</td>
<td>conv.</td>
<td>nr</td>
<td>nr</td>
<td>nr</td>
<td>-</td>
</tr>
<tr>
<td>NMP</td>
<td>A$^a$</td>
<td>conv.</td>
<td>nr</td>
<td>nr</td>
<td>nr</td>
<td>-</td>
</tr>
<tr>
<td>NMP</td>
<td>B$^c$</td>
<td>MW</td>
<td>cont.</td>
<td>&lt;1%</td>
<td>&lt;1%</td>
<td>-</td>
</tr>
<tr>
<td>Tol:NMP (4:1)</td>
<td>A$^a$</td>
<td>conv.</td>
<td>cont.</td>
<td>&lt;1%</td>
<td>none</td>
<td>-</td>
</tr>
<tr>
<td>Tol:NMP (3:1)$^d$</td>
<td>A</td>
<td>MW</td>
<td>cont.</td>
<td>13%</td>
<td>&lt;1%</td>
<td>5100</td>
</tr>
<tr>
<td>Tol:NMP (1:1)$^d$</td>
<td>B$^c$</td>
<td>MW</td>
<td>cont.</td>
<td>17%</td>
<td>13%</td>
<td>3600</td>
</tr>
</tbody>
</table>

$^a$GPC results of CHCl$_3$ fraction (1,2,4-trichlorobenzene at 135°C vs PS standards).
$^b$A: Pd$_2$(dba)$_3$, P(o–MeOPh)$_3$, PivOH, and CsCO$_3$ in 0.005:0.03:1:3
$^c$B: Pd(OAc)$_2$, P(o–MePh)$_3$, AcOH, K$_2$CO$_3$, and TBAB in 0.005:0.03:1:3:1
$^d$2-octylidodecyld derivative.

In optimizing the reaction conditions to increase yield and molecular weight, two different catalyst systems were used: "A", consisting of Pd$_2$(dba)$_3$, P(o–MeOPh)$_3$, pivalic acid (PivOH), and CsCO$_3$ system, and "B" consisting of palladium (II) acetate (Pd(OAc)$_2$), P(o–MePh)$_3$, acetic acid (AcOH), K$_2$CO$_3$, and tetrabutylammonium bromide (TBAB). Crude yields are not listed in this dissertation, but purified yields of fractions from different purification steps and remaining insoluble solids are reported. Classic and microwave methods were utilized, with the major difference being a significant reduction in reaction time needed for the latter. The results of this optimization are shown in Table 4.2.

All crude polymerizations were purified by precipitation into methanol, and impurities
removed by Soxhlet extraction. Initial attempts used methanol and hexanes to remove polar and non-polar impurities, with the desired material collected by dissolving the remaining solid in CHCl₃. However, these samples gave poor films. GPC showed a disperse and low molecular weight (2.6 – 5.1 × 10³) polymer with some impurities near the flow marker, indicative of molecular or solvent impurities.

The final polymer quality was greatly improved by the addition of two steps to the extraction protocol. Acetone was used after methanol and before hexanes to remove other impurities. After hexanes, THF was used to fractionate the desired polymer, followed by CHCl₃, then by chlorobenzene extraction fractionated the polymer into three relatively narrow dispersity polymer samples (see following Section 4.2.1.3). The chlorobenzene extraction for all copolymers did not yield enough material for use other than GPC characterization. The CHCl₃ fraction for all systems formed nice films and worked well in devices. The exception is pDT12PcoB, which had low yield in the CHCl₃ fraction, and so the THF fraction was used for devices and characterization.

![Figure 4.2: Soxhlet extractor diagram. Public domain image from http://commons.wikimedia.org/wiki/File:Soxhlet_extractor.png.](image)

The fractionation procedure was particularly helpful when using NMP as a solvent or cosolvent in the polymerizations. THF-extracted fractions contained a large amount of a viscous impurity, giving very unrealistic apparent yields and product that remained tacky even after being subjected to high vacuum and gentle heating. These fractions also visibly decomposed overnight at room temperature in sealed containers, changing from the deep blue of the product polymer to a dark brown. NMP was suspected to be the impurity,
however it is absent in the $^1$H NMR. The FTIR spectra of these THF fractions differ greatly from spectra of the pure polymer. Washing the crude polymer sample with excess water in an effort to remove the suspected NMP impurity, did not improve polymer purity or stability. The FTIR spectra of THF fractions of various ages did not differ from one another, including a sample that was freshly extracted and qualitatively showed no visible decomposition. This colorimetrically visible decomposition process may not involve the polymer itself, but rather in formation of a highly colored impurity.

4.2.1.3 Molecular Weight

The poor solubility of the hexyl substituted pDTP6PcoB and pDT6PcoB rendered them almost impossible to process by solvent evaporation. Even simple solvent evaporation onto glass gave cracked films. Accordingly, I switched to using dodecyl substituted variants, at the same time I shifted primarily to using the direct arylation methodology instead of Suzuki coupling. As the results in Table 4.3 show, even these copolymers do not give high molecular weights, and do give some amount of insoluble material that FTIR shows to be structurally very similar to the soluble fractions of the polymers, as discussed below.

**Table 4.3:** Molecular weight of fractionated DTP-alt-benzothiadiazole copolymers. Determined by high temp trichlorobenzene GPC against polystyrene standards.$^a$

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Extraction Solvent</th>
<th>$M_w$ (Da)</th>
<th>D</th>
<th>$X_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pDT12PcoB</td>
<td>THF</td>
<td>2600</td>
<td>1.12</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>CHCl$_3$</td>
<td>5100</td>
<td>1.31</td>
<td>9.6</td>
</tr>
<tr>
<td>pDTP12PcoB</td>
<td>THF</td>
<td>2600</td>
<td>1.37</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>CHCl$_3$</td>
<td>3400</td>
<td>1.27</td>
<td>5.6</td>
</tr>
<tr>
<td>pDTP8.12PcoB</td>
<td>THF</td>
<td>3700</td>
<td>1.27</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>CHCl$_3$</td>
<td>5100</td>
<td>1.26</td>
<td>7.0</td>
</tr>
</tbody>
</table>

$^a$Products from polymerization using the catalytic system “A” under microwave conditions. See the experimental section for more details.

These polymers were relatively short, 5-10 repeat units long for the weight-average chains. The low molecular weight of the benzothiadiazole alternating copolymers and the
isolated insoluble solid fraction obtained raises concerns over the possible presence of cross-linking. Interestingly, a previous preparation of pDT12PcoB by Janssen et al.\textsuperscript{34} utilizing Stille coupling yielded a similarly low molecular weight polymer described as having low solubility. Comparison between these results shows comparable yields and molecular weights, similar UV-Vis spectra and onsets, and similar redox potentials. $^1$H NMR of the polymers also match, with no visible evidence of cross-linking. Thus, if cross-linking could occur with DTP in direct-arylation, my ability to make substantial product using longer reaction times make major amounts of cross-linking unlikely: the low solubility of longer pDT12PcoB seems likely to have caused the polymer to precipitate before cross-linking could occur.

With cross-linking unlikely, and reaction condition variation giving no improvement on molecular weight (Table 4.2), solubility is likely the problem in obtaining longer chains. This is supported by extraction of higher weight fractions using chlorobenzene, but this new fraction for pDTP12PcoB only has a molecular weight of 4200 Da (D: 1.16, $X_w$: 6.7), large change in solubility for a slight increase in chain length. Again, the FTIR of the remaining insoluble portion matches well with the spectrum from the CHCl\textsubscript{3} fraction (Figure 4.3), consistent with the insoluble portion being mostly longer chains.

![Figure 4.3: ATR-FTIR spectra of pDTP12PcoB powder and the solid remaining after extraction.](image)

The replacement of hexyl with dodecyl yielded materials that were processible despite modest changes in molecular weight. Even the use of the large branching side-chain, 2-
octyldodecyl, yielded modest increase in molecular weight. The lack of influence of the solubilizing chain identity on molecular weight (despite the increase in processibility), and the large changes in solubility with small changes in chain length could be the result of an extremely rigid backbone. This is further investigated in the following sections.

4.2.2 DTP Copolymer Properties

4.2.2.1 Optical properties

As mentioned in Section 4.1, one goal for the copolymer series was preparation of a low-bandgap polymer, ideally one that absorbed around 500-900 nm, and with an $E_{\text{HOMO}}$ level around -5.3 eV. This gives the “ideal” $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ levels (-5.3 eV, -3.8 eV) for photovoltaic devices with PC$_{71}$BM (as discussed in Section 1.2.4).

Solution and solid state absorbance spectra in Figure 4.4 show the low-bandgap absorbance of the DTP-alt-benzothiadiazole copolymers in the visible region. The solid film spectra show redshifting and broadening of low energy absorbance peaks relative to solution phase spectra, a phenomenon typically associated with $\pi$-stacking and related local environment conditions. In the solid state, all three polymers have similar absorbance onsets of 1.67-1.70 eV, which in this dissertation will be considered to be their [optical] bandgap. The similarity is not surprising given their similar electronic structure. As will be shown in the next section, the onset of the longer wavelength band is not influenced by the pendant units, and thus should be independent between pDT12PcoB and pDTP1PcoB.

The solution absorptivities (M/cm per repeat unit) and the film absorption coefficients (1/cm by film thickness, determined by profilometry) show only minute difference in magnitude between the $N$-phenyl and the $N$-alkyl systems. All of these copolymers show large film absorption coefficients, $4.0 - 4.6 \times 10^4$, on the same order as reported for P3HT, $6 \times 10^4$ for the long wavelength band.$^{35}$ The observed low-bandgap absorbance, seen in Figure 4.4b, is in a good range with regard to the original plan for these systems. While the addition of $N$-phenyl units did not negatively impact the optical properties, it did fail to increase absorptivity.

The more blue-shifted onset of pDT12PcoB in the solution phase relative to both $N$-
Figure 4.4: UV-Vis spectra of DTP-alt-benzothiadiazole copolymers. a) 5.8 µg/mL in DCB. b) spin-coated films from 15 mg/mL DCB solutions at 1500 rpm, scaled by thickness.

Figure 4.5: Comparison of solution and film spectra for pDTP12PcoB and pDT12PcoB.

phenyl derivatives is quite notable. The possibility that pDT12PcoB has a larger amount of π-stacking in the solid state does not fit the observed, matching onsets in the solid-state spectra, thus the difference between N-alkyl and N-phenyl copolymers must be bigger in the solution phase than in the solid state. The dilute solution phase spectra of the N-phenyl derivatives exhibit broad peaks with weak but noticeable shoulders, whereas the dilute N-alkyl is does not.

Interestingly, the absorptivity of the DTP-alt-benzothiadiazole copolymers as a function of concentration (Figure 4.6) shows a larger deviation from Beer-Lambert behavior in the N-alkyl derivative versus both N-phenyl copolymers. The greater deviation in pDT12PcoB is consistent with greater geometrical changes upon aggregation of N-alkyl, since aggregation causes peak broadening and a decrease in absorptivity at $\lambda_{\text{max}}$. This is also supported
Figure 4.6: Absorbance spectra of DTP-alt-benzothiadiazole copolymers at various concentrations in DCB. a) pDT12PcoB b) pDTP12PcoB c) pDTP8.12PcoB, and d) relative intensity of peak as a function of concentration (by repeat unit).

by the qualitative shapes of the spectra upon increasing concentration. From low to high concentration the shape of the long wavelength band in the \(N\)-phenyl systems remain broad with evidence of shoulders, but the \(N\)-alkyl system shows red-shifting, broadening, and shoulder formation with increasing concentration. This seems to imply that the \(N\)-phenyl systems are more rigid than the \(N\)-alkyl ones, and more likely to retain a coplanar geometry in solution. The increased rigidity would reduce the amount of bond-rotation that would cause decreased conjugation, thus resulting in some less blue-shifted solution spectral contributions. This hypothesis I explored further in work described in Section 4.2.3.
Figure 4.7: Frontier orbital energy and vacuum levels of DTP-alt-benzothiadiazole copolymers. Top bars are vacuum levels of films relative to PEDOT:PSS on ITO coated glass. Numbers next to bands are energy levels determined by CV (UPS numbers in parentheses). UPS numbers determined from samples on PEDOT:PSS coated ITO. PC$_{71}$BM numbers taken from reference [36].

4.2.2.2 Experimental Frontier energy levels in DTP-Containing Copolymers

Cyclic voltammetry (CV) of dropcast polymer films can give the oxidation and reduction behavior and, when taken with respect to the ferrocene/ferrocenium (Fc/Fc$^+$) redox potential, can be related to the HOMO and LUMO energy levels respectively, using the formula $E_{MO} = -(E_{\text{redox}} + 4.8) eV$. This relates the redox potential to the vacuum energy of ferrocene.$^{37}$ This is a quick and versatile method, but does rely on assumptions about solution behavior. Ultraviolet photoelectron spectroscopy (UPS) can give $E_{HOMO}$ directly under conditions quite close to those in a photovoltaic device, as well as density of states and vacuum level of the solid material. For UPS, where only occupied states can be measured, or when electron affinity cannot be obtained from CV, the optical bandgap can be used to estimate $E_{LUMO}$ as the offset of the bandgap from $E_{HOMO}$; assuming the electronic bandgap is equivalent to the optical bandgap, the onset of absorbance in UV-Vis can be used to estimate $E_{HOMO} - E_{LUMO}$. Determination of these frontier orbital levels is important for predicting and rationalizing observed photovoltaic performance metrics, such as the maximum possible open-circuit potential, and the feasibility of charge-transfer to the
acceptor phase occurring: see the details discussed in Section 1.2.4.

Figure 4.8: Cyclic voltammograms of DTP-alt-benzothiadiazole copolymer films. Films dropcast from CHCl₃ onto Pt disk electrode, and run in acetonitrile (100 mV/s) as described in Section 6.2. a) pDT12PcoB, b) DTP12PcoB, and c) pDTP8.12PcoB.

$E_{HOMO}$ and $E_{LUMO}$ were determined for the copolymers using both dropcast film CV and UPS of samples (spin-coated from 10 mg/mL solutions in 1,2-dichlorobenzene) on PE-DOT:PSS coated ITO glass substrates. CV did not give a reduction signal, so $E_{LUMO}$ was estimated as the offset from $E_{HOMO}$ using the experimental optical bandgaps (the optical spectral onsets). These data are summarized in Figure 4.7. Interestingly, the $N$-phenyl polymer has an increased $E_{HOMO}$ relative to the $N$-alkyl, although previous studies report pendant aromatic groups to give lower $E_{HOMO}$. As described below, this behavior for pDT12PcoB and pDTP12PcoB is reproduced in the computational results comparing $N$-alkyl and $N$-phenyl single chains, indicating that this is purely a single-chain electronic
UPS also showed that pDT12PcoB has a lower vacuum level than either N-phenyl derivative relative to PEDOT:PSS on ITO coated glass. This means pDT12PcoB can form a larger interfacial dipole moment with the substrate, resulting in a large internal electric field that will assist with charge-separation and charge extraction.\textsuperscript{38}

### 4.2.2.3 Computational Modeling of D-A Polymer Geometric and Electronic Properties

The experimental results for the electronic absorption spectra of the DTP copolymers were supplemented with computational modeling of the electronic structure of model oligomers and periodic chains. The majority of the computations were performed using Gaussian 09\textsuperscript{39} to model the single chain electronic structure of the polymers using model structures, typically monomeric (n = 1), dimeric (n = 2), and n = 2.5. For most computations, optimized geometries were found using the default routines in Gaussian at the B3LYP/6-31G(d,p) level. Use of other functionals did not yield large differences in geometry and, as seen in Chapter 2, gave frontier orbital energy levels that reproduce the trends in experimental results while still completing in reasonable computational time. All systems were modeled in
vacuo with no solvent interaction effects. Frontier molecular orbital energy levels were taken directly from the ground state electronic structure results. While the accuracy of virtual orbital energy levels using Kohn-Sham orbitals is limited, the relative energy level trends were good enough for comparative purposes, as in Chapter 2. All molecular orbital and surface renderings were modeled in Avogadro\textsuperscript{40,41} using the POVray export option. Band structures of infinitely long single chains were computed by Prof. Bryan Wong (UC Riverside) in collaboration with our group.

Table 4.4: Comparison of experimental and computational orbital energy levels for various DTP polymers. Computations performed on dimeric systems at B3LYP/6-31(d,p).

<table>
<thead>
<tr>
<th>System</th>
<th>$E_{HOMO}$ (eV)</th>
<th>$E_{LUMO}$ (eV)</th>
<th>Expt – Comp</th>
<th>Expt – Comp</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>expt.</td>
<td>[comp.]</td>
<td>(eV)</td>
<td>expt.</td>
</tr>
<tr>
<td>pDT6P</td>
<td>-5.29 [-4.65]</td>
<td>0.64</td>
<td>-3.05 [-1.71]</td>
<td>1.34</td>
</tr>
<tr>
<td>pDTP6P</td>
<td>-5.15 [-4.42]</td>
<td>0.74</td>
<td>-2.72 [-1.72]</td>
<td>1.00</td>
</tr>
<tr>
<td>pDTB10P</td>
<td>-5.13 [-4.40]</td>
<td>0.73</td>
<td>-2.89 [-1.92]</td>
<td>0.97</td>
</tr>
<tr>
<td>pDT12PocB</td>
<td>-5.23 [-4.65]</td>
<td>0.58</td>
<td>-3.52 [-2.65]</td>
<td>0.87</td>
</tr>
<tr>
<td>pDTP12PcpB</td>
<td>-5.10 [-4.41]</td>
<td>0.69</td>
<td>-3.45 [-2.54]</td>
<td>0.91</td>
</tr>
<tr>
<td>Avg ±stddev:</td>
<td>0.68 ±0.06</td>
<td>1.01 ±0.18 eV</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The voltammetric experimental $E_{HOMO}$ and $E_{LUMO}$ were correlated with computationally predicted energy levels to establish a fairly accurate trend (empirical offsets HOMOs: -0.68 ±0.06 eV, LUMOs: -1.01 ± 0.18 eV, average across the series with the standard deviation of the differences as in Table 4.4). Interestingly, forcing a computationally planar structure does not change the predicted energy levels, so the experimental difference in MO energy levels is not due to moderate differences in conformation. The raised $E_{HOMO}$ of pDTP12PcoB is computationally reproduced on the single chains, thus it must be an electronic effect. However, the HOMO molecular orbital also has no density on the pendant portions, so the effect must be inductive in nature, similar to that described in Chapter 3 from aryl substitution. Molecular orbital density maps (Figure 4.10) show that the lower lying orbitals have some density delocalized onto the pendant rings, which may account for the differences in higher energy absorption band position between pDT12PcoB.
and pDTP12PcoB.

Figure 4.10: HOMO/LUMO orbital maps of the model structures for pDT12PcoB and pDTP12PcoB. Performed at B3LYP/6-31G(d,p).

The band structure computations of infinitely long chain models provide data more comparable to the actual polymers. The computations, seen in Figure 4.11, give accurate bandgap predictions, and allow quick comparison of the electronic band structure of the N-alkyl and N-phenyl systems. The only difference is a shifting of pDTP12PcoB bands to slightly higher energy, and introduction of new narrow conduction and valence bands around -0.4 and -6.4 eV. This arises from the pendant phenyl group, and do not mix with other bands, hence the band narrowness. The similarity is also confirmed in HOMO/LUMO orbital density maps of the two systems, as shown in Figure 4.10.

