Molecular Design, Characterization, and Implementation of Organic Semiconducting Oligothiophenes

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Molecular Design, Characterization, and Implementation of Organic Semiconducting Oligothiophenes

A Dissertation Presented

by

BENJAMIN P. CHERNIAWSKI

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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Polymer Science and Engineering
Molecular Design, Characterization, and Implementation of Organic Semiconducting Oligothiophenes

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DEDICATION

Dedicated to my friends, family, colleagues, and mentors whom have inspired and supported my love of science and discovery. Thank you all.

Special Thanks to:

Dr. Michelle Karpovich
for inspiring my passion for chemistry.

Mrs. Patricia Cherniawski
Mr. Michael Cherniawski
for being truly amazing parents. You have always nurtured the best in me.
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ABSTRACT

MOLECULAR DESIGN, CHARACTERIZATION, AND IMPLEMENTATION OF ORGANIC SEMICONDUCTING OLIGOTHIOPHENES

FEBRUARY 2018

BENJAMIN P. CHERNIAWSKI, B.A., VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY
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This work describes new self-assembly strategies and realizes new directions for rational side chain design in organic semiconductors. I examined the synthesis and structure property relations of monomers and dimers of a benchmark organic semiconductor system using a variety of linear alkyl side chains. I observed critical onsets for packing trends based on alkyl side chain length in both monomers and dimers. Monomer systems exhibited a pronounced even-odd effect manifesting directly from side chain length. In the dimer systems, I observed spontaneous bimolecular crystal formation with PC$_{61}$BM which undergoes an order-to-disorder transition at small side chain lengths. Combining these systematic structure-property studies, I designed and synthesized a set of BTTT dimers with variable substitution of long and short side chains. These systems displayed solid-state packing behaviors unique to their side chain pattern, both in neat films and in blends with fullerene derivatives. As these oligomers provide excellent model systems for their polymer analogues, the translation of the structure-property lessons here will benefit small molecule systems and polymer systems alike. More broadly, this work identifies the utility and application of variable substitution for imparting order and ‘smart’ self-assembly in organic semiconductors or other organic crystalline materials.
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CHAPTER 1
ORGANIC SEMICONDUCTORS

1.1 Introduction

Organic semiconductors are gaining recognition as commercial materials due to low processing costs and greater flexibility in material design and application. Arguably, the greatest advantage of organic semiconductors (OSCs) is the low device fabrication cost afforded by solution processing.[2, 4-12] Unlike their silicon based counterparts, these materials can be readily dissolved and patterned through a variety of solution-based techniques. Solubility is not a prerequisite for organic semiconductor electronic function, but rather a beneficial property selected through chemical design.[13, 14] In fact, solution processability and the addition of solubilizing sidechains is so desirable, that they are present in the vast majority of organic systems (especially polymeric systems).

Beyond the primary motivation of solubility, side chains can be further exploited to facilitate, enhance, or reduce other chemical, physical, or electrical properties.[9] This immense tunability available in OSCs far surpasses that of inorganic semiconductors and is a major advantage inherent to this class of semiconducting materials.[15] The outstanding tunability and potential for specialization arises from nearly infinite combinations of side chains, backbones, and processing conditions. However, the benefits of OSC complexity also poses a daunting task to interpret.[6, 16] Still, advances in side chain engineering and optimization continues to drive new materials and revitalize older ones.
1.2 Polythiophene Semiconductors

The most prolific and researched systems in the field of polymer semiconductors are the polythiophenes. Poly-3-hexylthiophene (P3HT), polyquarterthiophene (PQT), and poly(2,5-bis-(3-hexylthiophen-2-yl) thieno[3,2-b]thiophenes) (PBTTT) are benchmark polythiophene materials that contain a regioregular thiophene backbone and pendant linear alkyl solubilizing groups.[17] This molecular structure assembles into 2-D lamella with the thiophene rings and alkyl chains oriented edge-on relative to the substrate. By increasing the number of unsubstituted thiophene rings in the backbone from P3HT (fully alkylated) vs PQT (50% substitution), crystallinity and order improves in the solid state. Additionally, the incorporation of fused rings as seen in PBTTT reduces the rotational freedom of the backbone and further improves crystallinity.[17] Of the three polymers shown in Figure 1, PBTTT is a particularly outstanding candidate due to its high degree of order in the solid state. PBTTT is a ‘liquid crystalline’ polymer; implying it its backbone is very stiff and planar and has the ability to melt-crystallize into large highly ordered crystalline domains of 10-15 nm.[17] Due in part to its high degree of order and backbone planarity, PBTTT is also a benchmark semiconductor that exhibits high charge-transport efficiencies (~0.5 cm²/Vs) providing an excellent electronic platform for experimentation.[17]
1.3 Oligomers as Model Systems

OSCs can be divided into small-molecule and polymer systems. Polymer systems typically benefit from superior processing, but are plagued by packing frustrations in the solid state.[18] Even the one of the most crystalline polymers, PBTTT, can only grow crystalline domains of 10-15 nm.[17] The entropic disorder inherent to polymer systems limits the ability to grow crystals and thus the resolution of polymer-based structure-property studies. Additionally, polymers are also susceptible to batch-to-batch variation and regioregularity errors.[18] Small molecules, however, are highly crystalline, chemically pure, systems which allow atomically precise characterization of local packing and crystallization.[19] Blurring the lines between these two categories are oligomer systems.[5, 18, 20-22] Oligomers are small molecule analogues of the parent polymer systems with the same chemical structure and can be studied as standalone or model systems.[20, 22] In separate studies, our group used oligomers of PQT[22] and PBTTT[20] to gain a better understanding of their parent polymers. Among the many advantages of oligomer model studies, single crystal x-ray analysis reveals details about the backbone conformations and side chains behavior not accessible in polymer studies.[23] Additionally, oligomers have also proved essential for determining the effective conjugation length of their parent polymers.[20, 22] In this dissertation, I will show how they can be further exploited to understand the structure-property relations of linear side chains and their influence on crystal packing, thin film microstructure and morphology of PBTTT oligomers.