Excited state behavior was modeled using time-dependent DFT (TDDFT), with either 3, 6, or 9 excited states. A majority of the TDDFT computations also used B3LYP/6-31G(d,p), but some were repeated using a range-separated hybrid (RSH) functional (CAM-B3LYP). RSH functionals compensate for inaccurate asymptotic exchange behavior in DFT with hybrid functionals.42–45 While my systems are not large enough to cause significant errors in
the ground state when using B3LYP, TDDFT drastically underestimated transition energies for the dimeric models. This is a common problem when using TDDFT with traditional hybrid functionals,\textsuperscript{42–45} and thus the dimeric models were repeated using an RSH function, with the results shown in Figure 4.12b.

**Figure 4.11:** Computed band structures of DTP-alt-benzothiadiazole copolymer series (Bryan Wong–UC Riverside).

**Figure 4.12:** Predicted transition energies of pDT12PcoB and pDTP12PcoB imposed over experimental solution spectra. a) n = 1 (B3LYP/6-31G(d,p)), and b) n = 2.5 models (CAM-B3LYP/6-31G(d,p)).

TDDFT of monomeric and n = 2.5 systems were performed, but the monomeric systems alone were sufficient to predict the two major transitions (Figure 4.12a). The computational results concur with experiments in giving pDTP12PcoB and pDT1PcoB with similar optical bandgaps and with a lack of influence by the pendant on the single-chain absorbance. The higher energy bands do not differ significantly in predicted position between the two systems.
There are other transitions involving these orbitals that do differ more significantly in band position, but their oscillator strength is extremely low, and thus would not contribute in the single isolated chains.

Table 4.5: Major transitions in \( n = 1 \) systems for pDT12PcoB.

<table>
<thead>
<tr>
<th></th>
<th>Weight</th>
<th>Energy (eV)</th>
<th>( f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO → LUMO</td>
<td>0.50</td>
<td>2.19</td>
<td>0.32</td>
</tr>
<tr>
<td>HOMO-1 → LUMO+1</td>
<td>0.48</td>
<td>3.37</td>
<td>0.78</td>
</tr>
</tbody>
</table>

Table 4.6: Major transitions in \( n = 1 \) systems for pDTP12PcoB.

<table>
<thead>
<tr>
<th></th>
<th>Weight</th>
<th>Energy (eV)</th>
<th>( f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO → LUMO</td>
<td>0.50</td>
<td>2.16</td>
<td>0.31</td>
</tr>
<tr>
<td>HOMO-1 → LUMO+1</td>
<td>0.48</td>
<td>3.36</td>
<td>0.80</td>
</tr>
</tbody>
</table>

For my systems, the B3LYP computations showed large amounts of ICT character, due to large contribution from more isolated orbitals to yield unrealistically large ICT behavior. The addition of RSH functionals resulted in more orbitals in the configuration interaction that resulted in a more suppressed ICT character, and transition energies much close to experimental \( \lambda_{\text{max}} \) (Figure 4.12b). The small size of the monomeric models likely creates
a screening effect, which balances out the error from not using RSH functionals.

4.2.3 Computational Modeling of DTP Copolymer Conformational Potential Energy Surfaces

The large quinoidal character in the benzothiadiazole unit could be the cause of solubility-limiting rigidity of some of the DTP copolymers, due to the increased amount of double bond character in the inter-ring bonds. This hypothesis is supported by extensive literature evidence for solubility induced low molecular weights in benzothiadiazole-containing polymers, shown in Table 4.7. The strong trend shows systems that have no side-chain in the 3-position of the flanking thiophene rings are almost consistently low molecular weight systems (<7K g/mol), whereas those with side-chains in the 3-position that will sterically hinder the benzothiadiazole from laying coplanar are consistently very high molecular weight systems.

This is not the case with benzotriazole, where reported polymers are consistently higher molecular weight systems, even without sterically hindering 3-position substituents.\textsuperscript{56–58}

Considering the decreased aromaticity of the triazole ring, and the larger amount of benzenoid character in the benzene ring,\textsuperscript{29,59} it follows the trend that benzotriazole should have decreased quinoidal character.

To study this, I attempted to characterize the rigidity of the subunits using potential energy surfaces about the bond-rotation axes, and relate this to the solubility trends seen. The rigidity of model systems was predicted by generating the potential energy surface (PES) along a bond rotation pseudo-reaction coordinate between different aromatic rings. This was carried out as a relaxed potential energy surface scan, where the system is optimized at each fixed torsional angle. The height of the barrier to rotation, barrier curvature, and relative energy of the minima can be related to the rigidity of the system. The barrier height is the activation energy needed to rotate about the bond, the barrier curvature will affect the rigidity of deviation from a minima, and the relative energy between minima will affect the Boltzmann distribution between two conformers. A similar and more in-depth computational study was recently published to determine the likely conformation of a polythiophene system.\textsuperscript{60} Additional studies have also used a similar approach to predict the
Table 4.7: Reported molecular weights for various benzothiadiazole copolymers.

<table>
<thead>
<tr>
<th>System</th>
<th>$M_w$ (kDa)</th>
<th>ref</th>
<th>System</th>
<th>$M_w$ (kDa)</th>
<th>ref</th>
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<td>31.2</td>
<td>[47]</td>
</tr>
<tr>
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<td>[48]</td>
<td><img src="image4" alt="System 4" /></td>
<td>65.3</td>
<td>[49]</td>
</tr>
<tr>
<td><img src="image5" alt="System 5" /></td>
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<td>[50]</td>
<td><img src="image6" alt="System 6" /></td>
<td>260.0</td>
<td>[51]</td>
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<tr>
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<td>[52]</td>
<td><img src="image8" alt="System 8" /></td>
<td>43.0</td>
<td>[53]</td>
</tr>
<tr>
<td><img src="image9" alt="System 9" /></td>
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<td>[49]</td>
<td><img src="image10" alt="System 10" /></td>
<td>56.1</td>
<td>[54]</td>
</tr>
<tr>
<td><img src="image11" alt="System 11" /></td>
<td>2.4</td>
<td>[34]</td>
<td><img src="image12" alt="System 12" /></td>
<td>11.5</td>
<td>[54]</td>
</tr>
<tr>
<td><img src="image13" alt="System 13" /></td>
<td>2.7</td>
<td>[49]</td>
<td><img src="image14" alt="System 14" /></td>
<td>23.0</td>
<td>[46]</td>
</tr>
<tr>
<td><img src="image15" alt="System 15" /></td>
<td>6.9</td>
<td>[49]</td>
<td><img src="image16" alt="System 16" /></td>
<td>4.8</td>
<td>[55]</td>
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<tr>
<td><img src="image17" alt="System 17" /></td>
<td>5.8</td>
<td>[48]</td>
<td><img src="image18" alt="System 18" /></td>
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<tr>
<td><img src="image19" alt="System 19" /></td>
<td>2.3</td>
<td>[48]</td>
<td><img src="image20" alt="System 20" /></td>
<td>9.4</td>
<td>[48]</td>
</tr>
<tr>
<td><img src="image21" alt="System 21" /></td>
<td>2.8</td>
<td>[49]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
relative rigidity of different excited states,\textsuperscript{61} or the effect of substituents in bithiophene.\textsuperscript{62}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure}
\caption{PES scan around indicated bond rotation for terthiophene structures. Performed at B3LYP/6-31G(d,p).}
\end{figure}

To calibrate this technique, I used terthiophene control model structures and found the expected results: inclusion of methyl groups, as shown in Figure 4.14 (to mimic regioregularity in P3HT), decreases the barrier to rotation, and brings the conformational minima closer in energy. For comparative purposes, the energies are plotted as the difference from the lowest energy state, so no enthalpic energy differences between the methylated and non-methylated models are considered. Relating this directly to solubility is difficult as 3-alkylthiophenes as a class of materials do not begin to become soluble until the chains are butyl or larger.\textsuperscript{63,64}

A similar and more exaggerated effect can be seen in the DTP systems. While $N$-hydro DTP has a curve similar to terthiophene, $N$-ethyl DTP not only has severely reduced rotational barriers (on the order of $kT$ at room temperature), but also has additional barriers at 0° and 180°. This means $N$-ethyl DTP will not only remain perturbed from being co-planar, but will likely rotate and should therefore be more soluble. $N$-Phenyl DTP shares similar positions of minima and barriers with $N$-ethyl, however the rotational barriers are much higher, closer to those in $N$-hydro DTP, and with much steeper barrier curvatures. Therefore, $N$-phenyl DTP should be more rigid and less prone to bond rotation and essentially locked into a planar conformation. This difference in rigidity between the systems is a likely culprit for the solubility difference between pDT12PcoB and pDTP12PcoB.

The results of these methods applied to dithienyl benzothiadiazole, dithienyl benzene,
and dithienyl benzotriazole are shown in Figure 4.14b. Relative to dithienylbenzene, dithienylbenzothiadiazole has a larger barrier to rotation with minima at 0, 180, and 360°, where as dithienylbenzene does not. The difference in energy between the 0° and 180° states could be due to hydrogen bonding or simply sterics. However, the PES scan of benzothiadiazole and benzotriazole shows little difference in the barrier heights, and actually shows a more stable 180° state.

While benzotriazole itself has more aromatic character in the benzenoid ring, I found that these model systems do not show increased quinoidal character in their bond lengths, bond-orders, or electron density along the backbone bonds. Extending to longer model systems does not change this, and PES scans for other inter-ring bonds show the same trends. Benzothiadiazole and benzotriazole chains are equally as rigid, and so chain rigidity is likely not the source of the limited solubility in the DTP-alt-benzothiadiazole copolymers.

The source of solubility problems is rooted in the benzothiadiazole unit (since I found that experimentally incorporating an alkylated dipyrrlopyrrole in place of benzothiadiazole gives much better solubility, see Section 4.2.5). It could be the interaction of the unit with the solvent, and the reason the sterically interfering substituents increase solubility is by blocking access of the solvent to the benzothiadiazole. Benzotriazole, with a smaller dipole moment, and more non-polar 2-position attachment, could much better compatibility with solvent and more easily solubilized. This also fits the case of the outliers in the molecular weight trend of Table 4.7, where the longer non-benzothiadiazole portions dilute the amount
of unfavorable interactions with solvent and thus are more easily solubilized.

4.2.3.1 Deducing Chain Rigidity in DTP-Copolymers

Although the computational PES studies do not show rigidity as causing DTP copolymer solubility problems, they do show a large difference in rigidity of the $N$-alkyl and $N$-phenyl DTP systems. This is consistent experimentally with the absorbance data, previously shown in Figure 4.6, suggesting the $N$-alkyl systems undergo a larger geometrical change in solution than $N$-phenyl, likely due to a decreased rigidity. This is further supported with photoluminescence (PL) measurements done on highly diluted solutions. The Stokes shift of the spectral data can be related to the chromophore rigidity, as a larger stokes shift indicates larger geometrical changes between the excited and ground states. The quinoidal character of the excited states for these systems implies this geometrically would favor a coplanar conformation, and larger shifts would indicate larger deviations from this geometry. Since pDT12PcoB has the largest Stokes shift (512 meV), it must have the largest geometry change and thus the least rigid ground state. Since the PL spectra for all three DTP polymers virtually overlap, the difference in Stokes shift comes solely from the more blue-shifted absorbance of pDT12PcoB in solution.

4.2.4 Photovoltaic Devices with DTP-Copolymer Active Layers

4.2.4.1 Morphology

The morphologies of the DTP-alt-benzothiadiazole copolymers were studied with a variety of diffraction techniques, and their topologies probed with conducting AFM. Powder XRD of dropcast films was obtained to give an idea of order, while transmission electron microscopy (TEM) and grazing incidence wide-angle x-ray scattering (GIWAXS) gave more detailed information. TEM was carried out by Dr. Lang Wei from the Lahti group, and GIWAXS was carried out by Dr. Xiaobo Shen from the Russell group.

Powder XRD required thick dropcast films in order to give adequate diffraction strength for any analysis. Spin-coated films, while similar to device preparation conditions, were too thin to give any measurable signal. Grazing incidence X-ray diffraction (GIXRD),
where the source is fixed at a large-angle so that the beam only interacts with the surface, was attempted to increase the signal, but did not effectively diffract with the spin-coated films. The gonio-scan XRD of pDTP12PcoB, Figure 4.16a, shows a broad diffraction peak corresponding to a d-spacing of 6.8 Å, while pDT12PcoB shows only background from the glass substrate. Interestingly, GIXRD (Figure 4.16b) shows a new diffraction peak, once again only in pDTP12PcoB, with a d-spacing of 28.5 Å. This is close to the length of a dodecyl chain, and is likely to arise from a lamellar type packing. Overall, in dropcast films it appears that pDTP12PcoB orders more readily than pDT12PcoB.

TEM diffraction using dropcast films on graphite coated copper mesh, Figure 4.17, shows diffraction in both pDT12PcoB and pDTP12PcoB films. In pDT12PcoB, there is a diffraction spot on a ring corresponding to a d-spacing of 3.7 Å, which is consistent with a π-π
stacking distance. pDTP12PcoB shows a spot with d-spacing of 6.7 Å (likely the same contact seen previously in the powder XRD, Figure 4.16), and another a d-spacing of 4.8 Å. Both d-spacings are fairly large for a π-π stacking interaction. Possibly the N-phenyl substituent has increased the π-π stacking distance in the backbone of the polymer, or the 6.7 Å spacing is an alternating repeat stacking for the backbone. In either case, the presence of sharper diffraction spots and numerous higher-order diffraction spots for pDTP12PcoB are both signs of more regular crystallites in larger proportions than in pDT12PcoB.

GIWAXS of annealed spin-coated films on PEDOT:PSS coated silicon wafers for pDT12PcoB, Figure 4.18a, shows a very strong out-of-plane diffraction with a d-spacing of 28.3 Å and associated second and third order peaks, plus a weaker but narrow in-plane diffraction peak with a 3.7 Å d-spacing. The spacing and plane-orientation of the diffractions fit well with the evidence from the other scattering experiments that suggests lamellar and π-π stacking respectively: the orientation dependence indicates the polymers chains lie on the substrate in an edge-on orientation. In contrast, pDTP12PcoB has a strong, but broad out-of-plane GIWAXS peak with a 4.8 Å d-spacing, which corresponds with the TEM results. If this is indeed a π-π stacking peak, pDTP12PcoB must be oriented in a predominately face-on orientation relative to the substrate, but the broad nature of the peak and the circular diffraction pattern indicate that the film contains many small crystallites with random orientation. The lack of an observed lamellar peak suggests the crystallites to be π-π
stacked aggregates without regular lamellar sheet formations. A schematic representation of the proposed morphologies of pDT12PcoB and pDTP12PcoB is shown in Figure 4.19. Blended films of the copolymers and PC$_{71}$BM (1:1.1 w/w) were also tested by GIWAXS (Figure 4.18c,d) and found to resemble the pure polymer films, with the superposition of a diffuse PC$_{71}$BM peak over the polymer signal. Therefore, the addition of fullerene does not perturb the polymer crystallites, or produce new nanostructures.

The difference in vacuum levels seen in the UPS of the N-alkyl versus N-phenyl polymer films (described previously in Section 4.2.2.2) could be due to the different orientation of the polymers on the substrate. An edge on orientation would allow access of the thiophene sulfur to the surface for a larger interfacial dipole moment to form. However, the face-on orientation of pDTP12PcoB would seem to be more favorable in devices, since the π-π stacking direction perpendicular to the substrate is the predominant interchain charge-carrier hopping pathway in solar cells.

pDTP8.12PcoB, the copolymer with a branching side-chain, consistently showed no diffraction peaks in any of the above measurements. Despite the presence of more pronounced shoulders in its solid film UV-Vis absorbance (described previously in Section 4.2.2.1), there are no regular repeating structures to cause diffraction. This amorphous aggregation presumably is the cause of its degraded device performance, described in the
Figure 4.18: GIWAXS diffraction of DTP-alt-benzothiadiazole copolymer films. Showing a) neat pDT12PcoB, b) neat pDTP12PcoB, c) pDT12PcoB and PC$_{71}$BM (1:1.1 w/w), and d) pDTP12PcoB and PC$_{71}$BM (1:1.1 w/w). Films on PEDOT:PSS coated silicon wafers. Courtesy of X. Shen.

4.2.4.2 Photovoltaic Performance of DTP-Containing Copolymers

Table 4.8: Photovoltaic device preparation conditions for DTP-alt-benzothiadiazole copolymers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Donor (mg/mL)</th>
<th>PC$_{71}$BM (mg/mL)</th>
<th>RPM</th>
<th>Annealing (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pDT12PcoB</td>
<td>18</td>
<td>20</td>
<td>2500</td>
<td>5 min</td>
</tr>
<tr>
<td>pDTP12PcoB</td>
<td>12</td>
<td>14</td>
<td>1000</td>
<td>15 min</td>
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</tbody>
</table>

Photovoltaic devices of pDT12PcoB, pDTP12PcoB, and pDTP8.12PcoB were prepared and optimized by Dr. Lang Wei (preparation described in Section 6.2). The polymers were readily soluble in chlorobenzene, but the solutions had low viscosity, and care was needed to optimize the film thickness for best power conversion efficiency (PCE). A brief period of annealing was needed to maximize performance in pDT12PcoB and pDTP12PcoB, but...
while pDTP12PcoB was not negatively affected by longer annealing times, pDT12PcoB was found to decrease in performance if annealed for longer than 5 min, despite the increase upon initial annealing. Given the rigid nature of pDTP12PcoB, it is likely pDT12PcoB undergoes reorganization more readily and phase-separates to a greater degree.

Table 4.9: Photovoltaic performance of devices with DTP-alt-benzothiadiazole copolymers. Average device performance was taken from 10 effective devices, aside from DTP8.12PcoB which is the best achieved.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$V_{oc}$ [σ] (V)</th>
<th>$J_{sc}$ [σ] (mA/cm$^2$)</th>
<th>FF [σ] (%)</th>
<th>PCE [σ] (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pDT12PcoB</td>
<td>0.70 [0.01]</td>
<td>10.87 [0.44]</td>
<td>66.56 [1.08]</td>
<td>4.99 [0.08]</td>
</tr>
<tr>
<td>pDTP12PcoB</td>
<td>0.49 [0.01]</td>
<td>11.03 [0.54]</td>
<td>60.75 [0.43]</td>
<td>3.39 [0.14]</td>
</tr>
<tr>
<td>pDTP8.12PcoB</td>
<td>0.54</td>
<td>6.81</td>
<td>37.67</td>
<td>1.38</td>
</tr>
</tbody>
</table>

Once optimized preparation conditions were found, device performance was found to be very reproducible and consistent. The optimized performance results are shown in Table 4.9, and the best $I-V$ curves shown in Figure 4.20. Both short-circuit current ($J_{sc}$) and fill-factor (FF) were found to be high for both pDT12PcoB and pDTP12PcoB, both close to values reported for high performance PTB7 based devices. The difference in performance is due to difference in the open-circuit voltage ($V_{oc}$), where pDT12PcoB has a 0.2 V larger $V_{oc}$. This 0.2 V difference is consistent with the difference in $E_{HOMO}$ between the two systems, and the $V_{oc}$ for both are close to the maximum theoretical $V_{oc}$, 0.70 and 0.50 V for pDT12PcoB and pDTP12PcoB respectively (taken as $E_{LUMO}^{acceptor} - E_{HOMO}^{donor}$ using UPS numbers shown in Figure 4.7). This strongly suggests the difference in $V_{oc}$ between the materials arises.
purely from inherent energy level differences between the two, and not due to morphological differences.