1.4 Morphology and Microstructure of Organic Semiconductors

Microstructural characterization is essential to understanding the device performance and application of organic semiconductors (OSC).[24-26] However, morphologic and microstructural features span a range of size-scales from angstrom to micron where atomic, molecular, and
aggregated interactions are all interrelated and further convoluted by the disordered and weakly interacting materials that typify OSCs.[6, 16] Additionally, the near-limitless variability in chemical structure, processing, and blend composition necessitate case by case evaluation to extract meaningful microstructure-device relations.[10, 27, 28] Despite the nuanced and system-specific morphologies that dominate the field of OSCs, some over-arching guidelines provide targeted direction for device fabrication. In OPV devices, for example, molecular orientation, domain size, purity and connectivity require careful curation to reach their highest potential and in organic field-effect transistors (OFET), efforts to control microstructure are typically focused on orientation, crystallinity, and defect density.[14, 26, 29] Further complicating these issues in both polymer and small molecule systems are multicomponent blends. Ideally, the effects of component interactions could be separated from the microstructural changes in the system, but deconvoluting the two is non-trivial. Nevertheless, blended systems and a detailed understanding of their electronic, structural, and morphologic properties are necessary for the field of OPVs and the emerging fields of doped OSCs and organic electrochemical transistors.[4, 7, 30-33] Regardless of the application, proper implementation OSCs can only be accomplished through precise control and characterization of molecular conformations, crystal packing, and film microstructure. Control of these elements are governed principally by the chemical structure.

1.5 Structure Property Relations of Organic Semiconductors

In order to gain a more holistic view of the structure property relations in OSCs each structural variable must be carefully dissected and isolated. In this dissertation, I focus on the influence of linear alkyl side chain size and substitution pattern on the PBTTT oligomer system.
1.5.1 Side Chains

Primarily, side-chains are incorporated to enable solution processing of otherwise insoluble OSCs.[9] Initially, they were assumed to have little effect on performance.[9] This idea was quickly amended as system optimization began to include tuning side chains. Researchers now acknowledge that varying side chain size, type, topology (linear, branched), location, and density can drastically alter a system.[9, 34-36] Specifically, side chains effect chemical (solubility, backbone planarity, oxidative stability), morphologic ($\pi$-stacking orientations, phase separation), and electronic (conjugation length, charge-transport) properties.[2, 9, 37, 38] The immense complexity of the problem is multiplied by the unique chemical properties of each different backbone/polymer whose chemical, morphologic, and electronic effects cannot be uncoupled for the side chains they possess. Knowledge of sidechain effects is greatly underrepresented in the field due to this inherent complication. However, current research is slowly untangling the web of interactions to which side chains are attributed an ever-growing list of phenomena. These phenomena manifest at the macro, micro, and molecular scale making evaluation and eventual prediction necessary for future material design and engineering.

1.5.2 Intercalation

Among side chain phenomena, a rare and unique interaction, called intercalation, has been reported between both polymers and oligomers of PBT TT with the acceptor PCBM.[39-42] This interaction, defined as intercalation, occurs when the sidechains promote the inclusion of PCBM into the repeating crystalline lattice of the donor (thiophene) phase. This interaction has been characterized in great detail for both the polymer and oligomer system and presents a very unique opportunity for fundamental study of the P-N interface among other applications.[24, 43] Behavior consistent with intercalated systems was first reported in 2003[44], however it wasn’t until 2007
when McCullough et al.[42] was the first to identify the phenomena as “fullerene caging” (intercalation). In 2008, the polymer PBTIT became the poster child for intercalated systems, due to its especially high crystallinity and Organic Field Effect Transistor (OFET) performance.[45] Simulations based on Grazing Incidence X-ray Diffraction (GIXD) even produced a molecular model of the intercalated co-crystal.[3]

During this time, the research community recognized this intimate contact allows for exceptional quantity and quality of the interfacial area between phases in organic photovoltaics (OPVs).[46, 47] In the following years, many publications emerged to characterize and employ this well-defined interaction; with hopes of exploiting the especially large interfacial area.[3, 24, 25, 39-43, 46-51] Unfortunately, the interaction that so greatly increases the charge separation events also results in significant and detrimental recombination.[52] Further study revealed that intercalation inherently forbids pure phases of the donor material.[50] Without the pure phase, holes have no energetic driving force to leave the interface and are subject to high probability of recombination.[52] Despite the apparent limitations in the OPV performance, intercalation provides one of the best fundamental systems for studying solar cell processes due to its well defined structure, interaction, and opto-electronic behavior.[43] In my thesis work, I will continue to explore the fundamental properties of intercalation with oligomer systems as a self-assembly strategy in OSCs.

1.6 Applications of Oligothiophenes in Organic Semiconductors

OSC materials are most often integrated into organic field effect transistor (OFET) and organic photovoltaic (OPV) devices where efficient operation in both devices is inherently linked to the chemical and microstructural properties of the organic film, also called the active layer.[7, 15]
1.6.1 Organic Photovoltaic Principles [4, 7]

Solution processed OPV active layers are typically a percolating network of donor and acceptor phases know a bulk heterojunction (BHJ). Once light is absorbed to form an exciton, the BHJ allows the exciton to migrate to an interface and for subsequent separation and charge generation. Finally, these free charges must transport through the BHJ to an electrode for collection. Within the PV process, precise control of the BHJ microstructure (e.g.; interfaces, domain size/purity, connectivity, and interaction between phases) is essential to optimize performance.

Among the continuing attempts to improve control of the blended film microstructure, fullerene intercalation emerged as a promising candidate. In intercalated systems, the PCBM is intimately mixed at the molecular level within a donor matrix, often improving the crystalline order of the donor.[53] Additionally, fully intercalated blends allow for the fullerene and donor to experience the largest possible interfacial area while still maintaining connectivity. In the OPV process, this would eliminate the need for excitons to migrate to an interface because donor and acceptor molecules are co-crystalized into a single phase. However, OPV devices of intercalated systems revealed the benefits in efficient charge generation from intimate contact of the P-type (polymer) and N-type (fullerene) domains are far outweighed by an extensive loss in free carriers due to geminate recombination; leading to lower than expected PCEs.[24]

1.6.2 Organic Field Effect Transistor Principles [15, 47]

In both OPVs an OFETs, the ability to transport charges through the active layer is essential the device operation. In OFETs, the active layer is polarized by a gate electrode and dielectric to from charge carriers within 5 nm of the dielectric interface. Two other electrodes, the source and drain, are in contact with the active layer directly and an applied voltage causes charges to be injected from the source, drifted through the active layer, then collected at the drain. Only when gate
voltage is applied are charges transported efficiently. OFETs provide an excellent device architecture to study metal-organic interfaces, oxidative stability, interfacial defects, and other substrate effects. However, and possibly most importantly, it allows for direct correlation between charge transport performance and the crystal packing/microstructure of the active layer. [54]

1.7 Summary and Outlook

1.7.1 Summary

The major underlying theme of this dissertation is:

*The implementation of side chains to drive self-assemble in semiconducting small molecules.*

To accomplish this, we first needed to characterize the intrinsic conformational preferences of the BTTT molecule. Chapter 2 focuses on this concept. After understanding the molecule at an atomistic scale, we can begin to piece together the intermolecular driving forces which work in tandem with the molecular design and intramolecular interactions to drive self-assembly. This fundamental work, presented largely in Chapter 2, establishes a baseline for future alternations to the molecular structure.