![I-V curves for DTP-alt-benzothiadiazole copolymers as highest performing devices prepared by Dr. Lang Wei.](image)

**Figure 4.20:** I-V curves for DTP-alt-benzothiadiazole copolymers as highest performing devices prepared by Dr. Lang Wei.

In principle, the benefits of the interfacial dipole moment in pDT12PcoB and the face-on orientation of pDTP12PcoB could be a trade-off that accidentally imbues both systems with similar fill-factors performance. The external quantum efficiency (EQE) data shows that pDT12PcoB has larger efficiency near the neat polymer $\lambda_{\text{max}}$, while pDTP12PcoB has a broader wavelength range that has a more consistent intensity. The N-phenyl systems seem to be more efficient at harvesting the band-edge photons, consistent with their observed tendency to $\pi$-$\pi$ stack more.

Interestingly, the branched side-chain variant pDTP8.12PcoB has a $V_{oc}$ equal to that of its electronically equivalent pDTP12PcoB, but with a vastly lower $J_{sc}$ and FF. This fits with the amorphous nature of pDTP8.12PcoB, which is likely not to provide as many conducting pathways for charge carriers to move easily for longer distances, thus increasing the series resistance. The absorptivity and EQE of the pDTP8.12PcoB films in comparison to pDTP12PcoB support this. Since the same number of photons are absorbed by equivalent films of the two polymers, they should generate the same number of excitons, but the EQE is significantly lower for pDTP8.12PcoB.
4.2.5 Variants of the DTP Polymers

The low solubility and modest absorbance of the benzothiadiazole copolymers led to the exploration of replacing the acceptor unit with electronically appropriate alternatives. Raymond Devaughn of the Lahti group developed methodology to replace benzothiadiazole with diketopyrrolopyrrole (DPP), specifically with 3,6-di(2-thienyl)-2,5-didecylpyrrolo[3,4-c]pyrrole-1,4-dione. This allowed an easy substitution of benzothiadiazole with the same direct-arylation methods.

The resulting polymer pDTP12PcoDPP10, had a substantial molecular weight of $21.5 \times 10^3$ g/mol and a dispersity of 2.82. The absorbance of the polymer also had a much higher absorptivity for the long-wavelength band compared to the benzothiadiazole systems. However, DPP based polymers tend to aggregate, especially with linear side-chains. Preparation of devices by Dr. Lang Wei from concentrated solutions led to films with visible defects. While decreasing the concentration remedied this, the resulting films were too thin to absorb well and gave poor performance. Preparation of systems with branched side-chains will decrease aggregation, but could also disrupt the ordering of the polymer chains.

Benzotriazole was previously disregarded due to computations from Prof. Bryan Wong showing an unfavorably larger bandgap, but I decided to use it to test the solubility difference between a benzotriazole and a benzothiadiazole (albeit that the former can have solubilizing

Figure 4.23: Structure of pDTP8.12PcoBTr8.12.

alkyl groups). The work of a visiting scholar, Sevki Cever of the Cirpan group at Middle East Technical University in Turkey, provided a dibromo monomer for use in direct-arylation polymerization. The resulting polymer, pDTP8.12PcoBTr8.12 (Figure 4.23), was soluble in acetone and hexanes. I was able to purify the sample by simple column chromatography to yield a fraction with a molecular weight of $16.6 \times 10^3$ g/mol and a dispersity of 1.36. The resulting polymer had a deep orange-red color, indicative of the larger bandgap, but also exhibited drastically different solubility from the benzothiadiazole-containing copolymers.

I also did some testing of completely different chemistry to make DTP copolymers with electron acceptors by preparation of homopolymers. The flanking thiophenes on the DTP unit allow electrochemical or oxidative polymerization. Oxidation by either a chemical oxidant or electrochemistry generates radical cations that can couple as for EDOT polymer-
ization shown in Scheme 4.5, and with thiophenes on either side this will result in polymeric systems. This is a potentially very straightforward and simple route to polymers.

**Figure 4.24:** Comparison of experimental and computational $E_{HOMO}$, $E_{LUMO}$ for DTP polymers. a) Structure of DTP homopolymers, and b) comparison of experimental and computational $E_{HOMO}$, $E_{LUMO}$ for DTP polymers (determined by CV of dropcast films and optical bandgap from UV-Vis spectrum, computations at B3LYP/6-31G(d,p) of n = 2 models).

Treatment of $N$-hexyl and $N$-(p-hexyloxyphenyl) DTP monomers with FeCl$_3$ gave pDT6P and pDTP6P. These are very harsh conditions, but did yield polymer samples that were red powders, indicative of their larger bandgap relative to the donor-acceptor systems. Elemental analysis showed a large iron contamination, which precludes use in devices. However, collaborative experiments with UMass Lowell in using horseradish peroxidase in preparation of homopolymers could result in more defect-free systems.
pDTB10P was synthesized to begin exploration of tuning electronic properties of the pendant units. The electron withdrawing ester was predicted by DFT computations at the B3LYP/6-31G(d,p) level (Figure 4.24b, Table 4.4) to slightly reduce the bandgap of the homopolymer system from 2.7 eV to 2.5 eV, and was confirmed experimentally by CV and UV-Vis (Figure 4.24b, Table 4.4).

Scheme 4.7: DTP homopolymers prepared by electrochemical methods onto ITO coated glass. Triarylamine prepared by Paul Homnick using N-(4-bromophenyl)-DTP via Buchwald-Hartwig coupling.

Use of electrochemical polymerization also allows one to prepare insoluble polymer films directly on an electrode from monomers with no solubilizing groups. This allowed me to utilize monomers without solubilizing groups by polymerization directly onto ITO coated glass. This technique gave me the opportunity to test attaching other electronically interesting groups onto the pendant position, in this case triarylamines. Triarylamines can be
oxidized to give persistent radicals that should couple to backbone polarons much like the Sugawara systems\textsuperscript{22} (mentioned previously in Section 4.1). A simple \textit{N}-tolyl homopolymer was also made electrochemically in the same manner as a control. The result of both polymerizations was an insoluble thin yellow film on the ITO coated glass electrode.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4_25.png}
\caption{Different color states of electrochromic DTP polymer films. a) pDTTP, and b) pDTNAr3P.}
\end{figure}

Both films were found to be electrochromic when immersed in clean electrolyte solution (0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile): scanning the potential caused drastic color changes in the films. For the \textit{N}-tolyl system, the film changes from yellow to deep-blue during oxidation, with a single redox peak in the voltammogram (Figure 4.26a). The yellow color can be restored by cycling to negative potentials. The triarylamine system, however, had multiple redox peaks when scanning to positive voltages (as shown in Figure 4.26b), each one accompanied by a separate color state: yellow (neutral), green (oxidation state 1), blue (oxidation state 3), and purple (oxidation state 4). It is possible that oxidation of the triarylamine results in a radical cation that couples with polarons in the backbone that results in a separate state, both in color and energy. Further oxidation of the backbone would lead to bipolaron formation, which would not couple with the pendant radical cation. The disruption of this coupled state could lead to the different color state and the extra redox peak. I modeled these states computationally using a dimeric model structure at the UB3LYP/6-31G(d,p) level (spin-density shown in Figure 4.27), and confirmed the initial oxidation would occur in the backbone, forming polarons (state 1), followed by oxidation of the triarylamine center, generating radical cations that positively couple to the backbone polarons (state 2), followed by further backbone oxidation that results in bipolarons (state 3). It is possible the initial green state (1) is simply an aggregate effect of the
blue state (2) over the neutral yellow film. However, this does not explain the corresponding peak in the voltammogram. Confirmation that this is a separate state would require study by spectroelectro-chemical measurements of the absorbance as a function of potential, to see the different bands forming and disappearing. TDDFT of the various oxidation state models could be used to assign these peaks as I did in Section 2.2.

Figure 4.26: Voltammograms of DTP polymer films from electrochromic experiment. a) pDTTP, b) pDTNAr3P (with I$_2$ redox potential), and c) EPR of I$_2$ doped pDTNAr3P powder.

Scraping the triarylamine polymer from the electrode and oxidizing with I$_2$ vapor resulted in a single EPR peak with a g-value of 2.0048 after 2 h of doping, which is close to that of p-doped polythiophene, and higher than polypyrrole. There is also no resolved hyperfine coupling, which means it is not nitrogen centered, and thus is likely purely contained on the backbone, and in close proximity to sulfur atoms. Since the redox potential of iodine matches with the onset of the first oxidation curve in the voltammagram, this supports the computational prediction that backbone oxidation occurs first. Further study of deeper oxidation states, as well as conformation of the nature of the different color states has not
been possible due to the difficulty in obtaining more monomer.

4.3 Summary

Dithienylpyrrole is a promising donor-unit in low-bandgap p-type polymers for organic photovoltaic applications. This dissertation work showed that it can be incorporated into active layer polymers that yield high fill-factor, high $J_{sc}$, and maximum $V_{oc}$, the photovoltaic devices, and demonstrates the viability of oligomeric and lower molecular weight polymers for use in devices. The comparable performance of pDT12PcoB and pDTP12PcoB also demonstrates the low electronic impact of the pendant unit, aside from the increase $E_{HOMO}$ resulting in lower $V_{oc}$. The substitution of pendant phenyl groups does increase the rigidity and order seen in the polymer samples and yields systems with increased amounts of order,
despite destabilized $E_{HOMO}$. Computational modeling of rigidity led to the determination that rigidity is not the likely source of low solubility, further confirmed by experimental systems lacking benzothiadiazole. Other variations utilizing dithienylpyrrole were also explored, and interesting optoelectronic properties demonstrated.

4.4 References


(40) Avogadro: an open-source molecular builder and visualization tool., version 1.1.1.


(52) He, Y.; Zhao, G.; Min, J.; Zhang, M.; Li, Y. *Polymer* **2009**, *50*, 5055–5058.


CHAPTER 5
SUMMARY AND RECOMMENDATIONS FOR FUTURE WORK

5.1 Summary

I developed a series of low-bandgap polymers absorbing close to the “ideal” bandgap of 1.5 eV by copolymerizing an electron-donating and electron-withdrawing unit to yield copolymers with a low-bandgap “push-pull” of 1.7 eV. These copolymers were oligomeric in nature, but still gave very promising photovoltaic performance, with power conversion efficiencies up to 5%. The ability to vary substitution in a controllable way and tune solubility and/or electronic properties was explored through orthogonal pendant positions, the influence of a pendant phenyl unit in the copolymers yielded a system with increased order in the solid state, although this has not at this point led to improvement in the final photovoltaic devices.

I used computational modeling to study and predict the electronic properties of fluorenone, thienothiophene, and dithienylpyrrole donor-acceptor systems. This made it possible to narrow the wide number of possible material choices. The ability to control, engineer, and predict orbital energy levels is of major importance when designing new materials. The ability to computationally predict not just molecular orbital energy levels, but other properties of the system such as UV-Vis transitions, unpaired spin-density, and changes in dipole moment is important not just for designing new individual molecules and polymers, but in understanding how they work in the bulk as electronic materials.

5.2 Proposed Future Work

5.2.1 Correlation of $\Delta \mu_{ge}$ to Correct Physical Processes

Following the results from Section 3.4, it is worth further investigation to understand better what physical processes are influenced by a larger value of ground-to-excited state dipole change ($\Delta \mu_{ge}$), and indeed whether such a relationship holds true for a wider variety of systems.
An informatics approach for a variety of reported photovoltaic polymers would reveal more about whether $\Delta \mu_{ge}$ correlates to macroscopic properties: $J_{sc}$ and PCE. Further investigation of these systems using transient absorbance spectra would further reveal if $\Delta \mu_{ge}$ correlates to exciton quenching and charge-separation decay kinetics.

**Figure 5.1:** State diagram showing operation in organic photovoltaics. $G_D^*$: excitation of donor material. $D^*$: excited state of donor material. $k_{relax}$: charge-transfer from donor to acceptor, and CT: the resulting charge-transfer state. $k_{CS}$ (and $k_{CS}^*$): separation of electron and hole, and CS: the resulting charge-separation state. $k_r$ repopulation of CT state from CS state. Reproduced from Ref. [1] with permission\(^a\) from the Nature Publishing Group.

\(^a\)License 3546191165159

Yu et al. already determined the decay kinetics for their PTB series of polymers through transient absorption spectroscopy, and showed that the performance differences likely originate from differing rates of exciton and charge-separation decay pathways. This makes these systems worthwhile targets to investigate the hypotheses proposed in Section 3.4: particularly, whether changing $\Delta \mu_{ge}$ could be a result of unfavorable state changes as opposed to decreased barriers to separation. Lowering the charge-transfer (CT) state energy by stabilizing the charges would lead to increased recombination (due to decreased $k_{CS}$ in Figure 5.1), and a more likely chance of free charges in the CS state recombining back into the CT state (larger $k_r$). This would explain the faster decay dynamics of the CS state in the transient absorbance spectra of the systems with decreased photocurrent. The longer exciton decay could be explained by a more stable *intramolecular* charge-transfer (ICT) state that is less likely to undergo *intermolecular* charge-transfer due to a decreased energetic offset between
states that is below the exciton splitting energy.

The above hypotheses could be probed by computational modeling of the above mentioned states. The ICT state can be modeled from relaxation of the first excited state, while the CT state can be computed by modeling a polymer:fullerene interface, as has been done previously.\textsuperscript{3–6} Correlation of the state energies to $\Delta \mu_{ge}$ would give an computable relationship of a molecule that more accurately correlates to the complicated interfacial kinetics of a final device.

5.2.2 Mechanistic Role of Triphenylphosphine in Paal-Knorr Condensations

Triphenylphosphine (PPh\textsubscript{3}) is a well known oxaphile, and the results from Section 4.2.1.1 lead me to believe this oxaphilic behavior is responsible for the observed enhancement of the Paal-Knorr condensation. The use of Ph\textsubscript{3}PO and Ph\textsubscript{3}PBr\textsubscript{2} to assist in condensations of 1,3,4-oxadiazoles has been previously reported.\textsuperscript{7–9} Determining the role of PPh\textsubscript{3} in the Paal-Knorr condensations would aid in the preparation of oxaphilic reagents for use in the condensation of dithienylpyrrole and other pyrrole based molecules. Such a reagent and understanding of the mechanism could assist with condensations of other heterocycles that are not as simple or that require harsh conditions, as will be discussed below.

Under the conditions used in Chapter 4, it is possible PPh\textsubscript{3} is being activated in some manner. pTSA is a non-oxidizing sulfonic acid derivative, and likely not capable of oxidizing or activating phosphine. It is possible to hydrolyze pTSA, generating sulfuric acid, which is capable of oxidation and may generate Ph\textsubscript{3}PO, but whether this occurs under these conditions is unknown.

The mechanisms reported for 1,3,4-oxadiazole condensation do not appear to be applicable to pyrrole condensation: it’s likely furan would form rapidly due to the intramolecular nature of the cyclization and elimination steps occurring faster than intermolecular attack by the primary amine (Scheme 5.1). The de-aromatization of furan in order to recondense with the primary amine is very unlikely to occur (but may be possible\textsuperscript{10}). The procedures in Section 4.2.1.1 were all heated, whereas the oxadiazole condensations were capable of being run at room temperature. The need for heat may support this mechanism. More thorough reaction conditions, such as removal of pTSA and/or acetic acid are suggested to determine
if they play a significant role in this mechanism. Aliquots of the PPh$_3$ condensation at various points, quenched into cold methanol, then subjected to mass spectral analysis and $^{13}$P NMR could be used to determine the fate of PPh$_3$.

An alternative mechanism (bottom route in Scheme 5.1) could result from the oxidized triphenylphosphine condensing with a primary amine to form an iminophosphorane, which could undergo an Aza-Wittig reaction with one of the ketones: generating the initial imine more readily by releasing triphenylphosphine oxide. After tautomerization this can quickly condense with the other ketone (due to the intramolecular nature of the attack), and eliminate water to form the final pyrrole. As the initial and likely slower intermolecular step is assisted with the iminophosphorane, and the quicker, intramolecular steps already lead to pyrrole with less probability of furan formation, this seems the likely route. A summary of these two routes is shown in Scheme 5.1.

Preliminary work was attempted to confirm this by purposefully generating the iminophosphorane through a Kirsanov reaction using PPh$_3$ and N-bromosuccinimide (NBS) to form triphenylphosphoniumbromide, followed by addition of the primary amine before adding the other Paal-Knorr reagents. However, this attempt had low conversion, with
most starting materials remaining. The solvent needed to prepare the Kirsanov reagent (dichloromethane) was not as effective for a Paal-Knorr condensation, and it is difficult to tell whether or not the change in solvent caused the lack of reactivity in the Paal-Knorr. The lack of enhancement reported in oxadiazole condensation with PPh$_3$Br$_2$ does suggest this to not be a likely pathway, assuming the same mechanism applies (despite the successful use when generated in situ). The iminophosphane could be prepared and isolated separately instead of in situ, both to confirm its formation and for use in subsequent reactions.

5.2.3 Dithienylpyrrole Variations

5.2.3.1 Preliminary Work on 1,3,4-Triazoles for Increased $V_{oc}$

The difference in performance between the $N$-alkyl and $N$-aryl polymers, pDT12PcoB and pDTP12PcoB, was a decreased $V_{oc}$ caused by the destabilized $E_{HOMO}^{donor}$ of pDTP12PcoB, likely from inductive effects of the pendant phenyl unit (a result similar to that seen in Chapter 3). Lowering the $E_{HOMO}$ of the DTP unit would yield an increased $V_{oc}$ that could raise the solar cell performance of the DTP copolymers to have comparable power conversion efficiencies to those of higher performing materials, such as PTB7, while retaining the orthogonal pendant tuning point.

However, as I showed in Section 4.2.5, adding electron withdrawing units to the pendant phenyl does not greatly change the inductive effect, and only allows tuning of $E_{LUMO}$ of the monomeric unit. To vary the $E_{HOMO}$ level, backbone modifications will be needed.

![Figure 5.2: Structure of proposed 2,5-dithienyl-1,3,4-triazole.](image)

Conversion of pyrrole to 1,3,4-triazole (Figure 5.2) is an option worth pursuing. The structure is analogous to popular thiazoles and thiadiazoles being used for weakly electron-donating groups in low-bandgap, “push-pull” copolymers in organic electronic materials.
1,3,4-Triazoles themselves have seen sparing use before\textsuperscript{10} in organic conjugated materials and could represent a new class of high performing materials.

Computationally, a combination of my and Bryan Wong’s computations found the conversion from pyrrole to triazole to decrease $E_{HOMO}$ by 0.4 eV in a donor-benzothiadiazole copolymer model, with negligible increase in the bandgap. Thus, a 2,5-dithienyl-1,3,4-triazole copolymerized with benzothiadiazole should yield a copolymer close to the “ideal” bang-gap for a PC$_{71}$BM based device, with an increase in $V_{oc}$ and no decrease in photocurrent.

\begin{center}
\includegraphics[width=0.8\textwidth]{Scheme52.png}
\end{center}

\textbf{Scheme 5.2:} Retrosynthesis of 1,3,4-triazole derivative, with preliminary work.

I attempted to make a 2,5-dithienyl-1,3,4-triazole through a route similar to that used for the DTP units (Scheme 5.2). Preparation of the sym-bis(2-thiopheneacyl)hydrazine precursor was straightforward with high yield. However, I could not successfully condense this with an aniline derivative to prepare the final monomeric unit. Similar chemistry has been previously accomplished,\textsuperscript{10} although under much harsher conditions than I attempted. More mild conditions should be feasible given the previous work on condensation of oxadiazoles,\textsuperscript{7,9,13} and my findings for PPh$_3$ assisted condensations of pyrrole (Section 5.2.2).

The need for a new synthetic route may be in order, despite the ease and yield of the initial step. However, given the promising computational results of the material, the synthetic effort would be worthwhile.
5.2.3.2 Varying Optical and Electronic Properties through Pendant Variation

In Chapter 4, I described efforts to tune the electronic and optical properties of conjugated polymers through pendant variation. Based on the results of that chapter, the influence of a pendant aryl group on the polymer properties and morphology is well understood, and further manipulation can be carried out.

My long term goal for the DTP monomer was to include pendant stable radicals for the preparation of spin-polarized polymer samples. Stable radicals can be deeply colored and can undergo rapid and reversible charge-transfer: both properties could be of great use in organic photovoltaics.

I conducted preliminary work in preparation of pendant nitronyl nitroxide stable radicals (Scheme 5.3), previously prepared by another group. I computationally predicted the high-spin coupling of charge-carriers in the backbone of oligomeric samples, which should induce spin-polarization of these mobile charge-carriers, as briefly described in Section 4.1.

However, the current synthetic targets lack solubilizing groups, and could yield an intractable solid. The use of electropolymerization directly onto an electrode, much like in Section 4.2.5, is feasible to prepare initial samples for characterization. However, the inclu-
sion of solubilizing groups and preparation of polymer samples that are solution processable is preferable for preparation of photovoltaic devices and applications elsewhere.

Debra Sondak of the Lahti group worked on preparation of nitronylnitroxide groups with long alkyl chains for use in amorphous stable organic radical materials. This work could be adapted and applied to this preparation to prepare a solubilized pendant radical DTP monomer, similar to \(N\)-alkoxyphenyl-DTP. Another possibility is copolymerization of the stable radical monomer with another monomer that has solubilizing groups, such as \(N\)-dodecyloxyphenyl-DTP or 3,4-dihexylthiophene (Figure 5.3). However, this would increase the distance between pendant radical sites and thereby decrease electron-electron spin-coupling of a backbone charge carrier. Further computations would be needed to determine if this is a feasible route.

The other long term goal for DTP was the preparation of donor-acceptor systems, where the electron-withdrawing unit is moved from the backbone to a pendant position. This is an idea that has been presented previously in the literature.\(^{20–24}\) The “push-pull” architecture currently in wide use is thought to suffer from problems of decreased persistence length and extent of conjugation.\(^{25}\) This follows from the “push-pull” architecture using isolated orbitals to yield low-bandgaps, resulting in a narrow band-width in the band structure of the final polymer chain, which will increase localization of charge-carriers and decrease charge-carrier mobility.\(^{25}\)

Initial efforts by other groups yielded polymeric materials with promising properties and bandgaps, but moderate performance limited by low fill-factors.\(^ {21,22}\) However, more recent
progress has yielded more promising materials and photovoltaic device performance. The former systems utilized amorphous units, in particular triarylamines and dialkylfluorenes, which are the likely sources of the low fill-factors, and thus the low power conversion efficiencies.

A DTP based unit with a pendant acceptor would have the benefit of increased order in the solid state and ability for pendant variation, thus making it a good candidate for further exploration of this motif. Some possibilities for future consideration are presented in Figure 5.4.

![Figure 5.4: Potential pendant acceptor systems based around dithienylpyrrole.](image)

5.3 References


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CHAPTER 6
EXPERIMENTAL PROCEDURES

6.1 Materials

Tetrahydrofuran (THF) and toluene were freshly distilled from sodium/benzophenone under nitrogen atmosphere unless otherwise stated. All other materials and solvents were used as received. Polymerization apparatuses were assembled in a glove-bag under a dry nitrogen environment. Microwave reactions were performed using a CEM START SYNTH microwave reactor, with stock CEM microwave reaction vessels, either 10 mL or 35 mL reaction volume. All microwave procedures were carried out using the “MAX POWER” setting and with a pressure limit of 300 PSI, unless otherwise stated. All reactions were carried out under nitrogen atmosphere unless otherwise stated. Melting points were obtained using a hot block apparatus and are uncorrected.

6.2 Instrumentation

All compounds were characterized by $^1$H NMR at 400 MHz using a Bruker Avance 400 spectrometer (chemical shifts reported as $\delta$ in ppm downfield of tetramethylsilane, and coupling constants $J$ reported in hertz). Mass spectral data were obtained at the University of Massachusetts Mass Spectrometry Facility, which is supported in part by the National Science Foundation. Polymer molecular weights and dispersities were obtained using a Polymer Laboratories PL-220 high-temperature GPC using 1,2,4-trichlorobenzene at 135°C, calibrated against polystyrene standards.

UV-Vis measurements were carried out using a Shimadzu UV-3600 in standard 1 cm pathlength quartz cuvettes for solutions, and on microscope coverslips for solid films. Thickness of polymer films was determined using a KLA Tencor Alpha-Step IQ profilometer. Photoluminescence was carried out using a Photon Technology International QuantaMaster 30 with 0.5 mm slit width setting, unless otherwise stated. Cyclic voltammetry was performed
using a BASi EC Epsilon potentiostat in a three electrode configuration, with Ag/Ag\(^+\) reference electrode, platinum counter electrode and platinum disk working electrode. Ferrocene/ferrocenium (Fc/Fc\(^+\)) was used as an external standard, with measurements carried out using dry, stock acetonitrile or dichloromethane (DCM) electrolyte solutions containing 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte.

X-ray diffraction (XRD) measurements were carried out on using polymer films dropcast on microscope slides from 1,2-dichlorobenzene (DCB), using a X’Pert Powder X-ray diffractometer with Cu source, Ni filter and 1/2° slit. Grazing incidence X-ray diffraction (GIXRD) measurements were carried out at 1.5° incidence angle and with a 1/16° slit. Transmission electron microscopy (TEM) images and diffractograms were obtained by Dr. Lang Wei of the Lahti group, using a JEOL JEM-2000FX transmission electron microscope. Samples were prepared by dropcasting polymer solutions (15 mg/mL in DCB) onto carbon-coated copper grids (Electron Microscopy Sciences, carbon film on 400 square mesh copper grid) and left to dry overnight.

Computations were carried out using Gaussian 09.\(^1\) Polymeric species were approximated as model systems (with n = 1, 2, and 2.5). Band structures of k-space repeat unit along 1-D chains were performed by Prof. Bryan Wong (UC Riverside) in collaboration with our group. Charge-separation was modeled using methods and scripts from the literature,\(^2\) involving the volumetric difference of excited and ground state total electron density. All molecular orbital and surface renderings were modeled in either Avogadro\(^3,4\) using the POVray export option, or in GaussView,\(^5\) using default parameters unless otherwise stated.

Photovoltaic devices and external quantum efficiency (EQE) measurements were prepared and characterized by Dr. Lang Wei of the Lahti group. Solutions of polymer and PC\(_{71}\)BM in different ratios were prepared using chlorobenzene or DCB as solvent. All solutions were stirred overnight at 55 °C inside a glovebox(nitrogen, <1 ppm of O\(_2\), <1 ppm of H\(_2\)O) and were heated to 80 °C for 15 min to promote complete dissolution.

Typical photovoltaic devices were fabricated by the following structure: glass/indium tin oxide(ITO)/PEDOT: PSS(40 nm)/DTP donor-accepter copolymer: PC\(_{71}\)BM /LiF(1.5 nm)/Al (100 nm). Before spin coating, the ITO substrates (20 Ω/sq, Thin Film Devices Inc) were cleaned using Mucasol detergent (Aldrich, pH 13), deionized water, acetone, and
then isopropyl alcohol sequentially with 10 min of ultrasonication in each step. The cleaned ITO surface was exposed to UV/ozone treatment for 20 min. For thermal annealing step, the devices were placed directly onto a hot place (the temperature was depend on different polymers) and heated for several minutes before deposition.

Photovoltaic measurements were also carried out inside a glove box under nitrogen atmosphere (<1 ppm of oxygen, <1 ppm of water). Current density-voltage (I-V) measurements were made using a Keithley 2400 source-meter unit while illuminating the device with AM 1.5G solar simulator (Newport 91160, 100 mW/cm², calibrated using silicon reference cells with KG5 window). The mask that was used gave an effective device area of 0.06 cm².

External quantum efficiency (EQE) measurements were obtained in air under room temperature using a Newport system. Before the measurements, all the devices were well encapsulated.

6.3 General Procedures

General Procedure for Paal-Knorr Condensation

1,4-Di(2-thienyl)-butane-1,4-dione and a primary amine (2 equivalents) were dissolved in toluene:acetic acid (10:1, 0.1 M in the dione). p-Toluenesulfonic acid (1 equivalent) and PPh₃ (1 equivalent) were added, and the mixture was heated under reflux in a Dean-Stark apparatus for 24-48 hours. The resulting reaction mixture was slowly poured into saturated aqueous sodium bicarbonate solution, and extracted with ethyl acetate. The organic portions were collected and washed with saturated aqueous sodium bicarbonate solution. The organic portions were collected, dried over anhydrous Na2SO₄, filtered, and solvent removed under vacuum. The resulting crude solid was purified by column chromatography on silica with a hexanes:ethyl acetate gradient to yield the pure product.

General Procedure for Microwave Assisted Paal-Knorr Condensation

1,4-Di(2-thienyl)-butane-1,4-dione and a primary amine (2 equivalents) were dissolved in toluene:acetic acid (1:1, 1 M in the dione). p-Toluenesulfonic acid (1 equivalent) and PPh₃ (1 equivalent) were added, and the mixture was microwaved at 170°C for 10 min. The
resulting reaction mixture was slowly poured into saturated aqueous sodium bicarbonate solution and extracted with ethyl acetate. The organic portions were collected and washed with saturated sodium bicarbonate solution. The organic portions were collected, dried over anhydrous Na$_2$SO$_4$, filtered, and solvent removed under vacuum. The resulting crude solid was purified by column chromatography on silica with a hexanes:ethyl acetate gradient to yield the pure product.

**General Procedure for Direct Arylation Polymerization**

The following method was adapted from a literature procedure. The arene (DTP derivatives, 1 eq), aryl dibromide (electron-withdrawing monomer, 1 eq), CsCO$_3$ (3 eq), pivalic acid (1 eq), Pd$_2$(dba)$_3$ (0.5 mol%), and P(o−MeOPh)$_3$ (3 mol%) were placed in a flame-dried round bottom flask or microwave vessel under inert atmosphere inside a glove bag. THF (0.01 M in DTP for classic, 0.1 M for microwave) was added and the reaction was heated at reflux with protection from light for 2-7 days, or microwaved at 170°C for 2 h. The crude mixture was precipitated into cold excess methanol and collected by filtration. The resulting crude solid was purified by sequential Soxhlet extraction using methanol, acetone, then hexanes to remove undesired material and low molecular weight portions. The remaining solid was then collected by Soxhlet extraction with THF and CHCl$_3$. For each of these fractions, the solvent was removed under vacuum to yield the purified copolymer, which then was further subjected to high vacuum and gentle heating for 1 h to remove residual solvent.

**General Procedure for Suzuki Polymerization**

The aryl dibromide (1 eq), aryl diboronic acid (1 eq), sodium t-butoxide (2 eq), and Pd(PPh$_3$)$_4$ (3 mol%) were placed in a flame-dried round bottom flask, and degassed by evacuating and backfilling with N$_2$ three times. Freshly distilled toluene was added and the reaction was heated at reflux for three days with protection from light. The crude reaction mixture was poured into a 2:1 brine:toluene mixture, thoroughly mixed, then the organic layer separated and again washed with brine. The organic portions were combined, dried over anhydrous Na$_2$SO$_4$, filtered, and solvent removed in vacuo. The resulting crude solid was then dissolved in minimal CHCl$_3$, precipitated into methanol, and collected by filtra-
The resulting crude solid was purified by sequential Soxhlet extraction using methanol and then hexanes to remove undesired material. The remaining solid was then collected by Soxhlet extraction with CHCl$_3$, and the solvent removed under vacuum to yield solid copolymer, which was dissolved with minimal CHCl$_3$ and precipitated into ethanol, filtered, washed with methanol, and finally dried under high vacuum with gentle heating to yield the final purified copolymer.

**General Procedure for Oxidative Polymerization**

An appropriate monomer was dissolved in sparged CHCl$_3$ (0.01 M in monomer). Anhydrous FeCl$_3$ (4 eq) was placed in an addition funnel and dissolved in minimal nitromethane: this solution was then added slowly to the monomer solution. The reaction mixture was stirred for 2-7 days, then poured into an equal volume of saturated aqueous ammonium hydroxide and stirred for 30 min. The organic portion was decanted and washed with 0.1 M aqueous ethylenediamine tetraacetic acid (EDTA) solution. The organic portions were collected, dried over anhydrous Na$_2$SO$_4$, filtered, and the solvent removed under vacuum. The resulting crude solid was purified by Soxhlet extraction with methanol and hexanes. The remaining solid was then collected by Soxhlet extraction with CHCl$_3$, and the solvent removed under vacuum to yield the purified polymer. The resulting solid was placed under high vacuum with gentle heating for 1 h to remove residual solvent.

**6.4 Synthetic Procedures**

4-Dodecyloxy nitrobenzene

4-Nitrophenol (5 g, 36 mmol), anhydrous K$_2$CO$_3$ (10 g, 72 mmol), and NaI (catalytic) were added to a dry round bottom flask, dissolved in 2-butanone (100 mL), and then heated to reflux. 1-Dodecylbromide (7.4 mL, 30 mmol) was added in one portion and the reaction heated at reflux overnight. The resulting mixture was poured into excess water and extracted
with ethyl acetate. The organic fractions were collected and dried over anhydrous Na$_2$SO$_4$, and the solvent removed under vacuum. The crude solid was purified by passing through a plug of silica using hexanes as an eluent to yield the product as a pale off-white solid (8.5 g, 77% yield). $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.20 (dd, 2H, J=2.16, J=7.12), 6.95 (dd, 2H, J=2.16, J=7.12), 4.06 (t, 2H, J=6.56) 1.83 (p, 2H, J=6.96), 1.48 (m, 2H), 1.28 (m, 16H), 0.89 (t, 3H, J=6.64). Mp = 39-41° C.

4-Dodecyloxylaniline

The following method is adapted from a literature procedure. $^7$ p-Dodecyloxynitrobenzene (3.0 g, 9.75 mmol) and Fe(acac)$_3$ (0.11 g, 0.29 mmol) were dissolved in methanol (25 mL), and then heated to reflux. Hydrazine hydrate (1.42 mL, 29.2 mmol) was added in one portion, and the mixture heated at reflux overnight. The solvent was removed from the crude mixture under vacuum and the remaining solid redissolved in dichloromethane and filtered through a plug of Celite. The filtrate solvent was removed under vacuum to yield the product as a pale off-white solid of sufficient purity to use without further treatment (2.11 g, 78% yield). $^1$H NMR (CDCl$_3$ 400 MHz) δ 6.76 (d, 2H, J=8.64 Hz), 6.65 (d, 2H, J=8.64 Hz), 3.89 (t, 2H, J=6.6 Hz), 3.42 (s, 2H), 1.77 (m, 2H), 1.45 (m, 2H), 1.28 (m, 16H), 0.88 (t, 3H, J=6.60). Mp = 44-46° C.

2-Octyldodecylbromide

The following method is adapted from a literature procedure. $^8$ PPh$_3$ (80 mmol, 20.1 g) and 2-octyldodecanol (15 g, 50 mmol) were dissolved in dichloromethane (50 mL), then cooled to 0° C. N-Bromosuccinimide (13.3 g, 75 mmol) was added portionwise, and the final reaction mixture was stirred for 15 min, then allowed to warm to room temperature and stirred
overnight. The solvent was removed from the reaction mixture under vacuum, and the resulting solid was extracted with hexanes. The combined hexanes fractions were reduced in volume under vacuum, and purified by column chromatography on silica gel using hexanes as an eluent to yield the product as a colorless oil (12.2 g, 67% yield). ¹H NMR (CDCl₃, 400 MHz) δ 3.47 (d, 2H, J=4.76), 1.83 (m, 1H), 1.46 (m, 4H), 1.29 (m, 28H), 0.90 (t, 6H, J=7.12).

4-(2-Octyldodecyloxy)nitrobenzene

4-Nitrophenol (2.5 g, 18 mmol), anhydrous K₂CO₃ (2.7 g, 20 mmol), and NaI (catalytic) were added to a dry round bottom flask, dissolved in 2-butanone (100 mL), and then heated to reflux. 2-Octyldodecylbromide (5.8 g, 16 mmol) was added in one portion and the reaction heated at reflux overnight. The mixture was poured into excess water and extracted with ethyl acetate. The organic fractions were collected and dried over anhydrous Na₂SO₄, then the solvent removed under vacuum. The crude residue was purified by column chromatography on silica gel using a hexanes to dichloromethane gradient to yield the product as a pale off-white, waxy solid (3.77 g, 50% yield). ¹H NMR (CDCl₃, 400 MHz) δ 8.21 (dd, 2H, J=2.16, J=7.12), 6.96 (dd, 2H, J=2.16, J=7.12), 3.94 (d, 2H, J=4.76), 1.83 (m, 1H), 1.46 (m, 4H), 1.29 (m, 28H), 0.90 (t, 6H, J=7.12).

4-(2-Octyldodecyloxy)aniline

The following method is adapted from a literature procedure.⁷ 4-(2-Octyldodecyl)nitrobenzene (2.5 g 5.96 mmol) and Fe(acac)₃ (0.11 g, 0.32 mmol) were dissolved in methanol (15 mL), and the resulting mixture heated to reflux. Hydrazine hydrate (1.5 mL, 32 mmol) was added
in one portion and the mixture heated at reflux overnight. The solvent was removed from
the crude mixture under vacuum, and the resulting residue redissolved in dichloromethane
and filtered through a plug of Celite. The filtrate solvent was removed under vacuum to
yield the product as a pale off-white, waxy solid of sufficient purity for subsequent use (2.0
g, 86% yield). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.26 (d, 2H, J=8.88) 7.01 (d, 2H, J=8.88) 3.96
(t, 2H, J=4.76), 1.83 (m, 1H), 1.46 (m, 4H), 1.29 (m, 28H), 0.90 (t, 6H, J=7.12).

1,4-Di(2-thienyl)-butane-1,4-dione

The following method is adapted from a literature procedure.$^9$ 3-Benzyl-5-(2-hydroxyethyl)-
4-methylthiazolium chloride (cat. 8 mol%, 23.2 mmol, 6.3 g) and anhydrous potassium
acetate (6.9 g, 70.1 mmol) were dissolved in dry THF (300 mL) under an inert atmosphere.
2-Thiophenecarboxaldehyde (31.6 g, 25.6 mL, 280.8 mmol) was added, and the reaction was
heated. Before a full reflux was achieved, divinyl sulfone (16.6 g, 14.6 mL, 140.4 mmol)
was added dropwise over the course of an hour. The reaction mixture was then heated
at reflux for 48 h. The reaction mixture was then hot filtered, and the collected solid
washed with CHCl$_3$. The filtrate and washings was collected and reduced in volume under
vacuum to remove most of the THF to aid in later extraction. The crude solution was
diluted with CHCl$_3$ and washed with 1 M aqueous HCl solution, then washed with saturated
sodium bicarbonate solution. The organic portions were collected and filtered through a
plug of Celite, dried over anhydrous Na$_2$SO$_4$, filtered, and solvent removed under vacuum.
The crude solid was recrystallized from ethanol, and the crystals washed with minimal
diethylether to yield cream-colored crystals (8.6 g, 24% yield). $^1$H NMR (CDCl$_3$, 400 MHz)
$\delta$ 7.83 (d, 2H, J=3.76 Hz), 7.66 (d, 2H, J=4.8 Hz), 7.17 (t, 2H, J=4.28 Hz), 3.41 (s, 4H).
Mp = 129-131° C.