Chapter 3 and 5 leverage the fundamental baseline to generate powerful structure property conclusions through a systematic study of side chain length. Although the systematic monomer and dimer experiments are simple in both chemistry and concept, this sort of deep exploration into the influence of side chains is largely underrepresented in the field. In the monomer system, we learned that alkyl chains are exclusively responsible in determining the registration between layers of molecules. Additionally, we also observe the ability for side chains to interdigitate in a variable-substitution monomer, which provided an exciting concept for the work in the final chapter. In the systematic dimer study (Chapter 5), we predicted a sufficiently short alkyl chain would prevent
intercalation. However, we observed instead an order to disorder transition at small side chains where dimers and fullerene are still intercalated, but not crystalline. Much of the preliminary work for the systematic dimer study was supported by Chapter 4 where we extensively characterize BTTT-2-12:PC₆₁BM blended thin films at a variety of blend ratios. Careful microstructure characterization of fullerene blends in Chapter 4 was well worth the effort as it provided an excellent comparative platform for the structure-property relations observed in systematic dimer series and variable-substitution dimers studied in Chapter 5 and 6, respectively.

Finally, in a beautiful combination of fundamental work in Chapters 2 and 4, and the structure property-exploration in Chapters 3 and 5, we apply our knowledge of the BTTT system to synthesize and characterize variable-substitution dimers. These molecules have varying patterns of short and long chains which display a myriad of assembly behaviors as neat films, and as blends with PC₆₁BM.

1.7.2 Outlook

In a broader sense, this dissertation also builds a compelling molecular design guide for future side chain engineering. In OSCs, improvements in electronic properties can be gained by reducing disorder and improving crystallinity. This dissertation provides new approaches for improving the crystallinity and order in both small molecule and polymer systems. In BTTT dimers, the most crystalline systems which still adopt a favorable crystal packing is the BTTT-4-12-12-4 which has side chains of varying lengths. This molecule shows improve crystallinity in the thin film as well as unprecedented order in the intercalated co-crystal. Translating this to a polymer system would not require new chemistries or challenging synthesis and could yield a interdigitated and intercalated system like that observed in BTTT-4-12-12-4.
Additionally, the extensive study in intercalated systems is also relevant to new directions in the field of OSCs. Recently, OPVs have been surpassed by other solution based technologies and the research teams in these areas are already beginning to pivot to new OCS applications. One of the most promising fields is doped OSC. Doped OSCs currently are poorly understood although their potential for application in thermoelectrics and/or organic electrochemical transistors is well recognized. Essential to these new technologies is the interaction of the OSC with a secondary dopant molecule, analogous to OPV active layers. However multicomponent blending almost always results in disruption of the microstructure, molecular packing, and charge transport properties. Although doping can be accomplished with many OSC systems, device performance leaves much to be desired. One strategy to overcome disruptions in blended microstructures, intercalation and specifically, co-crystal formation is covered in detail in this dissertation. The benefit realized by intercalation is the intimate and multicomponent mixing required for the field of doping which can be accomplished without disrupting the crystallinity, microstructure, or connectivity of the OCS. Building a more complete understanding of the packing forces which allow co-crystal formation will undoubted lead to new, more intelligent, molecular design to address the challenges presented in both new and old areas of OCS research.

Finally, future work in these systems includes, new side chain chemistries, ternary blends, study of self-assembly and templating through blending or thermal cycling, and implementation of new side chain patterns into polymer systems. A new class of side chains that are particularly interesting is the ethylene glycol based chains. These chains are more water, ion, and biologically compatible and will likely be a popular choice for new interdisciplinary work between OCS and biology.[11] In future work, we also would like to blend multiple dimers together and compare the solid-state behavior in films of variable side chain dimers with blends of BTTT-2-4 molecules and BTTT-2-
This concept could be expanded to explore the blending behavior of any binary, ternary, or quaternary blend of dimers and/or fullerenes. Finally, the lessons learned from the variable-substitution in Chapter 6 provide a tantalizing direction for improving polymer crystallinity through side chain patterning.

1.8 Dissertation Overview

- Chapter 1
  Introduction, Summary, Outlook, and Overview.

- Chapter 2
  Collaborators: Stephen Lopez, Ilhan Yavuz, Lei Zhang, Kendall Houk, Sean Parkin

We report substituent effects on conformational preferences and hole mobilities of 2,5-bis-(thiophen-2-yl) thieno[3,2-b]thiophenes (BTTT) monomer and dimer, and hexyl derivatives. We employ single-crystal X-ray diffraction, computational analysis, and thin-film transistors to explore the difference between monomer, dimer, and effect of hexyl substitution. The hexyl-substituted molecules show marked differences in solid-state packing compared to the unsubstituted analogs. Most notably, the alkylated monomer crystal structure exhibits terminal thiophenes in the syn conformation. In contrast, the unsubstituted monomer adopts the more conventional anti conformation. The hexyl-substituted dimer, however, features a mixture of syn and anti thiophenes. Gas-phase conformational analysis of oligomers using density-functional theory calculations rationalize the intramolecular conformational preferences. We simulate thin-film hole mobilities and find excellent agreement with experiment. Theoretical results support our hypothesis that alkyl side chains cause these small molecules to adopt orientations more favorable for charge transport, as observed by an order of magnitude enhancement in hole mobilities upon hexyl substitution of the monomer.
• Chapter 3

Collaborators: Edmund Burnett, Sean Parkin

A series of poly(2,5-bis-(3-alkylthiophen-2-yl) thieno[3,2-b]thiophenes) (PBTTT) monomers with varying alkyl side-chain lengths are synthesized, characterized, and tested in p-channel organic field-effect transistors (OFETs). We observe an even-odd material properties effect with the alkyl side-chain length variation. We characterize even-odd effects by differential scanning calorimetry (DSC), single crystal X-ray diffraction (SCXRD), grazing-incident X-ray diffraction (GIXD), and hole mobility measurements. SCXRD reveals the crystal packings in even and odd monomers are different, a finding corroborated by the trend in thermal transitions. The morphology of the thin films does not correspond to the single crystal morphology for the odd-type molecules. We attribute this new thin film packing to our observed hole mobilities in OFETs.

• Chapter 4

Collaborators: Martina Causa, Eliot Gann, Brooke Kuei, Ester Buchaca-Domingo, Yao Liu, Liang Ma, Natalie Stingelin, Enrique Gomez, Christopher McNeill, Natalie Banerji

We characterize the morphology and device performance of intercalated blends of 2,5-bis(3-dodecylthiophen-2-yl)thieno[3,2-b]thiophene (BTTT) dimers and phenyl-C61-butyric acid methyl ester (PCBM). Our previous work shows that PCBM spontaneously intercalates into pBTTT dimers. In this work, we employ grazing incidence x-ray diffraction (GIXD), transmission electron microscopy (TEM), UV-Vis, photoluminescence (PL), and differential scanning calorimetry (DSC) to rationalize performance trends in organic photovoltaic (OPV) and field-effect transistor (OFET) devices. Characterization of the full range of blend fractions reveals a complex evolution of morphology which defines the observed OFET and OPV performance trends. GIXD reveals 3 distinct crystalline phases: interdigitated BTTT, intercalated/co-crystal, and clustered PCBM.
Additionally, through a combination of techniques we report a new amorphous mixed phase morphology unique to this system at low wt% blends of BTTT.

- Chapter 5

**Collaborators: Edmund Burnett, Detlef Smilgies, Steve Rosa, Sean Parkin**

Polymer/fullerene bimolecular crystal formation has been investigated using a variety of conjugated polymers and fullerenes to understand the design rules that influence donor-acceptor interaction. Modifications of the polymer by varying the substitution side chain position, density, and branching have demonstrated the importance of the “pocket” dimensions (free volume between side chains where the fullerene resides) for controlling intercalation. Yet the effect of pocket height has not been systematically explored due to the solubility limitations in polymers. In this report, we present the first experimental investigation into the effect of the pocket height by synthesizing poly[2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene] (PBT) dimers with varied side chain lengths and track the morphological changes of the dimer/fullerene blends using grazing-incidence X-ray scattering, thermal measurements, and photoluminescence quenching. We identify two regimes: 1) oligomers with side chains \( \geq \) heptyl (C7) form bimolecular crystals and 2) oligomers with \( \leq \) hexyl (C6) form intercalated amorphous blends. This work provides the first observation of an order-to-disorder transition mediated by side chain length in donor-fullerene intercalated blends.

- Chapter 6

**Collaborators: Edmund Burnett, Detlef Smilgies, Sean Parkin**

Building on the work from all the previous chapters, I describe the synthesis and characterization of variable-substitution BTTT dimers as crystals, thin films, and blends with PC\(_{61}\)BM. Variable-substitution dimers are synthesized with two butyl (C4) and two dodecyl (C12) chains in varying substitution patterns along the backbone to yield BTTT-4-4-12-12, BTTT-12-4-4-12, and BTTT-
4-12-12-4. Attempted synthesis and failure analysis is also described for the remaining, BTTT-4-12-4-12 molecule. Characterization by SCXRD, DSC, and GIXD reveals that each system exhibits different crystal packing and intercalation behavior. In neat films, we observe mostly an interdigitated lamellar morphology although the 4-4-12-12 pattern does not appear to be interdigitated. When blending with fullerene, the 12-4-4-12 does not intercalate and instead form pure domains of oligomer. Most interestingly, BTTT-4-12-12-4:fullerene blends interdigitates and intercalates to form co-crystal domains with the highest crystalline order and fidelity yet observed.
CHAPTER 2

ALKYL SUBSTITUTION ON THE BTTT SYSTEM

![Diagram of Monomers and Dimers with R = H and R = C₆H₁₃]

Figure 2. Molecules used in this chapter. Shown in all-anti conformations with adjacent sulfurs opposing one another.

2.1 Introduction

Sidechain substitution on the backbone of organic semiconductors, particularly thiophenes, is fairly well understood. As discussed previously, each backbone and side chain combination constitutes a different system with properties that cannot be entirely predicted, however, the existing body of research has matured enough to establish basic design rules and property predictions.[2, 18, 35, 55, 56] These studies often leverage the crystal structures of the oligomers.[18, 20-22, 30, 57-80] I have identified a recurring theme in reported crystal structures: terminal thiophenes in many of these oligomer systems, oligo-quarterthiophene[22] and oligo-BTTT[20] for examples, adopt syn (adjacent thiophene sulfurs on the same side) conformations. This is contrary to how these systems are typically depicted in the literature.

The majority of oligothiophene publications report interior alpha-coupled thiophenes as the expected anti (adjacent sulfurs on opposing sides) conformation in the single crystal.[20-22, 30, 57-59, 61, 64-69, 71-76, 81-86] Exceptions exist, but typically are substituted with multiple chains, bulky groups, or flanked by relatively strongly interacting units.[63, 75, 86] However, the terminal
thiophene conformation is much less consistent and is undoubtedly influenced by substitution patterns and solid-state interactions. Many examples of terminal thiophenes in both anti[20, 22, 30, 57-59, 63-67, 69, 71, 73-76, 81-86] and syn[20-22, 61, 63, 66-68, 71, 72, 75, 82, 86] conformations exist in the literature.

By carefully characterizing the effects of alkyl substitution in the BTTT system by characterizing hexyl-substituted and unsubstituted monomers and dimers (Figure 2), I hope to refine these predictions and establish a strong fundamental foundation for further study on the BTTT system. Of particular interest is the effect of substitution on backbone conformation. Understanding the intramolecular interactions will help future design of planar backbones and identify optimum positions for substitution to facilitate backbone planarity or control self-assembly. Single-crystal X-ray diffraction (SCXRD), and computational analysis will determine the backbone-sidechain interactions within this system. Secondly, we expect the device performance to vary with substitution. Transistor performance in organic semiconductors is inherently linked to the molecular arrangement and the disorder (static and dynamic) present in the film; both of which manifest from the molecular structure. Thin-film transistors and computational simulations will explore the structure-property relationships devices.