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2,5-Di(2-thienyl)-pyrrole

![Structure of 2,5-Di(2-thienyl)-pyrrole]

The following method is adapted from a literature procedure.\textsuperscript{10} 1,4-Di(2-thienyl)-butane-1,4-dione (1.0 g, 4 mmol), ammonium acetate (3.0 g, 40 mmol), PPh\textsubscript{3} (4 mmol, 1.0 g) and p-toluenesulfonic acid (4 mmol, 0.76 g) and dissolved in glacial acetic acid (4 mL). The mixture was heated to 100° C and stirred over night. The crude mixture was carefully poured into saturated aqueous sodium bicarbonate (vigorous foaming), and extracted with ethyl acetate. The organic portions were collected and washed with more saturated aqueous sodium bicarbonate solution. The organic portions were then collected, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered, and the solvent removed under vacuum. The resulting crude solid was purified by column chromatography on silica gel using a hexanes to ethyl acetate gradient to yield the product as a yellow solid (0.85 g, 92% yield). \textsuperscript{1}H NMR numbers (CDCl\textsubscript{3}, 400 MHz) δ 8.76 (s, 1H), 7.17 (d, 2H, J=4.88), 7.12 (d, 2H, J=3.64), 7.03 (dd, 2H, J=5.06, J=3.64), 6.43 (d, 2H, J=5.06). Mp = 79-80° C.

N-Dodecyl-2,5-di(2-thienyl)-pyrrole

![Structure of N-Dodecyl-2,5-di(2-thienyl)-pyrrole]

Sodium hydride, NaH, (60% in mineral oil, 0.21 g of solid for 5.2 mmol net NaH) was suspended in dry THF (50 mL) under inert atmosphere. 2,5-Di(2-thienyl)pyrrole (0.85 g, 3.2 mmol) was added in one portion, and the mixture stirred until gas evolution ceased. The mixture was then gently heated, while dodecylbromide (0.9 mL, 3.2 mmol) was added dropwise, and the reaction then allowed to stir overnight at room temperature. The crude mixture was poured into excess water and extracted with ethyl acetate. The organic portions were combined and dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, and the solvent removed under vacuum. The crude residue was purified using column chromatography on silica gel with a hexanes
to ethyl acetate gradient to yield the product as a yellow oil (0.82 g, 64% yield). $^1$H NMR 
(CDCl$_3$, 400 MHz) δ 7.33 (dd, 2H, J=1.48, 4.88 Hz) 7.10 (dd, 2H, J=6.36, 4.88 Hz), 7.08 
(dd, 2H, J=1.48, 6.36 Hz), 6.35 (s, 2H), 4.08 (t, 2H, J=6.45 Hz), 1.88 (m, 2H), 1.45 (m, 
2H), 1.24 (m, 16H), 0.88 (t, 3H, J=6.60 Hz). MS (FAB, m/z): found 399.2054, calculated for 
C$_{24}$H$_{33}$NS$_2$ 399.2054.

$N$-(4-Dodecyloxyphenyl)-2,5-di(2-thienyl)-pyrrole

Prepared using the general procedure for Paal-Knorr condensation, using p-dodecyloxyaniline 
(2 eq, 0.6 g, 2 mmol) to yield a yellow solid (0.24 g, 50% yield). $^1$H NMR (CDCl$_3$, 400 MHz) 
δ 7.23 (d, 2H, J=8.84 Hz), 7.06 (dd, 2H, J=1.04, 5.12 Hz), 6.94 (d, 2H, J=8.84 Hz), 6.84 
(dd, 2H, J=3.60, 5.08 Hz), 6.60 (dd, 2H, J=1.04, J=3.60), 6.55 (s, 2H), 4.02 (t, 2H, J=6.6 
Hz), 1.84 (m, 2H), 1.49 (m, 2H), 1.29 (m, 16H), 0.89 (t, 3H, J=6.64 Hz). MS (FAB, m/z): 
found 491.2317 calculated for C$_{30}$H$_{37}$NOS$_2$ 491.2316. Mp = 104-105° C.

$N$-(p-(2-Octyldodecyloxy)phenyl)-2,5-di(2-thienyl)-pyrrole

Prepared with p-(2-octyldodecyloxy)aniline (2 eq, 1.5 g, 8 mmol) using the general procedure 
for Paal-Knorr condensation, to yield a waxy yellow solid (1.55 g, 64% yield). $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.23 (d, 2H, J=8.84), 7.07 (dd, 2H, J=1.08, J=5.12), 6.94 (d, 2H, 
J=8.84), 6.85 (dd, 2H, J=3.60, J=5.08), 6.60 (dd, 2H, J=1.08, J=3.60), 6.55 (s, 2H), 3.89 
(d, 2H, J=5.84), 1.82 (m, 1H), 1.49 (m, 4H), 1.29 (m, 28H), 0.90 (t, 6H, J=5.92). HR-MS
(FAB+, m/z): found m/z = 603.3587, calculated for C_{38}H_{53}ONS m/z = 603.3568. Mp = 51-54° C.

Poly(\(N\)-(p-dodecyloxyphenyl)-2,5-di(2-thienyl)-pyrrole-alt-
-4,7(2,1,3-benzothiadiazole)) (pDTP12PcoB)

\[
\begin{align*}
\text{OC}_{12}H_{25} & \quad \text{S} \quad \text{S} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{S} & \quad n
\end{align*}
\]

Prepared using the general procedure for direct arylation polymerization under microwave conditions, using \(N\)-(p-dodecyloxyphenyl)-2,5-di(2-thienyl)-pyrrole (0.14 g, 0.29 mmol) and 4,7-dibromo-2,1,3-benzothiadiazole (0.08 g, 0.29 mmol) in THF (20 mL). CHCl_3 fraction yielded a dark blue powder (20 mg, 11%). GPC: \(M_w = 3.5 \times 10^3\) g/mol, \(\bar{D} = 1.27\). \(^1\)H NMR spectrum in Appendix B.

Poly(\(N\)-dodecyl-2,5-di(2-thienyl)-pyrrole-alt-
-4,7(2,1,3-benzothiadiazole)) (pDT12PcoB)

\[
\begin{align*}
\text{C}_{12}H_{25} & \quad \text{S} \quad \text{S} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{S} & \quad n
\end{align*}
\]

Prepared using the general procedure for direct arylation polymerization under microwave conditions, using \(N\)-dodecyl-2,5-di(2-thienyl)-pyrrole (0.82 g, 2.0 mmol) and 4,7-dibromo-2,1,3-benzothiadiazole (0.60 g, 2.0 mmol) in THF (25 mL). THF fraction yielded a dark purple powder (55 mg, 5%). GPC: \(M_w = 2.6 \times 10^3\) g/mol, \(\bar{D} = 1.12\). \(^1\)H NMR spectrum in Appendix B.
Poly(N-(p-(2-octyl-dodecyloxyphenyl))-2,5-di(5-thienyl)-pyrrole-alt-4,7(2,1,3-benzothiadiazole)) (pDTP8.12PcoB)

Prepared using the general procedure for direct arylation polymerization under microwave conditions, using N-(p-(2-octyl-dodecyloxy)phenyl)-2,5-di(2-thienyl)-pyrrole (0.50 g, 0.83 mmol) and 4,7-dibromo-2,1,3-benzothiadiazole (0.24 g, 0.83 mmol) in THF (25 mL). CHCl₃ fraction yielded a dark blue powder (50 mg, 8%). GPC: $M_w = 5.1 \times 10^3$ g/mol, $\bar{D} = 1.26$. $^1$H NMR spectrum in Appendix B.

Poly(N-(p-(2-octyl-dodecyloxyphenyl))-2,5-di(5-thienyl)-pyrrole-alt-2(2-octyldodecyl)4,7(1,2,3-triazole)) (pDTP8.12PcoBTr8.12)

Prepared using the general procedure for direct arylation polymerization under microwave conditions, using N-(p-(2-octyldodecyloxy)phenyl)-2,5-di(2-thienyl)-pyrrole (97 mg, 0.16 mmol) and 4,7-dibromo-2-(2-octyldodecyl)-1,2,3-benzotriazole (90 mg, 0.16 mmol) in THF (20 mL). Acetone fraction was purified by column chromatography to yield a dark orange-red powder (0.10 g, 62%). GPC: $M_w = 16.6 \times 10^3$ g/mol, $\bar{D} = 1.36$. $^1$H NMR spectrum in Appendix B.
Poly(\(N\)-(p-dodecyloxyphenyl)-2,5-di(5-thienyl)-pyrrole-alt-3,6-di(2-thienyl)-2,5-didecylpyrrolo[3,4-c]pyrrole-1,4-dione) (pDTP12PcoDPP10)

Prepared using the general procedure for direct arylation polymerization under microwave conditions, using \(N\)-(p-dodecyloxyphenyl)-2,5-di(2-thienyl)-pyrrole (0.10 g, 0.20 mmol) and 3,6-di(5-bromo-2-thienyl)-2,5-didecylpyrrolo[3,4-c]pyrrole-1,4-dione (0.14 g, 0.20 mmol, provided by Ray Devaughn of the Lahti group) in THF (25 mL). CHCl\(_3\) Soxhlet fraction yielded a dark teal powder (40 mg, 19%). GPC: \(M_w\) 21.5 × 10\(^3\) g/mol, \(\bar{D}\) 2.82. \(^1\)H NMR spectrum in Appendix B.

4-Hexyloxy nitrobenzene

4-Nitrophenol (10.0 g, 90.8 mmol), NaOH (9.8 g, 230 mmol), and 1-bromohexane (28 mL, 200 mmol) were dissolved in absolute ethanol and heated to reflux. The reaction mixture was poured into excess water and the resulting precipitate was collected by filtration. The resulting crude solid was then purified by recrystallization from ethanol (95%) to yield a white solid (20.4 g, 80% yield). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.19 (d, 2H, \(J=9.08\) Hz), 6.94 (d, 2H, \(J=9.12\) Hz), 4.06 (t, 2H, \(J=6.56\) Hz) 1.84 (m, 2H), 1.48 (m, 2H), 1.36 (m, 4H), 0.92 (t, 3H, \(J=6.86\) Hz).

4-Hexyloxy aniline
4-Hexyloxynitrobenzene (20.0 g, 89.5 mmol) was dissolved in ethanol (100 mL) and heated to 50°C. Palladium on carbon (10% w/w, amount to cover a small spatula tip) was added, followed by dropwise addition of hydrazine hydrate (4.2 mL, 134 mmol). The reaction was then stirred for 12 h at room temperature. The solid suspension was filtered and washed with dichloromethane. The filtrate and washings were combined and the solvent removed under vacuum. The resulting crude solid was recrystallized from n-heptane to yield the product as a pale brown crystals (5.18 g, 30% yield). 

\[ \text{¹H NMR (CDCl}_3\text{, 400 MHz)} \delta 6.76 (d, 2H, J=8.12 \text{ Hz}), 6.65 (d, 2H, J=8.04 \text{ Hz}), 3.89 (t, 2H, J=6.36 \text{ Hz}), 3.45 (s, 2H), 1.76 (m, 2H), 1.46 (m, 2H), 1.34 (m, 4H), 0.90 (m, 3H). \]

**N-Hexyl-2,5-di(2-thienyl)-pyrrole**

Prepared in a similar manner to N-dodecyl-2,5-di(2-thienyl)pyrrole, with dry sodium hydride (95%, 39 mg, 1.6 mmol), 2,5-di(2-thienyl)pyrrole (0.25 g, 1.0 mmol), and 1-bromohexane (0.33 mL, 2.2 mmol) to yield product as a pale yellow oil (0.18 g, 60%). 

\[ \text{¹H NMR (CDCl}_3\text{, 400 MHz) } \delta 7.31 (dd, 2H, J=1.50, 4.90 \text{ Hz}) 7.09 (dd, 2H, J=6.34, 4.90 \text{ Hz}), 7.10 (dd, 2H, J=1.50, 6.34 \text{ Hz}), 6.35 (s, 2H), 4.10 (t, 2H, J=6.4 \text{ Hz}), 1.89 (m, 2H), 1.45 (m, 2H), 1.25 (m, 4H), 0.89 (t, 3H, J=6.61 \text{ Hz}). \]

**N-Hexyl-2,5-di(5-bromo-2-thienyl)pyrrole**

N-Hexyl-2,5-di(2-thienyl)-pyrrole (1.02 g, 3.2 mmol) was dissolved in THF and cooled to 0°C. N-Bromosuccinimide (1.15 g, 6.4 mmol) was added slowly, and the reaction was covered in foil, to protect from light, and stirred for 3 h. The reaction was poured into excess distilled water, and extracted with ethyl acetate. The organic portions were collected and dried over anhydrous Na$_2$SO$_4$ and the solvent removed under vacuum. The crude solid was purified
by column chromatography on silica gel using a hexanes to ethyl acetate gradient to yield the product as a pale yellow oil (1.50 g, 97%). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.28 (d, 2H, J=3.88 Hz) 7.13 (d, 2H, J=3.88 Hz), 6.30 (s, 2H), 4.10 (t, 2H, J=6.36 Hz), 1.87 (m, 2H), 1.43 (m, 2H), 131 (m, 4H), 0.93 (t, 3H, J=6.46 Hz).

$N$-(4-Hexyloxyphenyl)-2,5-di(2-thienyl)-pyrrole

![Chemical structure](image)

1,4-Di(2-thienyl)-butane-1,4-dione (1.0 g, 4.0 mmol), 4-hexyloxyaniline (0.85 g, 4.4 mmol), and p-toluenesulfonic acid (0.76 g, 4.0 mmol) were dissolved in toluene:acetic acid (1:1, 10 mL), and the mixture was microwaved at 170°C for 10 min. The reaction mixture was slowly poured into saturated aqueous sodium bicarbonate solution (vigorous foaming!) and extracted with ethyl acetate. The organic portions were collected and washed with more saturated sodium bicarbonate solution. The organic portions were collected, dried over anhydrous Na$_2$SO$_4$, and the solvent removed under vacuum. The resulting crude solid was purified by column chromatography on silica gel with a hexanes:ethyl acetate gradient to yield the product as a yellow solid (0.54 g 33% yield). $^1$H NMR (CDCl$_3$, 400 MHz), 7.22 (d, 2H, J=8.84 Hz), 7.05 (dd, 2H, J=1.04, 5.08 Hz), 6.93 (d, 2H, J=8.84 Hz), 6.83 (dd, 2H, J=5.04, 3.52 Hz), 6.59 (dd, 2H, J=1.00, 3.52 Hz), 6.54 (s, 2H), 4.01 (t, 2H, J=6.56 Hz), 2.34 (m, 2H), 1.83 (m, 2H), 1.50 (m, 2H), 1.38 (m, 2H), 0.93 (t, 3H, J=7.08 Hz). Mp = 102-104°C. MS (EI, m/z): found 407.137, calculated for C$_{24}$H$_{25}$NOS$_2$ 407.1377

$N$-(4-Hexyloxyphenyl)-2,5-di(5-bromo-2-thienyl)-pyrrole

![Chemical structure](image)
\(N\)-(4-Hexyloxyphenyl)-2,5-di(2-thienyl)-pyrrole (0.5 g, 1.22 mmol) was dissolved in dry THF (15 mL), and cooled to 0° C in an ice-bath. \(N\)-Bromosuccinimide (2 eq, 0.44 g, 2.45 mmol) was added portionwise, and the reaction allowed to stir at 0° C for 2 h with protection from light. The reaction was poured into excess water and extracted with \(\text{CHCl}_3\). The organic portions were collected and dried over anhydrous \(\text{Na}_2\text{SO}_4\), and the solvent removed under vacuum. The crude solid was recrystallized from ethanol to yield the product as yellow solid (0.36 g, 55% yield). \(^1\text{H NMR (CDCl}_3, 400 MHz), 7.18 \text{ (d, 2H, J}=8.84 \text{ Hz}), 6.95 \text{ (d, 2H, J}=8.84 \text{ Hz}), 6.78 \text{ (d, 2H, J}=4.04 \text{ Hz}), 6.47 \text{ (s, 2H), 6.37 \text{ (d, 2H, J}=4.04 \text{ Hz}), 4.04 \text{ (t, 2H, J}=6.56 \text{ Hz), 1.85 \text{ (m, 2H), 1.38 \text{ (m, 6H), 0.93 \text{ (t, 3H, J}=6.8 \text{ Hz). Mp = 95-97° C. MS (EI, m/z): found (562.9618, 564.96, 566.96), calculated for C}_{24}\text{H}_{23}\text{NOS}_2\text{Br}_2 562.9587.}\

\(N\)-(4-Hexyloxyphenyl)-2,5-di(5-boronate-2-thienyl)-pyrrole

\[
\begin{array}{c}
\text{OC}_6\text{H}_{13} \\
\text{(HO)}_2\text{B} \\
\text{S} \\
\text{N} \\
\text{S(HO)}_2\text{B} \text{ B(OH)}_2
\end{array}
\]

\(N\)-(4-Hexyloxyphenyl)-2,5-di(5-bromo-2-thienyl)-pyrrole (0.5 g, 0.8 mmol) was dissolved in dry THF and cooled to -78° C in a dry-ice/acetone bath. \(n\)-BuLi (2 eq, 2.5 M in hexanes, 0.7 mL) was added dropwise, and then the reaction was stirred for 30 min. The reaction was then allowed to warm to 0° C and stirred for another 30 min. Triisoproylboronate (4 equivalents, 0.8 mL, 3.6 mmol) was added in one portion, and the reaction was allowed to stir overnight. The reaction was poured into excess water and extracted with ethyl acetate. The organic portions were collected and dried over anhydrous \(\text{Na}_2\text{SO}_4\), filtered, and the solvent removed \textit{in vacuo} to yield a greenish solid that was used without further treatment in subsequent work (0.21 g, 51% yield).
3,6-Di(2-thienyl)-2,5-dihexylpyrrolo[3,4-c]pyrrole-1,4-dione

The following method is adapted from a literature procedure.\textsuperscript{11} 3,6-Di(2-thienyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (0.25 g, 0.8 mmol) and anhydrous K\textsubscript{2}CO\textsubscript{3} (0.34 g, 2.5 mmol) were placed in a dry round bottom flask, and then dissolved in dry N,N-dimethylformamide (DMF) (10 mL) under nitrogen. The reaction was heated to 110°C for 1 hour, then 1-bromohexane (0.41 g, 0.35 mL) was added dropwise, and the reaction was stirred overnight at 110°C. The reaction was then poured into excess water and stirred for 30 min, extracted with CHCl\textsubscript{3}, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered, and solvent removed under vacuum to yield a black solid (0.22 g, 62% yield). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \( \delta \) 8.92 (dd, 2H, J=1.04,4.04 Hz), 7.65 (dd, 2H, J=1.00,5.04 Hz), 7.29 (dd, 2H, J=4.04,5.08 Hz), 4.07 (t, 4H, J=7.80 Hz), 1.75 (m, 4H), 1.33 (m, 12H), 0.90 (t, 6H, J=7.52 Hz).