2.2 Synthesis of Substituted and Unsubstituted Oligothiophenes

3-bromothiophene 5, 2-hexyl-3-bromothiophene 6, and 2,5-di(trimethyltin)-thieno[3,2-b]thiophene 7 are commercially available. 2,5-Bis-(thiophen-2-yl)thieno[3,2-b]thiophene (1) 5-(triisopropylthiophe-2-yl) thieno[3,2-b]thiophene 10 was synthesized according to literature procedure.[80, 87] THF was dried over sodium and distilled. Suitable crystals for SCXRD were obtained though slow evaporation from Hexanes. Spectra in Appendix A.
Scheme 1 Synthesis of BTTT-1-H (1), BTTT-1-6 (2) and BTTT-2-6 (4).

2,5-Bis-(thiophen-2-yl)thieno[3,2-b]thiophene (1)[80]

2-bromothiophene (5) (0.772 g, 4.74 mmol), 2,5-bis-(trimethyltin)thieno[3,2-b]thiophenes (7) (1.03 g, 2.22 mmol), and Tetrakis(triphenylphosphine)palladium(0) (0.124 g, 0.107 mmol) were combined with toluene (100 mL) under N₂. The reaction was stirred and refluxed 15 hrs. After cooling to room temperature, methanol 50 mL was added and the product (1) was collected by gravity filtration and recrystallized twice with acetone to yield 1 (0.283 g, 42%) as a yellow-brown powder. Crystals suitable for X-ray analysis were grown in physical vapor transport. ¹H NMR shifts available in literature.[80]

2,5-Bis-(3-hexylthiophen-2-yl)thieno[3,2-b]thiophene (2)

Follows similar procedure to literature.[20, 22, 80] 2-bromo-3-hexylthiophene (0.58 g, 2.35 mmol), 2,5-bis-(trimethyltin)thieno[3,2-b]thiophene (0.5 g, 1.07 mmol), and Tetrakis(triphenylphosphine)palladium(0) (0.062 g, 0.0536 mmol) were combined with toluene (100 mL) under N₂. The reaction was stirred and refluxed 15 hrs. Toluene was removed under reduce pressure and hexanes was added. After gravity filtration, the mother liquor was collected and the compound (2, yellow solid) was purified by column chromatography on silica gel (hexanes). This yielded 2 (0.26 g, 52%) ¹H NMR (500 MHz, CDCl₃, δ) 7.26 (s, 2H), 7.24 (d, 2H), 6.99 (d, 2H), 2.83 (t, 4H), 1.71 (m, 4H), 1.42-1.28 (m, 12H), 0.92 (t, 6H)
2-(3-hexyl-5-bromothiophen-2-yl)-5-(3-hexylthiophen-2-yl)-thieno[3,2-b]thiophene (9)

2 (0.85 g, 1.80 mmol) was added to a stirring mixture of glacial acetic acid and chloroform (100 ml, 50:50. N-bromo-succinimide (0.33 g, 1.85 mmol) was added after 1 completely dissolved. The reaction was left in the absence of light at room temperature under N₂ to react for 15 hrs. To the reaction 100 ml of water was added and the product was extracted with hexanes. The organic layer was reduced under vacuum and the product was purified by column chromatography (hexanes). Since the material elutes close to the di-brominated product and unreacted product, purification was challenging. This yielded 9 (0.50g, 50%). 

1H NMR (500 MHz, CDCl₃, δ) 7.23 (s, 1H), 7.22 (d, 1H), 7.19 (s, 1H), 7.08 (d, 1H), 6.98 (d, 1H), 2.80 (t, 2H), 2.74 (t, 2H), 1.63 (m, 4H), 1.42-1.28 (m, 12H), 0.92 (t, 6H)

2,5-Bis-(3-hexylthiophen-2-yl)thieno[3,2-b]thiophene dimer (4)

9 (0.50 g, 0.91 mmol), hexamethylditin (0.139 g, 0.425 mmol), and Tetrakis(triphenylphosphine)palladium(0) (0.05 g, 0.0432 mmol) were combined with toluene (100 mL) under N₂. The reaction was stirred and refluxed 15 hrs. Toluene was removed under vacuum and hot hexanes was added. The compound (4, orange powder, red crystal) was purified by column chromatography on silica gel (hexanes). This yielded 4 (0.196 g, 45%). 1H NMR (500 MHz, CDCl₃, δ) 7.27 (s, 4H), 7.25 (d, 2H), 7.06 (s, 2H), 7.00 (d, 2H), 2.84 (m, 8H), 1.71 (m, 8H), 1.42-1.28 (m, 24H), 0.92 (t, 12H)

2-(5-triisopropylsilyl-thiophen-2-yl)-thieno[3,2-b]thiophene (10)

Synthesis of this compound is reported in literature.[87]

2-Bromo-5-(5-triisopropylsilyl-thiophen-2-yl)-thieno[3,2-b]thiophene (11)

10 (.20 g, 0.53 mmol) and N-bromo-succinimide (0.096 g, 0.53 mmol) was added to a stirring mixture of glacial acetic acid and chloroform (100 ml, 50:50 by vol). The reaction was left in the
absence of light at room temperature under N2 to react for 15 hrs. To the reaction 100 ml of water was added and the product was extracted with hexanes. The organic layer was reduced under vacuum and the product was purified by column chromatography (hexanes). This yielded 11 (0.2, 81%). 1H NMR (400 MHz, CDCl3, δ) 7.33 (d, 1H), 7.32 (s, 1H), 7.30 (s, 1H), 7.22 (d, 1H), 1.34 (m, 3H), 1.13 (d, 27H)

Scheme 2 Synthesis of 2-H (3)

2,5-bis-(5-triisopropylsilyl-thiophen-2-yl)-thieno[3,2-b]thiophene Dimer (12)

11 (.20 g, 0.44 mmol) and 5,5’-bis-(trimethylstanyl)-2,2’-bithiophene and Tetrakis(triphenylphosphine) palladium(0) (0.01 g, 0.008 mmol) were combined with toluene (80 mL) under N2. The reaction was stirred and refluxed 15 hrs. Product was recovered by precipitation into methanol followed by vacuum filtration. Recrystallized 2x from Toluene gave a red powder. This yielded 12 (0.15 g, 38%). Lack of solubility prevented NMR analysis. Confirmation of product by MALDI-ToF shows the correct 917.8 m/z (expected m/z 919.6).

2,5-Bis-(thiophen-2-yl)thieno[3,2-b]thiophene Dimer (3)

Deprotection of 12 (.1 g, 0.11 mmol) was performed by tetrabutylammoniumfluoride (8 eqv, 1M in THF) in a refluxing THF solution overnight. The product precipitated out of solution and was collected by vacuum filtration and washed with Hot Toluene and Hot THF. This yielded 3 as a red/orange powder (56 mg, 85%).This product was entirely insoluble except in boiling
trichlorobenzene. Confirmation of product by MALDI-ToF shows the correct 605.5 m/z (expected m/z 606.9).

Figure 3 MALDI-ToF of TIPS-BTTT-2-H (12) and BTTT-2-H (3)
2.3 Crystal Packing

The unsubstituted monomer (BTTT-1-H) crystallizes with the triclinic P1 space group with two crystallographically distinct half molecules in the asymmetric unit. It assumes the herringbone packing motif characterized by slipped edge-to-face interactions with an interplanar angle of 63° (Figure 4; a-c). Disorder within the unit cell could also be identified. The BTTT-1-H has two major disorders: first the whole molecule is disordered by a ~180° rotation about the long molecular axis (still anti-anti, but rotated relative to the neighboring monomers). Secondly, the central thienothiophene unit can be flipped relative to one or both of the end thiophenes (syn-anti or syn-syn). Predominantly, the BTTT-1-H molecule is anti-anti (adjacent sulfurs on opposing sides).
though with a small population of syn-syn and/or anti-syn conformation. This indicates that anti-anti is the preferred conformation for BTTT-1-H.

Despite many attempts, a BTTT-2-H (structure in Figure 5; b) crystal suitable for X-ray analysis could not be obtained. We expect BTTT-2-H to have many of the same features observed for BTTT-1-H as well as a variety of other linear unsubstituted thiophene small molecules; namely, a planar, all-anti conformation and herringbone packing motif.[58, 82, 83]

The alkylated monomer (BTTT-1-6) has space group P2₁/n, with a half molecule in the asymmetric unit and an end-to-face herringbone packing motif (Figure 4; d-f). The intermolecular backbone distance between adjacent molecules aligned along the b-axis do not indicate any close π–π interactions (>3.4 Å). Interestingly, the alkyl chains prevent rotational disorder of the terminal thiophene rings, but the central fused thienothiophene is disordered by a ~180° flip. The terminal thiophenes are predominantly in the syn-syn conformation (the preferred conformation), but with a large torsion angle of 38° with respect to the thienothiophene core.

The alkylated dimer (BTTT-2-6) crystallizes in space group P1 with one whole molecule in the asymmetric unit (Figure 4; g-i). The π–π distance in BTTT-2-6 is ~3.5 Å which also does not indicate significant π-interactions. This unusual packing has the hexyl chains curving away from a surprisingly planar backbone. The three hexyl groups on one side of the molecule interdigitate with hexyls on inversion-related molecules. The structure is severely disordered due to a complicated superposition of conformers. In brief, the disorder manifests from a 180° flip of one or both of the thienothiophenes. The thiophenes are again prevented from rotating due to alkylation, but experience small translational shifts depending on the adjacent thienothiophene conformation. Half of the molecule is predominantly anti-anti and the other half is 50/50 anti-syn/syn-anti. From what we observed in the hexyl-monomer preferences, the anti conformation is
unexpected; we address this in the computational analysis section. The 50/50 occupancy of the other thienothiophene occurs because both conformations are essentially equivalent in energy (anti-syn = syn-anti).

2.4 Optical and Electrochemical Properties

![Graphs showing UV-Vis spectra](#)

*Figure 5* Normalized UV-Vis spectra of the materials in chloroform [BTTT-2-H in hot TCB] (dashed red) and thin film on glass (solid black): a-d) BTTT-1-H, BTTT-2-H, BTTT-1-6, BTTT-2-6, respectively. Thin film of BTTT-2-H was evaporated (~20 nm), all other films were spin coated from chloroform solution.

The UV-Vis absorption spectra of the BTTT oligomers in chloroform solution (BTTT-2-H in hot trichlorobenzene) and thin films are shown in Figure 5. The solution maximum absorption of BTTT-1-H shows a red shift compared to BTTT-1-6; 373 and 350 nm respectively. The solid state
for both monomers show a blue shift compared to their solution spectra, and the BTTT-1-H shift is much larger than the BTTT-1-6 ($\Delta \lambda_{\text{max}} = 42$ nm and 8 nm respectively). The larger shift in the BTTT-1-H $\lambda_{\text{max}}$ is due to the H-aggregate arrangement in the solid state, as this phenomena is previously reported for this system.[80] The smaller blue shift of BTTT-1-6, may be due to weaker H-aggregation, the loss in backbone planarity imposed by the molecular packing, or a combination of these effects.

The dimers (b and d) show a red-shifted absorption compared to the monomers due to the extended conjugation.[88] Among the dimers, BTTT-2-H has a red shifted maximum absorption compared to the BTTT-2-6 due to its enhanced backbone planarity in solution. The solid state of BTTT-2-H is also strongly blue shifted ($\Delta \lambda_{\text{max}} = 68$ nm) from its solution state spectra; likely due to H-aggregation. The BTTT-2-6 spectra shows a broadening and redshift in the solid state. This lower energy absorption is evidence of a J-aggregate.[80]

<table>
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<th>Material</th>
<th>$\lambda_{\text{max}}$ Soln$^a$ [nm]</th>
<th>$\lambda_{\text{max}}$ Film$^b$ [nm]</th>
<th>OG$^c$ [eV]</th>
<th>IP$^d$ [eV]</th>
<th>EA$^e$ [eV]</th>
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</tbody>
</table>

$^a$Absorptions were measured from thin films on glass. $^b$Absorptions measured from methylene chloride solution. $^c$Determined from onset of absorption in the solution UV-Vis. $^d$Determined by cyclic voltammetry (CV) in chloroform. $^e$Estimated from the sum of OG and IP. $^f$Computed using B97d/def2-QZVP//B97d/def2-TZV

The optical band gap was determined by using the absorption edge from the solution spectra. Cyclic voltammetry was performed in dichloromethane with 0.1 M TBAPF6 as the electrolyte and a scan rate of 100 mV/s to determine the ionization potentials (IP) of the oligomers. Table 1 shows a summary of the electrochemically determined IP from the onset of oxidation as compared to ferrocene. The electron affinity (EA) was calculated by the sum of the IP and the optical gap (OG).
2.5 Computational Analysis of Backbone Conformations

Stephen Lopez, while in the Houk Group, calculated gas-phase optimized structures with the B97D density functional at the def2-TZV level of theory. Single-point energies were obtained from the optimized geometries with the B97D[89] functional and the large def2-QZVP basis set.[90] Following an experimental and theoretical approach previously used to understand the origin of paracrystalline disorder in PBTTT[35], the hexyl group of BTTT-1-H was replaced by methyl (1-Me) or ethyl (1-Et) groups to reduce computational expense.