3,6-Di(5-bromo-2-thienyl)-2,5-dihexylpyrrolo[3,4-c]pyrrole-1,4-dione

The following method is adapted from a literature procedure.\textsuperscript{12} 3,6-Di(2-thienyl)-2,5-dihexylpyrrolo[3,4-c]pyrrole-1,4-dione (0.38 g, 0.8 mmol) was dissolved in 1:1 CHCl\textsubscript{3}:acetic acid (10 mL), and stirred for 15 min. N-Bromosuccinimide (2 eq, 0.28 g, 1.6 mmol) was added, then the reaction was protected from light and stirred at room temperature for 48 h. The reaction was poured into excess methanol and filtered. The collected solid was then washed with methanol to yield the product as a tacky purple-black solid (0.38 g, 76% yield). \textsuperscript{1}H NMR (DMSO\textsubscript{−}d\textsubscript{6}, 400 MHz) \( \delta \) 8.48 (d, 2H, J=4.20 Hz), 7.55 (d, 2H, J=4.20 Hz), 3.89 (t, 4H, J=7.10 Hz), 1.74 (m, 4H), 1.33 (m, 12H), 0.90 (t, 6H, J=7.50 Hz).
The following method is adapted from a literature procedure.\textsuperscript{13}

2,7-Dibromofluorenone (1.1 g, 3.25 mmol), bis(pinacolato)diboron (1.88 g, 7.8 mmol), 1,1'-bis(diphenylphosphino)ferrocene (96 mg, 0.17 mmol), Pd(II)Cl\(_2\) (30 mg, 0.16 mmol), and anhydrous K\(_2\)CO\(_3\) (2.25 g, 16.2 mmol) were placed in a dry round bottom flask and de-gassed by evacuation and backfilling with nitrogen. Sparged 1,4-dioxane (25 mL) was added, and the reaction was heated at 100° C overnight. The solvent was removed under vacuum, and the crude solid redissolved in dichloromethane, and washed with distilled water. The organic portions were collected and washed with brine, dried over anhydrous MgSO\(_4\), and the solvent removed under vacuum. The crude solid was purified by column chromatography on silica gel using ethyl acetate and hexanes (1:4) as an eluent to yield the product as a yellow solid (0.55 g, 39% yield). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.13 (s, 2H), 7.94 (dd, 2H, J=1.00,7.56 Hz), 7.57 (dd, 2H, J=0.80,7.56 Hz), 1.34 (s, 24H).

Poly(N-(p-hexyloxyphenyl)-2,5-di(2-thienyl)-pyrrole-alt-3,6-di(2-thienyl)-2,5-dihexylpyrrolo[3,4-c]pyrrole-1,4-dione) (pDTP6coDPP6)

Prepared using the general procedure for Suzuki polymerization with N-(p-hexyloxyphenyl)-2,5-di(5-boronate-2-thienyl)-pyrrole (0.21 g, 0.41 mmol) and 3,6-di(5-bromo-2-thienyl)-2,5-dihexylpyrrolo[3,4-c]pyrrole-1,4-dione (0.26 g, 0.41 mmol) to yield a dark green powder (47 mg, 13% yield). GPC (CHCl\(_3\) versus PS standards): \(M_w\) 5.3 \(\times\) 10\(^3\) g/mol, D 1.32. UV-Vis and \(^1\)H NMR spectra in ?? and Appendix B.
Poly(\(N\)-(p-hexyloxyphenyl)-2,5-di(2-thienyl)-pyrrole-alt-4,7(2,1,3-benzothiadiazole)) (pDTP6PcoB)

Prepared using the general procedure for Suzuki polymerization using 2,1,3-benzothiadiazole-4,7-diboronic acid (0.24 g, 0.62 mmol) and \(N\)-(p-hexyloxyphenyl)-2,5-di(5-bromo-2-thienyl)-pyrrole (0.35 g, 0.62 mmol) to yield a dark blue powder (67 mg, 20% yield). GPC (CHCl\(_3\) versus PS standards): \(M_w\) 2.9 \(\times\) 10\(^3\) g/mol, \(\bar{\eta}\) 1.17. UV-Vis and \(^1\)H NMR spectra in ?? and ??.

Poly(\(N\)-hexyl-2,5-di(2-thienyl)-pyrrole-alt-4,7(2,1,3-benzothiadiazole)) (pDT6PcoB)

Prepared using the general procedure for Suzuki polymerization using 2,1,3-benzothiadiazole-4,7-diboronic acid (0.26 g, 0.68 mmol) and \(N\)-hexyl-2,5-di(5-bromo-2-thienyl)-pyrrole (0.32 g, 0.68 mmol) to yield a dark purple powder (85 mg, 28% yield). GPC (CHCl\(_3\) versus PS standards): \(M_w\) 5.2 \(\times\) 10\(^3\) g/mol, \(\bar{\eta}\) 1.28. UV-Vis in ??.

Poly(\(N\)-(p-dodecyloxyphenyl)-2,5-di(2-thienyl)-pyrrole-alt-2,7-9H-fluoren-9-one) (pDTP6PcoFO)
Prepared using the general procedure for Suzuki polymerization with 2,7-di(pinnocarborane)-fluoren-8-one (40 mg, 90 µ mol) and \( N-(p\)-hexyloxyphenyl)\)-2,5-di(5-bromo-2-thienyl)pyrrole (52 mg, 90 µ mol) to yield a brick red powder (3.5 mg, 6.7% yield). GPC (CHCl\textsubscript{3} versus PS standards): \( M_w \ 9.2 \times 10^3 \) g/mol, \( \bar{D} \ 2.24 \). UV-Vis and ATR-FTIR spectra in ??.

**Poly(\( N-(p\)-dodecyloxyphenyl)\)-2,5-di(2-thienyl)pyrrole-alt-2,7-9H-fluoren-9-yiliden-emalonitrile) (pDTP6PcoBCNFO)**

![Polymer structure](image)

pDTP6PcoFO (3.5 mg, 7.2 µ mol repeat unit), and dicyanomethane (2.9 mg, 43 µ mol) were added to a dry round bottom flask and degassed under vacuum. Dry dimethylsulfoxide (5 mL) was added, then the reaction mixture was heated to 110\textdegree C and stirred overnight. The mixture was poured into excess distilled water, and the resulting precipitate collected by filtration. The dark-brown solid was only soluble in \( N \)-methylpyrrolidone (NMP), and IR shows significant presence of fluorenone ketone peak. ATR-IR (neat, cm\textsuperscript{-1}) 1715 (s, C=O str). UV-Vis, and ATR-FTIR spectra in ??.

**3,6-Di(2-thienyl)-2,5-di(2-ethylhexyl)pyrrolo[3,4-c]pyrrrole-1,4-dione**

![Chemical structure](image)

The following method is adapted from a literature procedure.\textsuperscript{11} 3,6-di(2-thienyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (0.25 g, 0.8 mmol, provided by Ray Devaughn of the Lahti group) and anhydrous K\textsubscript{2}CO\textsubscript{3} (0.34 g, 2.5 mmol) were dissolved in dry DMF (6 mL)
under an inert atmosphere. The reaction was heated at 110° C with stirring 1 hour. 1-
Bromo-2-ethylhexane (0.48 g, 0.44 mL, 2.5 mmol) was added dropwise, followed by addition
of 18-crown-6 (catalytic, small amount to cover spatula tip). The reaction was then stirred
overnight at 110° C, poured into excess water and stirred for 1 hour. The resulting precipi-
tate was collected by filtration and washed with water, then methanol. The crude solid was
then purified by column chromatography on silica gel using a hexanes to dichloromethane
gradient to yield the product as a deep red powder (59 mg, 14 %). ¹H NMR (CDCl₃,
400 MHz) δ 8.90 (dd, 2H, J=1.16,3.92 Hz), 7.65 (dd, 2H, J=1.08, 5.00 Hz), 7.29 (dd, 2H,
J=3.92,5.00 Hz), 4.00 (d, 4H, J=7.2 Hz), 1.73 (m, 2H), 1.33 (m, 12H), 1.26 (m, 8H), 0.90
(t, 6H, J=7.52 Hz), 0.87 (t, 6H, J=7.2 Hz). MS (FAB, m/z): found 524.2, calculated for
C₃₀H₄₀N₂O₂S₂ 524.253.

3,6-Di(5-bromo-2-thienyl)-2,5-di(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione

The following method is adapted from a literature procedure.¹¹ 3,6-Di(2-thienyl)-2,5-di(2-
ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione (0.06 g, 0.11 mmol) was dissolved in CHCl₃ (10
mL), and cooled to 0° C. N-Bromosuccinimide (2 eq, 0.04 g, 0.22 mmol) was added por-
tionwise, and the reaction stirred at room temperature for 2 h with protection from light.
The reaction was poured into excess water, then extracted with dichloromethane. The or-
ganic portions were collected and dried over anhydrous Na₂SO₄, and the solvent removed
under vacuum. The crude solid was purified by column chromatography on silica gel using
a hexanes to dichloromethane gradient to yield a deep purple solid (57 mg, 77 % yield). ¹H
NMR (DMSO−d₆, 400 MHz) δ 8.48 (d, 2H, J=4.24 Hz), 7.56 (d, 2H, J=4.24 Hz), 3.88 (d,
4H, J=4.04 Hz), 1.70 (m, 2H), 1.40 (m, 12H), 1.23 (m, 8H), 0.91-0.89 (m, 12H). MS (FAB,
m/z): found M⁺ (680.11, 682.10, 684.11) and MH⁺ (681.11, 683.11, 685.11), calculated for

134
The following method is adapted from similar literature procedures.\textsuperscript{14,15} 2-Thiophenecarboxylic acid (0.25 g, 1.95 mmol) and pyridine (0.15 mL, 1.95 mmol) were dissolved in dry dichloromethane (25 mL) and placed under inert atmosphere. Thionyl chloride (0.14 mL, 1.95 mmol) was then added dropwise. The reaction mixture was heated at reflux for 2 h, then cooled to 0\textdegree C, and hydrazine hydrate (0.10 mL, 2.1 mmol) was added dropwise. The reaction was then stirred overnight at room temperature. The resulting precipitate was collected by filtration, and dried under vacuum with gentle heating to yield the product as a white solid (0.24 g, 97\% yield). \textsuperscript{1}H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 8.90 (dd, 2H, J=1.48,6.40 Hz), 8.50 (dd, 2H, J=1.56,7.80 Hz), 7.99 (dd, 2H, J=7.76,6.52 Hz), 6.86 (s, broad). ATR-IR (neat, cm$^{-1}$) 3257, 2585-3131 (N-H), 1940-2040 (aromatic overtone), 1483 (s, C=O str). MS (EI, m/z): found 252.0, calculated for C$_{10}$H$_8$N$_2$O$_2$S$_2$ 252.0027.

$N$-(4-Bromophenyl)-2,5-di(2-thienyl)pyrrole

1,4-Di(2-thienyl)-butane-1,4-dione (1.0 g, 4.0 mmol), 4-bromoaniline (1.38 g, 8 mmol), and p-toluene sulfonic acid (0.76 g, 4.0 mmol) were dissolved in toluene:acetic acid (1:1, 10 mL), and the mixture was microwaved at 170\textdegree C for 10 min. The reaction mixture was carefully poured into saturated aqueous sodium bicarbonate solution (vigorous foaming) and extracted with ethyl acetate. The organic portions were collected and washed with more saturated sodium bicarbonate solution. The organic portions were collected, dried over anhydrous Na$_2$SO$_4$,
filtered, and the solvent removed under vacuum. The resulting crude solid was purified by
column chromatography on silica gel with a hexanes:dichloromethane gradient to yield the
product as a tan solid (0.2 g, 13 %). ¹H NMR (CDCl₃, 400 MHz) δ 7.55 (d, 2H, J=8.6 Hz),
7.18 (d, 2H, 8.6 Hz), 7.12 (dd, 2H, J=1.16, 5.7 Hz), 6.88 (dd, 2H, J=5.7, 5.6 Hz), 6.58 (dd,
2H, J=1.16, 5.6 Hz), 6.53 (s, 2H).

4-(N-2,5-Di(2-thienyl)pyrrole)-benzoic acid methyl ester

Prepared using the general procedure for Paal-Knorr condensation, with 4-aminomethyl-
benzoate (2 eq, 2.5 g, 16 mmol) to yield a yellow solid (2.85 g, 97% yield). ¹H NMR (CDCl₃,
400 MHz) δ 8.09 (dd, 2H, J=1.84,8.52 Hz), 7.36 (dd, 2H, J=1.82,8.84 Hz), 7.10 (dd, 2H,
J=1.00,5.12 Hz), 6.83 (dd, 2H, J=3.64,5.08 Hz), 6.55 (s, 2H), 6.52 (dd, 2H, J=1.00,3.60 Hz),
3.98 (s, 3H).

N-(4-Hydroxymethylphenyl)-2,5-di(2-thienyl)pyrrole

Lithium aluminum hydride (0.33 g, 8.7 mmol) was suspended in dry THF (50 mL) and
cooled to 0° C. 4-(N-2,5-Di(2-thienyl)pyrrole)-benzoic acid methyl ester (0.74 g, 2 mmol)
was added, and the reaction stirred overnight. The reaction was poured cautiously over
crushed ice, then neutralized using 1 M aqueous HCl solution. The resulting precipitate was
collected by filtration and washed with water. The solid was dried under vacuum, yielding
the product as a gray-green powder (0.67 g, quantitative yield). ¹H NMR (CDCl₃, 400
MHz) $\delta$ 7.43 (d, 2H, $J=7.88$ Hz), 7.32 (d, 2H, $J=7.60$ Hz), 7.07 (d, 2H, $J=5.44$ Hz), 6.83 (t, 2H, $J=3.84$ Hz), 6.55 (s, 2H), 6.50 (d, 2H, $J=5.40$ Hz), 4.80 (s, 2H), 1.80 (br s, 1H).

$N$-(4-Formylphenyl)-2,5-di(2-thienyl)pyrrole

\[
\begin{array}{c}
\text{N} \\
\text{O} \\
\end{array}
\]

$N$-(4-Hydroxymethylphenyl)-2,5-di(2-thienyl)pyrrole (0.74 g, 2.2 mmol) was dissolved in minimal acetonitrile. Mn(IV)O$_2$ (0.96 g, 11 mmol) was added, and the reaction stirred for 24 h. The crude mixture was filtered through a pad of silica, and washed with dichloromethane. The filtrate was collected and solvent removed under vacuum. The crude solid was then purified by column chromatography on silica gel with a hexanes to dichloromethane gradient to yield a yellow solid (0.26 g, 35% yield). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 10.09 (s, 1H), 7.92 (d, 2H, $J=8.3$ Hz), 7.44 (d, 2H, $J=8.3$ Hz), 7.12 (dd, 2H, $J=0.9$, 5.1 Hz), 6.85 (dd, 2H, $J=5.1$, 3.6 Hz), 6.56 (s, 2H), 6.53 (dd, 2H, $J=1.0$, 3.6 Hz).

4-(N-2,5-Di(2-thienyl)pyrrole)benzoic acid

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\begin{array}{c}
\text{HO} \\
\text{O} \\
\end{array}
\]

The following method is adapted from a similar procedure.\textsuperscript{16} 4-(N-2,5-Di(2-thienyl)pyrrole)benzoic acid methyl ester (0.18 g, 0.49 mmol), potassium t-butoxide (0.11 g, 0.98 mmol), and distilled water (8 mg, 0.49 mmol) were dissolved in THF (25 mL) and heated at reflux over night. The reaction was poured into excess water and the resulting precipitate collected by filtration to yield the product as a tan solid (0.17 g, quantitative yield). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.05 (d, 2H, $J=8.40$ Hz), 7.50 (d, 2H, $J=8.40$ Hz), 7.32 (d, 2H, $J=4.32$ Hz), 6.89
(dd, 2H, J=4.32, 2.68 Hz), 6.66 (d, 2H, J=2.68 Hz), 6.59 (s, 2H).

4-(N-2,5-Di(2-thienyl)pyrrole)benzoic acid decyl ester

4-(N-2,5-Di(2-thienyl)pyrrole)benzoic acid (0.20 g, 0.57 mmol), 1-decanol (0.09 g, 0.60 mmol), N,N’-dicyclohexylcarbodiimide (0.18 g, 0.85 mmol), and 4-(N,N-dimethylamino)-pyridine (7 mg, 50 µmol) were placed in a round bottom flask under inert atmosphere, dissolved in dichloromethane that was freshly distilled from phosphorous pentoxide (15 mL), and stirred for 15 h. The crude mixture was poured into excess distilled water and extracted with dichloromethane. The organic portions were collected and dried over anhydrous Na₂SO₄, filtered, then the solvent removed under vacuum. The crude solid was purified by column chromatography on silica gel with a hexanes to dichloromethane gradient to yield the product as a yellow solid (0.12 g, 44%).

Poly(4-(N-2,5-di(2-thienyl)pyrrole)-benzoic acid decyl ester) (pDTB10P)

Prepared using the general procedure for oxidative polymerization with 4-(N-2,5-di(2-thienyl)pyrrole)-benzoic acid decyl ester (0.12 g, 0.25 mmol) to yield a deep red-orange powder (40 mg, 33 %). GPC: Mₘ 6.3 × 10³ g/mol, D 1.82.
**N-(Dimethyl-1,3-benzenedicarboxylato)-2,5-di(2-thienyl)pyrrole**

![Chemical Structure](image)

Dimethyl-5-amino-1,3-benzenedicarboxylate (1.25 eq, 0.525 g, 2.5 mmol), p-toluenesulfonic acid (0.38 g, 2.0 mmol), and 1,4-di(2-thienyl)-butyl-1,4-dione (0.5 g, 2.0 mmol) were dissolved in xylenes (25 mL) and heated at reflux in a Dean-Stark apparatus for 12 h. The reaction was allowed to cool, diluted with ethyl acetate, and then washed with saturated aqueous sodium bicarbonate. The organic portions were collected and dried over anhydrous MgSO₄, and the solvent removed under vacuum. The crude solid was purified by column chromatography on silica gel using a hexanes to ethyl acetate gradient, to yield the product as a yellow solid (0.513 g, 61% yield). ¹H NMR (CDCl₃, 400 MHz) δ 8.78 (s, 1H), 8.18 (s, 2H), 7.07 (dd, 2H, J=1.04,5.08 Hz), 6.82 (dd, 2H, J=3.56,5.08 Hz), 6.58 (dd, 2H, J=1.04,3.60 Hz), 6.55 (s, 2H), 3.93 (s, 6H).

**2,2"-Bis(4-[2,1,3-benzothiadiazole])-N-(4'-dodecyloxyphenyl)-2,5-di(5-thienyl)pyrrole**

![Chemical Structure](image)

N-(4-Dodecyloxyphenyl)-2,5-di(2-thienyl)pyrrole (0.145 g, 0.29 mmol), Pd₂dba₃ (1.3 mg, 1.4 µmol), pivalic acid (0.03 g, 0.29 mmol), CsCO₃ (0.30 g, 0.92 mmol), P(o–MeOPh)₃ (2 mg, 5.6 µmol), and 4-bromo-2,1,3-benzothiadiazole (0.18 g, 0.87 mmol) were dissolved in dry THF (20 mL) and stirred for 30 min under inert atmosphere. The reaction was then microwaved at 100°C for 1 hour. The reaction mixture was poured into excess water, then extracted with ethyl acetate. The organic fractions were collected and dried over anhydrous
Na₂SO₄, filtered, and the solvent removed under vacuum. The resulting crude solid was purified by column chromatography on silica gel using a hexanes to dichloromethane gradient to yield the product as a deep red solid (26 mg, 12% yield). ¹H NMR (CDCl₃, 400 MHz) δ 7.92 (d, 2H, J=3.88 Hz), 7.88 (d, 2H, J=8.6 Hz), 7.70 (d, 2H, J=7.08 Hz), 7.60 (t, 2H, J=8.16 Hz), 7.38 (d, 2H, J=8.48 Hz), 7.04 (d, 2H, J=8.84 Hz), 6.73 (s, 2H), 6.58 (d, 2H, J=3.84), 4.08 (t, 2H, J=6.2 Hz), 1.88 (m, 2H), 1.55 (m, 2H), 1.20 (m, 16H), 0.90 (t, 3H, J=6.6).

4,7-Bis(2-(N-(4-hexyloxyphenyl)-2,5-di(5-thienyl)-pyrrole))-2,1,3-benzothiadiazole

N-(4-Dodecyloxyphenyl)-2,5-di(2-thienyl)pyrrole (0.37 g, 0.75 mmol), Pd₂dba₃ (1.0 mg, 1.1 µmol), 4,7-dibromo-2,1,3-benzothiadiazole (0.07 g, 0.25 mmol), pivalic acid (0.02 g, 0.21 mmol), anhydrous CsCO₃ (0.30 g, 0.91 mmol), and P(o−MeOPh)₃ (2.1 mg, 5.6 µmol) were added to a dry round bottom flask, and de-gassed by evacuation and backfilling with nitrogen. Dry THF (20 mL) was added and the reaction heated at reflux for 2 days. The reaction was poured into excess water and extracted with CHCl₃. The organic portions were collected, dried over anhydrous Na₂SO₄, filtered, and the solvent removed under vacuum. The crude solid was purified by column chromatography on silica gel using a hexanes to dichloromethane gradient to yield the product as a deep maroon powder (0.08 g, 30% yield). ¹H NMR (CDCl₃, 400 MHz) δ 7.89 (d, 2H, J=4.00 Hz), 7.80 (d, 2H, J=7.80 Hz), 7.75 (s, 2H), 7.55 (d, 2H, J=7.84 Hz), 7.09 (d, 2H, J=5.04 Hz), 7.00 (d, 4H, J=8.76 Hz), 6.86 (dd, 2H, J=3.72,4.96 Hz), 6.68 (d, 2H, J=3.84 Hz), 6.65 (d, 2H, J=3.64 Hz), 6.59 (d, 2H, J=3.80 Hz), 6.54 (d, 2H, J=4.00 Hz), 4.04 (t, 4H, J=6.36 Hz), 1.86 (m, 4H), 1.50 (m, 4H), 1.29 (m, 24H), 0.90 (t, 6H, J=6.64 Hz). MS (FAB, m/z) found 1114.4368, calculated for C₁₆₆H₁₆₄N₄O₂S₅ 1114.4415.
4-Hexyloxyiodobenzene

\[
\begin{align*}
\text{OC}_6\text{H}_{13} & \quad \text{I} \\
\end{align*}
\]

p-Iodophenol (2.0 g, 9.0 mmol), anhydrous K\textsubscript{2}CO\textsubscript{3} (2.52 g, 18.2 mmol), and NaI (0.15 g, 1 mmol) were dissolved in 2-butanone (50 mL) and heated to reflux. 1-Bromohexane (1.92 mL, 13.6 mmol) was added dropwise, and the reaction heated at reflux overnight. The reaction was poured into excess distilled water and extracted with ethyl acetate. The organic portions were collected and dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered, and the solvent removed under vacuum to yield the product as a pale red oil (2.73 g, quantitative yield). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \(\delta\) 7.61 (d, 2H, \(J=8.71\) Hz), 6.69 (d, 2H, \(J=8.71\) Hz), 3.90 (t, 2H, \(J=6.47\) Hz), 1.83 (m, 2H), 1.34 (m, 6H), 0.89 (t, 3H, \(J=6.81\) Hz).

4-(\textit{N,N}-Bis(4-hexyloxyphenyl)amino)-1-bromobenzene

\[
\begin{align*}
\text{H}_3\text{C}_6\text{O} & \quad \text{N} \\
\text{OC}_6\text{H}_{13} & \quad \text{Br} \\
\end{align*}
\]

4-Hexyloxyiodobenzene (5.42 g, 17.8 mmol), 4-bromoaniline (1.28 g, 7.4 mmol), KOH pellets (1.99 g, 36 mmol), 1,10-phenanthroline (0.30 g, 1.78 mmol), and anhydrous Cu(I)I (0.30 g, 1.78 mmol, previously washed with THF in Soxhlet apparatus) were heated at reflux in a Dean-Stark apparatus for 3 days. The reaction mixture was cooled to room temperature, diluted with dichloromethane, and washed four times with distilled water. The organic portions were collected and dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered, and the solvent removed under vacuum. The crude solid was purified by column chromatography on silica gel using dichloromethane:hexanes (1:1) as an eluent to yield the product as a pale yellow solid (0.5 g, 25%). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \(\delta\) 7.25 (dd, 2H, \(J=2.14,9.10\) Hz), 7.04 (dd, 4H, \(J=2.24,9.00\) Hz), 6.84 (dd, 4H, \(J=2.28,9.04\) Hz), 6.80 (dd, 2H, \(J=2.16,9.12\) Hz), 3.95 (t, 4H,
J=6.56 Hz), 1.81 (m, 4H), 1.62 (m, 4H), 1.50 (m, 8H), 0.94 (m, 4H). MS (FAB, m/z): found (523.22, 525.22) calculated for C_{30}H_{38}BrNO_{2} 523.20859.

**2-(Tributylstannyl)-3,4-ethylenedioxythiophene**

![](image)

3,4-Ethylenedioxythiophene (EDOT) (0.5 g, 3.5 mmol) was dissolved in dry THF (30 mL), cooled to -78° C, treated with n-BuLi (2.5 M in hexanes, 1.4 mL, 3.5 mmol) and stirred for 1 hour at -78° C. Tributyltin chloride (1.04 mL, 3.85 mmol) was added in one portion, then the reaction mixture was allowed to warm to room temperature and stirred for 8 h. The solvent was then removed under vacuum, and the resulting residue was dissolved in hexanes and filtered. The filtrate was collected and the solvent removed under vacuum to yield the product as a yellow liquid (1.33 g, 83%). \(^{1}H\) NMR (CDCl\(_3\), 400 MHz) \(\delta\) 6.59 (s, 1H), 4.17 (m, 4H), 1.58 (m, 6H), 1.36 (m, 6H), 1.12 (m, 6H), 0.91 (t, 12H, J=7.32 Hz).

**2,5-Di(tributylstannyl)-3,4-ethylenedioxythiophene**

![](image)

EDOT (0.5 g, 3.5 mmol) was dissolved in dry THF (25 mL), cooled to 0° C, treated with n-BuLi (2.5 M in hexanes, 2.8 mL, 7.0 mmol), and stirred for 30 min at 0° C. Tributyltin chloride (2.08 mL, 7.7 mmol) was added in one portion, then the reaction mixture was allowed to warm to room temperature and react for 8 h. The solvent was then removed under vacuum, and the resulting residue was dissolved in a dichloromethane:water mixture. The organic layer was washed with saturated aqueous sodium bicarbonate solution, collected and dried over anhydrous MgSO\(_4\), filtered, and the solvent removed under vacuum to yield the product as a yellow liquid (2.51 g, 99%). \(^{1}H\) NMR (CDCl\(_3\), 400 MHz) \(\delta\) 4.12 (s, 4H), 1.58 (m, 12H), 1.36 (m, 12H), 1.12 (m, 12H), 0.91 (t, 24H, J=7.30 Hz).
2,2’-Bis(3,4-ethylenedioxythiophene)

EDOT (1.00 g, 7.0 mmol) was dissolved in dry THF (25 mL), cooled to -78°C, treated with n-BuLi (2.5 M in hexanes, 2.8 mL, 7.0 mmol) and stirred at -78°C for 1 hour. Fe(acac)₃ (2.48 g, 7.0 mmol) was dissolved in dry THF (25 mL) and heated to reflux. The lithiated solution was added via cannulae to the Fe(acac)₃ solution, then the reaction mixture was heated at reflux for 8 h. The crude mixture was concentrated under vacuum, and the resulting residue was dissolved in CHCl₃ and passed through a silica plug. The filtrate was collected and concentrated under vacuum. The crude solid then purified by column chromatography on silica gel with ethyl acetate:hexanes (10:90) as the eluent to yield the product as a yellow solid (0.86 g, 85%). ¹H NMR (CDCl₃, 400 MHz) δ 6.27 (s, 2H), 4.32 (m, 4H), 4.25 (m, 4H). MS (FAB, m/z): found 282.0, calculated for C₁₂H₁₀O₄S₂ 282.0020.

2,2’-(4-Phenylcarboxaldehyde)-5,5’-bis(3,4-ethylenedioxythiophene)

Anhydrous K₂CO₃ (0.79 g, 5.7 mmol), tetrabutylammonium bromide (0.58 g, 1.8 mmol), and Pd(OAc)₂ (38 mg, 0.17 mmol) were degassed in a round bottom flask by evacuating and backfilling with nitrogen. A solution of 2,2’-bis(3,4-ethylenedioxythiophene) (0.5 g, 1.8 mmol) and p-bromobenzaldehyde (0.72 g, 3.9 mmol) in DMF:water (10:1, 15 mL) was degassed with nitrogen sparging and added via cannulae into the flask containing the additives and catalyst. The resulting suspension was stirred for 15 min, then heated at 80°C with stirring 48 h. The reaction mixture was allowed to cool, then poured into excess water, neutralized with 1 M aqueous HCl solution, and the resulting precipitate collected by filtration.
The crude solid was purified by column chromatography on silica gel using dichloromethane as an eluent to yield a dark red solid (1.09 g, 39% yield). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.66 (s, 2H), 8.02 (d, 4H, J=8.32 Hz), 7.813 (d, 4H, J=8.08 Hz), 4.36 (m, 8H).

**3,4,5-Trimethoxybenzyl alcohol**

\[
\begin{array}{c}
\text{MeO} \\
\text{MeO} \\
\text{MeO} \\
\text{OH}
\end{array}
\]

NaBH\(_4\) (1.25 g, 33 mmol) was added to a solution of 3,4,5-trimethoxybenzaldehyde (6.0 g, 30 mmol) in absolute methanol (300 mL) and stirred for 2 h. The mixture was poured into an equal volume water and extracted with ethyl acetate. The organic fractions were collected and dried over anhydrous MgSO\(_4\), filtered, and the solvent removed under vacuum, yielding the product as a clear oil (6.0 g, 99%). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 6.57 (s, 2H), 4.59 (s, 2H), 3.83 (s, 6H), 3.81 (s, 3H).

**5-Bromomethyl-(1,2,3-trimethoxy)benzene**

\[
\begin{array}{c}
\text{OMe} \\
\text{MeO} \\
\text{MeO} \\
\text{Br}
\end{array}
\]

3,4,5-Trimethoxybenzyl alcohol (6.0 g, 30 mmol) and PPh\(_3\) (10.22 g, 39 mmol) were dissolved in dry THF (300 mL). \(N\)-Bromosuccinimide (6.94 g, 39 mmol) was added portionwise to the reaction mixture, which was then stirred for 12 h. The reaction mixture was poured into excess water, and then extracted with ethyl acetate. The organic fractions were collected and dried over anhydrous MgSO\(_4\), filtered, and then the solvent was removed under vacuum. The resulting residue was then purified by column chromatography on silica gel with ethyl acetate:hexanes (10:90) as an eluent to yield the product as a white solid (4.36 g, 55.6%). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 6.59 (s, 2H), 4.62 (s, 2H), 3.85 (s, 6H), 3.83 (s, 3H).
3,4,5-Trimethoxybenzyl triphenylphosphonium bromide

PPh₃ (2.41 g, 9.2 mmol) was added to a solution of 5-bromomethyl-(1,2,3-trimethoxy)benzene (2.0 g, 7.6 mmol) in dry THF (75 mL) and refluxed for 6 h. The resulting solid was collected by filtration, then washed with diethyl ether and hexanes to yield product as a white powder (4.0 g, 99%). ¹H NMR (CDCl₃, 400 MHz) δ 7.65 (m, 15H), 6.13 (s, 2H), 3.86 (s, 2H), 3.79 (s, 6H), 3.76 (s, 3H).

3,4,5-Trimethoxybenzyl tri-n-butylphosphonium bromide

P(n-Bu)₃ (1.02 mL, 4.1 mmol) was added to a solution of 5-bromomethyl-(1,2,3-trimethoxy)benzene (0.89 g, 3.4 mmol) in dry THF (25 mL) and heated at reflux for 6 h. The mixture was poured into water and extracted with ethyl acetate. The organic fractions were collected and dried over anhydrous MgSO₄, filtered, then the solvent was removed under vacuum to yield the product as a tan residue (1.49 g, 94%). ¹H NMR (CDCl₃, 400 MHz) δ 7.93 (s, 2H), 4.40 (d, 2H, J=15.12Hz), 3.97 (s, 3H), 3.89 (s, 6H), 2.50 (m, 6H), 1.45 (m, 6H), 1.39 (m, 6H), 0.93 (t, 12H, J=7.08 Hz).

2,2'-bis[(3,4-ethylenedioxy)thiophene]-5-carbaldehyde

2,2'-Bis(3,4-ethylenedioxy)thiophene (0.5 g, 1.8 mmol) and DMF (0.17 mL, 2.16 mmol) were dissolved in 1,2-dichloroethane (20 mL), placed under nitrogen, and then cooled to
0°C. POCl₃ (0.2 mL, 2.16 mmol) was then added dropwise, and the reaction allowed to warm to room temperature. The reaction was then heated to reflux and stirred for 18 h. The reaction was then poured into excess aqueous 1 M sodium acetate solution and stirred for 2 h. The organic layer was decanted and the aqueous layer was further extracted with dichloromethane. The organic portions were combined and dried over anhydrous MgSO₄, filtered, then the solvent was removed under vacuum. The crude product was then purified by column chromatography on silica gel using dichloromethane as an eluent to yield product as a yellow solid (0.17 g, 25%). ¹H NMR (DMSO-d₆, 400 MHz) δ 9.84 (s, 1H), 4.42 (m, 4H), 4.27 (m, 4H). MS (FAB, m/z) found 310.8, calculated for C₁₃H₁₀O₅S₂ 309.9969.

2,5-Dibromo-3,4-ethylenedioxythiophene

EDOT (3 g, 21 mmol) was dissolved in dry THF (150 mL), and then N-bromosuccinimide (7.48 g, 42 mmol) was added portionwise. The reaction was then stirred for 1 hour at room temperature, poured into excess water and extracted with diethyl ether. The organic portions were collected and dried over anhydrous MgSO₄, filtered, then the solvent was removed under vacuum. The crude solid was then recrystallized from ethanol to yield large tan crystals (6.07 g, 96%). ¹H NMR (CDCl₃, 400 MHz) 4.27 (s, 4H).

2-Bromo-1,3-bis-bromomethylbenzene

Prepared following a procedure described previously in literature.¹⁷ 2-bromo-m-xylene (1 g, 5.4 mmol) and N-bromosuccinimide (2.4 g, 13.5 mmol) were added to CCl₄ along with 2 drops of Br₂, and then heated at reflux for 4 h under lamp illumination. The reaction was then filtered, and the filtrate was collected and the solvent removed under vacuum. The
resulting oil was dissolved in minimal hexanes and placed in freezer, after which the resulting solid was filtered and collected to yield the product as pale tan crystals.

2-Bromo-1,3-di(triphenylphosphoniumbromidemethyl)benzene

Prepared following a procedure described previously in literature.\textsuperscript{17} 2-Bromo-1,3-bis-bromomethylbenzene (1 g, 2.9 mmol) was dissolved in xylenes (25 mL) and heated to reflux. PPh\textsubscript{3} (1.91 g, 7.3 mmol) was dissolved in another portion of xylenes (75 mL), and then added slowly to the refluxing solution. The reaction was then heated at reflux for another 4 h. The resulting off-white solid was collected by hot filtration with purity sufficient for further use (1.9 g, 76%).

2-Bromo-1,3-bis[2-(2-naphthyl)vinyl]benzene

Prepared following a procedure described previously in literature.\textsuperscript{17} 2-Bromo-1,3-di(triphenylphosphoniumbromidemethyl)benzene (1.11 g, 1.28 mmol) was placed in a three-neck round bottom flask and dissolved in methanol (100 mL). A sodium methoxide solution was prepared by carefully adding solid Na (0.5 g) to 50 mL of methanol (caution! fire hazard!). A second solution of 2-napthaldehyde (0.40 g, 2.56 mmol) in methanol (30 mL) was also prepared. The 2-napthaldehyde and sodium methoxide solutions were placed in separate addition funnels, and added alternatively a few drops at a time to the Wittig salt solution. After both solutions were depleted, the reaction was heated at reflux for 2 h. The reaction mixture was then poured into an equal volume of water and stirred for 20 min. The resulting precipitate was collection by filtration to yield the product as a tan solid (0.59
g, 60 % yield). Previous work established this material as a mixture of (E,E) and (E,Z) isomers, but adequate to use in the next synthetic step.\textsuperscript{17}

**9-Bromodinaphth[1,2-a;2',1'-j]anthracene**

![Chemical Structure](image)

Prepared following a procedure described previously in literature.\textsuperscript{17} 2-Bromo-1,3-bis(2-(2-naphtyl)vinyl)benzene (100 mg, 0.20 mmol) was dissolved in benzene (500 mL) along with a small crystal of solid iodine under inert atmosphere, then irradiated in a UV-irradiation vessel for 5 h. The benzene was removed under vacuum, and the crude solid washed with MeCN to yield the product as a tan solid. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) 11.1 (s, 1H), 8.93 (d, 2H, J=8.56 Hz), 8.68 (d, 2H, J=9.08 Hz), 8.09 (d, 2H, J=7.32 Hz), 8.05 (d, 2H, J=8.36 Hz), 8.01 (d, 2H, J=9.08 Hz), 7.95 (d, 2H, J=8.36 Hz), 7.64 (t, 2H, J=6.84 Hz), 7.53 (t, 2H, J=8.32 Hz).

**4-Bromo-2,6-di-tert-butylphenoxy-(trimethyl)silane**

![Chemical Structure](image)

4-Bromo-2,6-di-tert-butylphenol (1.0 g, 3.5 mmol) was dissolved in dry THF (15 mL), cooled to 0°C, treated with \textit{n}-BuLi (2.5 M in hexanes, 1.5 mL, 3.7 mmol), and then stirred for 10 min. Trimethylsilyl chloride (0.4 g, 0.5 mL, 3.7 mmol) was added dropwise, then the solution was heated at reflux for 1 h. The reaction mixture was then poured into excess water and extracted with ethyl acetate. The organic portions were collected and dried over anhydrous MgSO\textsubscript{4}, filtered, and the solvent was removed under vacuum. The crude solid
was recrystallized from hexanes to yield the product as clear white crystals (0.8 g, 64%). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.33 (s, 2H), 1.39 (s, 18H), 0.41 (s, 9H).