Figure 6. CV of BTTT oligomers in DCM with 0.1M Tetra-n-butylammonium hexafluorophosphate.
In order to evaluate the steric effects, van der Waals radii \(^1\) \(r_{\text{vdw}}\) [\(Sr_{\text{vdw}}: 1.8\ \text{Å}, \ Hr_{\text{vdw}}: 1.2\ \text{Å}\)] were used to identify critical interactions where interaction distances for atomic pairs is based on the sum of two \(r_{\text{vdw}}\). S-S, H-H, and S–H interactions were evaluated for their influence on the final conformation when rotating the terminal ring. For the BTTT-1-H system, only S-S interaction lengths were within the critical van der Waals distance. This suggests that H\(_{\text{aryl}}\)-H\(_{\text{aryl}}\) interactions are negligible and S–S lone pair repulsion dominates the intrinsic preference for the \textit{anti-anti} conformer of BTTT-1-H.

Table 2. Optimized Gas-Phase Geometries and Dihedral angles for BTTT-1-H, 1-Me and 1-Et. The dotted lines highlight important H\(_{\text{aryl}}\)-H\(_{\text{alkyl}}\) interactions unsubstituted BTTT-1-H monomer, 1-Me and 1-Et have global energy minima in the \textit{syn-syn} conformation with relatively large torsion angles, 38° and 39°, respectively. These structures agree with the BTTT-1-6 crystal structure (38° torsion angle observed in crystal packing).

<table>
<thead>
<tr>
<th>1-R</th>
<th>SCCS Dihedral</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTTT-1-H</td>
<td>168° [anti-anti]</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>1-Me</td>
<td>38° [syn-syn]</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>1-Et</td>
<td>39° [syn-syn]</td>
<td><img src="image" alt="Structure" /></td>
</tr>
</tbody>
</table>

Possible steric interactions were also evaluated for the 1-Me and 1-Et systems based on the \(r_{\text{vdw}}\).

The interaction distances for S-H\(_{\text{alkyl}}\), H\(_{\text{aryl}}\)-H\(_{\text{alkyl}}\), and S-S interaction were within the \(r_{\text{vdw}}\) sum. The H\(_{\text{aryl}}\)-H\(_{\text{alkyl}}\) interaction is shown by the dotted lines in Table 2. For the alkylated systems, these additional interactions cause increased torsion in the optimized \textit{syn-syn} conformation (~38°) vs the BTTT-1-H \textit{syn-syn} local minima (~32°), and outweighs the S-S repulsion to prefer the \textit{syn}
conformer. The relative free energies of syn and anti conformations for the monomer systems are given in Table 3.

**Table 3. The computed relative free energies, SCCS dihedral angles (ϕ₁ and ϕ₂) of BTTT-1-H, 1-Me, and 1-Et.**

<table>
<thead>
<tr>
<th>1-R</th>
<th>ΔG_{rel} (kcal·mol⁻¹)</th>
<th>SCCS (ϕ₁, ϕ₂)</th>
<th>ΔG_{rel} (kcal·mol⁻¹)</th>
<th>SCCS (ϕ₁, ϕ₂)</th>
<th>ΔG_{rel} (kcal·mol⁻¹)</th>
<th>SCCS (ϕ₁, ϕ₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-H</td>
<td>0.0</td>
<td>168, 168</td>
<td>0.8</td>
<td>173, 32</td>
<td>1.5</td>
<td>33, 33</td>
</tr>
<tr>
<td>1-Me</td>
<td>0.8</td>
<td>149, 149</td>
<td>0.3</td>
<td>145, 38</td>
<td>0.0</td>
<td>38, 38</td>
</tr>
<tr>
<td>1-Et</td>
<td>1.0</td>
<td>139, 139</td>
<td>0.5</td>
<td>139, 40</td>
<td>0.0</td>
<td>39, 39</td>
</tr>
</tbody>
</table>

We computed the torsional potential for BTTT-1-H and 1-Me to better understand how the unfavorable steric and orbital effects described above contribute to the overall torsional potentials about ϕ₁ and ϕ₂ (Figure 7).[37] 0° indicates a planar syn conformation and 180° indicates a planar anti conformation. The rotations all exhibit maxima at ±90° and 0°, which are the rotational barriers. In the red line (circles), BTTT-1-H shows a global minimum in the anti-anti conformation at approximately 180°. In the blue line (squares) with the conformers of 1-Me, the lowest energy conformer is syn-syn, and S–S repulsion causes substantial deviation from planarity.

With a better understanding of the relative energies of intramolecular interactions we can now address the observed conformational preferences in the solid state. BTTT-1-H prefers the planar, all-anti conformation because of S-S repulsion and planarizing contributions from π-electron delocalization. On the other hand, BTTT-1-6 intramolecular alkyl interactions outweigh the S-S repulsion and prompt this system to adopt the syn-syn conformation. In BTTT-2-6, we can rationalize the presence of the anti conformation. The 1-Me (blue squares) in Figure 7 best represents this interaction in the alkylated dimer. Although the global minimum is indeed a twisted
syn conformation, the system is constrained to a planar conformation in the crystal. Therefore, the thiophene-thienothiophene interactions can only adopt $0^\circ$ or $\pm 180^\circ$. Comparing these two energies, the **anti** conformation is lower in energy and is thus favored.

**Figure 7.** Torsional potentials (kcal mol$^{-1}$) for SCCS torsion (in degrees) for BTTT-1-H (red, circles) and 1-Me (blue, squares). Computed using B97d/def2-QZVP//B97d/def2-TZV.