3,5-Di-t-butyl-4-(trimethylsilyloxy)phenylboronic acid

4-Bromo-2,6-di-tert-butylphenoxy-(trimethyl)silane (1.0 g, 2.8 mmol) was dissolved in dry THF, cooled to -78°C, treated with n-BuLi (2.5 M in hexanes, 1.2 mL, 3.0 mmol), and then stirred for 20 min. Triisopropylborate (1.4 mL, 6.0 mmol) was then added in one portion, and the mixture stirred for another 20 min. The mixture was then poured into excess water, neutralized with 1 M aqueous HCl solution, stirred for 2 h, and then extracted with ethyl acetate. The organic fractions were collected, dried over anhydrous MgSO$_4$, filtered, then the solvent removed under vacuum. The crude product was recrystallized from ethyl acetate:hexanes (60:40) to yield the product as a white solid (0.12 g, 14%). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.18 (s, 2H), 1.44 (s, 18H), 0.44 (s, 9H).

9-(3',5'-di-t-butylphenol)-dinaphth[1,2-a;2',1'-j]anthracene

9-Bromodinaphth[1,2-a;2',1'-j]anthracene (100 mg, 0.20 mmol), 3,5-di-t-butyl-4-(trimethylsilyloxy)phenylboronic acid (70 mg, 0.22 mmol), sodium t-butoxide (40 mg, 0.40 mmol), and Pd(PPh$_3$)$_4$ (24 mg, 0.021 mmol) were placed in a round bottom flask and de-gassed with by evacuating and backfilling with nitrogen three times. Freshly distilled
Toluene was added (10 mL) and the reaction was refluxed for 48 h. The mixture was poured into brine:toluene (2:1) and extracted with toluene. The organic portions were collected, dried over anhydrous MgSO$_4$, filtered, then the solvent removed under vacuum. The crude solid was then purified by column chromatography on silica gel using ethyl acetate:hexanes (20:80) as an eluent, and once again using dichloromethane:hexanes (60:40) as an eluent to yield the product as yellow solid. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 11.07 (s, 1H), 9.03 (d, 2H, $J$=8.4 Hz), 8.08 (d, 2H, $J$=7.08 Hz), 8.02 (d, 2H, $J$=8.36 Hz), 7.90 (d, 2H, $J$=8.60 Hz), 7.87 (d, 2H, $J$=8.84 Hz), 7.76 (d, 2H, $J$=8.84 Hz), 7.60 (t, 2H, $J$=7.08 Hz), 7.52 (t, 2H, $J$=8.34 Hz), 7.37 (s, 2H), 1.52 (s, 18 H). MS (FAB, m/z): found 582.3, calculated for C$_{44}$H$_{38}$O 582.2922. When dissolved in DCM at room temperature and treated with PbO$_2$, a persistent grey-green color resulted: the solution gave a persistent EPR spectrum consistent with $a$(H1) = 1.77 gauss (2 H) and $a$(H2) = 0.90 gauss (1 H), g = 2.0048(2). The solution could be evaporated in air and reconstituted to yield the same spectrum for about 24 h.

2-3,4-Ethylenedioxythiophene-2-boronic acid

EDOT (2.0 g, 14.0 mmol) was dissolved in dry THF (30 mL), cooled to -78°C, treated with $n$-BuLi (2.5 M in hexanes, 6.2 mL, 15.5 mmol), then stirred for 1.5 h. Triisopropylborate (6.47 mL, 28 mmol) was then added in one portion. The mixture was then allowed to warm to room temperature and stirred overnight. The reaction was then poured into excess water, neutralized with 1 M aqueous HCl solution, and then extracted with dichloromethane. The organic layers were collected, dried over anhydrous MgSO$_4$, filtered, then the solvent removed under vacuum to yield the product as a dark red residue that was used as is in subsequent steps (1.29 g, 50%). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 6.33 (s, 1H), 4.20 (s, 4H).
2,5-Bis(4-benzaldehyde)-3,4-ethylenedioxythiophene

Tetrabutylammonium bromide (4.5 g, 14 mmol), Pd(OAc)$_2$ (0.27 g, 1.2 mmol), and anhydrous K$_2$CO$_3$ (5.8 g, 42 mmol) were placed in a round-bottom flask and degassed by evacuation and backfilling with nitrogen three times. EDOT (2.0 g, 14 mmol) and p-bromobenzaldehyde (5.72 g, 31 mmol) were dissolved in a DMF:H$_2$O mixture (10:1, 100 mL) and sparged with nitrogen for 5 min. The solution was cannulated into the solids, and the mixture stirred with heating at 80°C for 48 h. The reaction mixture was allowed to cool, then poured into excess water and neutralized with 1 M aqueous HCl solution. The resulting precipitate was collected by filtration. The crude solid was purified by dissolving in minimal, hot CHCl$_3$ and slowly adding hexanes to precipitate the product as a brick-red solid (2.45 g, 49%). $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 10.00 (s, 2H), 7.95 (d, 4H, J=8.32 Hz), 7.89 (d, 4H, J=8.60 Hz), 4.46 (s, 4H).

2,5-Bis(4'(4"-nitrophenylethenyl)phenyl)-3,4-ethylenedioxythiophene

2,5-Bis(4-benzaldehyde)-3,4-ethylenedioxythiophene (0.5 g, 1.4 mmol) and 4-nitrobenzyl tri-n-butylphosphonium bromide (1.25 g, 3.0 mmol) were dissolved in dry THF (30 mL). Sodium t-butoxide (0.58 g, 6.0 mmol) was dissolved in dry THF (10 mL) and the resulting solution was added dropwise to the reaction mixture. The reaction mixture was heated at reflux overnight, then poured into excess water and stirred for 20 min. The mixture was neutralized with 1 M aqueous HCl solution and the resulting precipitate was collected by filtration. The crude solid was purified by recrystallization from toluene to yield the product as a brick-red solid.
powder (0.27 g, 33%). \(^1\)H NMR (DMSO-\textit{d}_6, 400 MHz) \(\delta\) 8.24 (d, 4H, J=8.84 Hz), 7.88 (d, 4H, J=8.84 Hz), 7.75 (dd, 8H, J=8.56,18.9 Hz), 7.55 (d, 2H, J=16.4 Hz), 7.45 (d, 2H, J=16.4 Hz), 4.46 (s, 4H). Mp > 220°C. MS (FAB, m/z) found 587.9, calculated for C\(_{34}\)H\(_{24}\)N\(_2\)O\(_6\)S \(588.1355\). UV (CH\(_2\)Cl \((\epsilon = \log(M^{-1}cm^{-1}))\): 447 (5.62). PL (CH\(_2\)Cl\(_2\), 443 nm): 515 nm.

2,5-Bis(3,4,5-trimethoxystyryl)thiophene

\[
\begin{array}{c}
\text{MeO} \\
\text{MeO} \\
\text{MeO} \\
\text{OMe} \\
\text{OMe} \\
\text{S}
\end{array}
\]

2,5-Dibromothiophene (0.31 g, 1.3 mmol), 3,4,5-trimethoxystyrene (0.5 g, 2.5 mmol), tri(o-tolyl)phosphine (70 mg, 0.23 mmol), Pd(OAc)\(_2\) (26 mg, 0.16 mmol), and triethylamine (0.36 mL, 2.5 mmol) were placed in a round bottom flask and de-gassed by evacuation and backfilling with nitrogen. Dry DMF (25 mL) was added and the reaction mixture was heated at 85°C for 48 h. The reaction mixture was poured into excess water, and neutralized with 1 M aqueous HCl solution. The resulting solid was collected by filtration, dissolved in dichloromethane, and then passed through a plug of Celite. The filtrate was then concentrated under vacuum and purified by column chromatography on silica gel using ethyl acetate:hexanes (50:50) mixture as an eluent to yield the product as a bright orange powder (0.1 g, 16%). \(^1\)H NMR (DMSO-\textit{d}_6, 400 MHz) \(\delta\) 7.42 (d, 2H, J=15.88 Hz), 7.13 (s, 2H), 6.91 (s, 4H), 6.86 (d, 2H, J=16.2 Hz), 3.84 (s, 12H), 3.68 (s, 6H). Mp = 62-64°C. UV (CHCl\(_3\) \((\epsilon = \log(M^{-1}cm^{-1}))\): 404 nm (4.24). PL (CHCl\(_3\), 405 nm): 432, 570 nm.

Poly(3,4-ethylenedioxy-2,5-thienylene-vinylene-alt-phenylene-vinylene)

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{S} \\
\text{n}
\end{array}
\]

2,5-Dibromo-3,4-ethylenedioxythiophene (1.5 g, 5.0 mmol), 1,4-divinylbenzene (0.6 g, 5.0 mmol), tri(o-tolyl)phosphine (0.28 g, 0.9 mmol), Pd(OAc)\(_2\) (67 mg, 0.3 mmol), and triethylamine (1.4 mL, 10 mmol) were added to a round bottom flask and de-gassed by evacuation
and backfilling with nitrogen. Dry DMF (50 mL) was added and the reaction was heated at 80°C for 48 h. The reaction mixture was poured into methanol (200 mL), and the resulting precipitate was collected by filtration. The crude solid was subjected to Soxhlet extraction with methanol and then hexanes, and the resulting residue extracted using CHCl₃. The solvent in the CHCl₃ extracts were removed under vacuum to yield the product as a black flaky powder (0.70 g, 50%). GPC (CHCl₃ versus PS standards): Mₑ 2.1 × 10³ g/mol, D 1.27.

**1,4-Dihexyloxybenzene**

The following method is adapted from a literature procedure.¹⁸ Hydroquinone (10 g, 90.8 mmol), and NaOH (9.08 g, 230 mmol) was dissolved in absolute ethanol (60 mL), and heated to reflux. 1-Bromohexane (28 mL, 200 mmol) was added, and the reaction heated at reflux for 12 h. The reaction was poured into excess distilled water, and the resulting precipitate collected by filtration. The crude solid was recrystallized from 95% ethanol to yield the product as a white solid (20.41 g, 80%). ¹H NMR (CDCl₃, 400 MHz) δ 6.82 (s, 4H), 3.90 (t, 4H, J=6.60 Hz), 1.79 (m, 4H), 1.45 (m, 4H), 1.33 (m, 8H), 0.92 (t, 6H, J=4.28). MS (FAB, m/z): found 278.4, calculated for C₁₈H₃₀O₂ 278.2246.

**1,4-Di(bromomethyl)-2,5-dihexyloxybenzene**

The following method is adapted from a literature procedure.¹⁹ 1,4-Dihexyloxybenzene (2.0 g, 7.0 mmol) and paraformaldehyde (1.34 g, 42 mmol) were suspended in glacial acetic acid (20 mL). The suspension was stirred for 45 min until all solids were fully dissolved.
Hydrobromic acid (47%, 4 mL) was added and the mixture was heated at 70°C for 2 h. The resulting precipitate was collected by filtration and the resulting crude solid recrystallized from hexanes to yield the product as pale-yellow needle crystals (2.01 g, 62% yield). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta \) 6.86 (s, 2H), 4.55 (s, 4H), 3.99 (t, 4H, J=6.56 Hz), 1.82 (m, 4H), 1.51 (m, 4H), 1.37 (m, 8H), 0.93 (t, 6H, J=7.08 Hz). MS (FAB, m/z): found (462.3, 464.3, 466.3), calculated for C\(_{20}\)H\(_{32}\)Br\(_2\)O\(_2\) 462.0769.

2,5-Dihexyloxy-1,4-bis(diethylphosphonatomethyl)benzene

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{OC}_6\text{H}_{13} & \quad \text{OC}_6\text{H}_{13} \\
\text{OEt} & \quad \text{OEt} \\
\text{P} & \quad \text{P} \\
\text{EtO} & \quad \text{EtO}
\end{align*}
\]

1,4-Di(bromomethyl)-2,5-dihexyloxybenzene (1.5 g, 3.2 mmol) and triethylphosphite (3.32 mL, 19.4 mmol) were dissolved in toluene (25 mL) and heated at reflux for 4 h. Triethylphosphite and toluene were removed by vacuum distillation to leave the product as a clear oil (1.31 g, 78%). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta \) 6.88 (s, 2H), 3.95 (t, 8H, J=5.32), 3.88 (t, 4H, J=6.32), 3.13 (d, 2H, J=20.2Hz), 1.72 (m, 4H), 1.43 (m, 4H), 1.29 (m, 8H), 1.17 (t, 12H, J=5.56 Hz), 0.88 (t, 6H, J=6.80 Hz). MS (FAB, m/z): found 578.4, calculated for C\(_{28}\)H\(_{52}\)O\(_8\)P\(_2\) 578.3137.

Poly(3,4-ethylendioxythiophene-alt-2,5-dihexyloxy-1,4-divinylbenzene

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{S} & \quad \text{O} \\
\text{OC}_6\text{H}_{13} & \quad \text{H} \quad \text{C}_6\text{O} \\
\text{n} & \quad \text{n}
\end{align*}
\]

2,5-Dihexyloxy-1,4-bis(diethylphosphonatomethyl)benzene (1.31 g, 2.5 mmol) was dissolved in dry THF (500 mL) under nitrogen. Sodium hydride (0.5 g, 20 mmol) was added, and the reaction was stirred for 20 min. 3,4-Ethylendioxy-2,5-thiophenedicarbaldehyde (0.5 g, 2.5 mmol) was added, and the reaction was heated at reflux overnight. The reaction mixture was poured into a solution of conc. HCl (3 mL) in methanol (500 mL), and the solvent
removed under vacuum. The resulting orange solution becomes an insoluble black solid
upon solvent removal. A brown appearance can be partially restored with sodium doping
by adding small amounts of solid sodium to a solution of the powder in toluene. However,
this does not persist in air once the solvent is removed again.

1,4-Bis(bromomethyl)-2,3,5,6-tetrafluorobenzene

1,4-Dimethyl-2,3,5,6-tetrafluorobenzene (1.0 g, 5.6 mmol), and N-bromosuccinimide (2.5 g,
14.0 mmol) were dissolved in CCl₄ (30 mL) in a dry round bottom flask. Br₂ (1 drop) was
added as an initiator, and the reaction was heated at reflux under illumination for 4 h. The
reaction was hot filtered, and the filtrate collected. The solvent was removed under vacuum,
and the crude solid purified by recrystallization from ethanol to yield the product as white
crystals (1.3 g, 68%). MS (EI, m/z): found (332.9, 334.9, 336.9), calculated for C₈H₄Br₂F₄
333.8616. Mp = 117-122° C.

1,4-Bis(diethylphosphonatomethyl)-2,3,5,6-tetrafluorobenzene

1,4-Bis(bromomethyl)-2,3,5,6-tetrafluorobenzene (0.3 g, 0.9 mmol) was dissolved in tri-
ethylphosphite and heated at reflux for 4 h. Triethylphosphite was removed by vacuum
distillation and the resulting residue recrystallized from n-heptane to leave the product as
a white powder (0.22 g, 54%). MS (EI, m/z): found 450.1, calculated for C₁₆H₂₄F₄O₆P₂
450.298.
Poly(3,4-ethylenedioxythiophene)-alt-2,3,5,6-tetrafluoro-1,4-divinylbenzene

1,4-Bis(diethylphosphonatomethyl)-2,3,5,6-tetrafluoro-benzene (0.30 g, 0.66 mmol) was dissolved in dry THF (150 mL) under inert atmosphere. NaH (0.07 g, 2.64 mmol) was added, and the reaction was stirred for 20 min. 3,4-Ethylenedioxy-2,5-thiophenedicarbaldehyde (0.13 g, 0.66 mmol) was added, and the reaction was stirred overnight. The reaction was poured into an equal volume of distilled water, and the resulting precipitate collected by filtration to yield the product as an orange-red powder (54 mg, 24%). GPC (CHCl₃ versus PS standards): $M_w \approx 1.3 \times 10^3$ g/mol, $D$ 1.04. UV (THF): 479 nm.

6.5 References


(3) Avogadro: an open-source molecular builder and visualization tool., version 1.1.1.


APPENDICES
APPENDIX A

$^1$H NMR OF DITHIENYLPYRROLE POLYMERIC SYSTEMS

Figure A.1: $^1$H NMR spectrum of pDT12PcoB. CDCl$_3$, 400 MHz.
Figure A.2: $^1$H NMR spectrum of pDT12PcoB (aromatic region). CDCl$_3$, 400 MHz.

Figure A.3: $^1$H NMR spectrum of pDT12PcoB (alkyl region). CDCl$_3$, 400 MHz.
Figure A.4: $^1$H NMR spectrum of pDTP12PcoB. CDCl$_3$, 400 MHz.

Figure A.5: $^1$H NMR spectrum of pDTP12PcoB (aromatic region). CDCl$_3$, 400 MHz.
Figure A.6: $^1$H NMR spectrum of pDTP8.12PcoB. CDCl$_3$, 400 MHz.

Figure A.7: $^1$H NMR spectrum of pDTP8.12PcoB (aromatic region). CDCl$_3$, 400 MHz.
Figure A.8: $^1$H NMR spectrum of pDTP8.12PcoBTr8.12. CDCl$_3$, 400 MHz.

Figure A.9: $^1$H NMR spectrum of pDTP8.12PcoBTr8.12 (aromatic region). CDCl$_3$, 400 MHz.
Figure A.10: $^1$H NMR spectrum of pDTP12PcoDPP10. CDCl$_3$, 400 MHz.

Figure A.11: $^1$H NMR spectrum of pDT6PcoB. CDCl$_3$, 400 MHz.
Figure A.12: $^1$H NMR spectrum of pDT6PcoB (aromatic region). CDCl$_3$, 400 MHz.

Figure A.13: $^1$H NMR spectrum of pDTP6PcoB. CDCl$_3$, 400 MHz.
Figure A.14: $^1$H NMR spectrum of pDT6PcoB (aromatic region). CDCl$_3$, 400 MHz.

Figure A.15: $^1$H NMR spectrum of pDTB10P. CDCl$_3$, 400 MHz.
Figure A.16: $^1$H NMR spectrum of pDTB10P aromatic region. CDCl$_3$, 400 MHz.
Figure B.1: UV-Vis absorbance of pDT6PcoB and pDTP6PcoB. Solutions in CHCl₃ (1000x diluted from 3 mg/mL stock), and films dropcast from 0.3 mg/mL CHCl₃ solutions onto glass substrates.
Figure B.2: UV-Vis absorbance of pDT6PcoDPP. Solution in CHCl$_3$ (1000x diluted from 3 mg/mL stock). Film dropcast from 0.3 mg/mL CHCl$_3$ solution onto glass substrate.

Figure B.3: UV-Vis absorbance of pDT6PcoFO. Solution in CHCl$_3$ (1000x diluted from 2.5 mg/mL stock). Film dropcast from 0.25 mg/mL CHCl$_3$ solution onto glass substrate.
Figure B.4: UV-Vis absorbance of pDTB10. Solution in CHCl$_3$ (1000x diluted from 3 mg/mL stock). Film dropcast from 0.3 mg/mL CHCl$_3$ solution onto glass substrate.

Figure B.5: IR spectra of THF fractions from polymerization run in NMP, compared to the CHCl$_3$ fraction, and reference polymer from a cleaner reaction.
APPENDIX C
UV-VIS AND FLUORESCENCE SPECTRA OF EDOT SYSTEMS

Figure C.1: UV-Vis and PL spectra of 2,5-bis(3,4,5-trimethoxystyryl)thiophene.
Figure C.2: UV-Vis and PL spectra of \((\text{NO}_2\text{PVP})_2\text{EDOT}\) (2,5-Bis(4'(4''-nitrophenylethinyl)phenyl)-3,4-ethylenedioxythiophene).

Figure C.3: UV-Vis spectra of EDOT copolymers.
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