**Figure 8.** Transfer curves of BGBC thin film transistors of (a) BTTT-1-H, (b) BTTT-2-H, (c) BTTT-1-C6, and (d) BTTT-2-C6.
2.6 Effects of Alkylation on Charge Transport

We characterized charge transport in thin-film organic field-effect transistors (OFETs). Electrical measurements were performed under ambient conditions using a standard probe station. Thin-film OFETs were fabricated in a bottom-gate, bottom-contact geometry by spin coating 10 mg/ml solution of oligothiophenes in chloroform at 3000 rpm for 60 s. The hole mobilities calculated in the saturated regime, threshold voltages, and current on/off ratios can be seen in Figure 8. The measured mobilities of BTTT-1-H, BTTT-1-C₆ and BTTT-2-C₆ are 3.2 x 10⁻⁴, 5.2 x 10⁻³, and 2.5 x 10⁻³ cm²/Vs, respectively.

Both BTTT-1-C₆ and BTTT-2-C₆ have comparable mobilities in the thin film, however the BTTT-1-H film is an order of magnitude lower than the alkylated oligomers. Stephen Lopez performed charge transport simulations to understand the lower mobility of BTTT-1-H compared to BTTT-1-C₆ and BTTT-2-C₆.

<table>
<thead>
<tr>
<th>Material</th>
<th>λ   (meV)</th>
<th>σ   (meV)</th>
<th>J   (meV)</th>
<th>μₐₗₜ   (cm²/Vs)</th>
<th>μₑₓᵖ   (cm²/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTTT-1-H</td>
<td>420</td>
<td>80</td>
<td>6</td>
<td>2.3 x 10⁻⁴</td>
<td>3.2 x 10⁻⁴</td>
</tr>
<tr>
<td>BTTT-1-C₆</td>
<td>618</td>
<td>56</td>
<td>170</td>
<td>1.0 x 10⁻³</td>
<td>5.2 x 10⁻³</td>
</tr>
<tr>
<td>BTTT-2-C₆</td>
<td>638</td>
<td>54</td>
<td>104</td>
<td>6.3 x 10⁻³</td>
<td>2.5 x 10⁻³</td>
</tr>
</tbody>
</table>

Stephen Lopez, while in the Houk Group, also simulated the morphologies using classical molecular dynamics (MD) simulations (with AMBER[91]) and charge-carrier dynamics using kinetic Monte Carlo[92] (kMC) simulations (using VOTCA[93]), based on Marcus Theory.[94] We calculated the charge-transport properties, reorganization energies (λ), energetic disorder (σ), electronic-coupling (J) distributions and the hole-mobilities (μₑₓᵖ) for these BTTT oligomers. The
reorganization energies are calculated by the four-point rule\cite{7} using the B3LYP\cite{95} density functional using the 6-311G(d,p) basis set. The energetic disorder is obtained from the distribution of site-energy differences calculated by the Thole\cite{96} model. The electronic-coupling between molecular dimers are calculated using ZINDO\cite{97} semi-empirical methods.

\[ \Delta g = 1.4\% \quad \Delta g = 1.8\% \quad \Delta g = 2.7\% \]

**Figure 9.** (Top row) crystal structures of BTTT-1-H, BTTT-1-C6, and BTTT-2-C6 with principal charge transport direction indicated in red. Hexyl side-chains are represented with green sticks for clarity. (Bottom row) snapshot crystal configurations before (left) and after (right) introducing thermal disorder with AMBER molecular dynamics. BTTT-1-H (red), BTTT-1-C6 (green), BTTT-2-C6 (blue) with the simulated paracrystalline disorder parameter, $\Delta g$. Credit Stephen A. Lopez.

The initial configurations were constructed as multiple copies of the unit cells in three crystallographic directions (Figure 9). We used 1560, 1536 and 1536 molecules for BTTT-1-H, BTTT-1-C6, and BTTT-2-C6 respectively. The initial crystal models are equilibrated at 300 K in an NPT ensemble for 6 $\text{ns}$ followed by a production run lasting 10 $\text{ns}$. The predicted morphologies are shown in Figure 9 where the hexyl side chains are shown as green sticks for clarity. kMC simulations are performed on snapshots of the MD trajectories based on Marcus theory. We sought to understand the origin of the mobilities by employing molecular dynamics simulations. Figure 9 shows the initial configurations (left box) and the snapshots of representative
disordered morphologies of BTTT-1-H, BTTT-1-C₆, and BTTT-2-C₆ materials (right box). Under each of these snapshots is the paracrystalline disorder parameter \( \Delta g = \delta/\langle d \rangle \). Here, \( \delta \) is the standard deviation and \( \langle d \rangle \) is average of intermolecular distance distributions between oligomer centroids within the snapshot.

The BTTT-1-H morphology remains visibly ordered after MD equilibration. However, BTTT-1-C₆ and BTTT-2-C₆ morphologies are relatively changed after MD equilibration. These have paracrystallinity values of 1.4%, 1.8% and 2.7% respectively. The structural disorder leads to fluctuations in energetic landscapes during charge-transport, which enhances energetic disorder in these thin films. The energetic disorder parameter can be predicted by computing the site energy differences. The site-energy difference is defined as the difference between HOMO energies of the system during charge-transfer. The distributions of site energies of the equilibrated morphologies are shown in the SI of ref [5]. The energetic disorder is calculated from the standard deviations of these data distributions.

The simulated mobilities (summarized in Table 4) were in good agreement of \( \mu_{\exp} \) and correctly predict the lower performance of the BTTT-1-H. This is in line with our previous study that established a methodology by which hole mobilities can be computed within an order of magnitude of the experimental mobility.[98] BTTT-1-H features molecules arranged in a herringbone packing, while BTTT-1-C₆ and BTTT-2-C₆ monomers are slip-stacked. The herringbone packing minimizes orbital overlap (\( J \)); it is nearly two orders of magnitude lower than those of BTTT-1-C₆ and BTTT-2-C₆ (6 vs 170 and 104 meV, respectively).

The alkyl chains provide stabilizing intermolecular dispersive interactions that result in slip-stacked arrangements for BTTT-1-C₆ and BTTT-2-C₆ and enhanced overlap integrals. According to Marcus Theory, hopping rate is proportional to \( J^2 \), and the low \( J \) in BTTT-1-H is responsible for
the low mobility relative to BTTT-1-C₆ and BTTT[2-C₆], despite the more favorable reorganization energy (420 vs. 618 and 638 meV, respectively).

2.7 Conclusion
I synthesized unsubstituted and hexyl-substituted monomers and dimers of the PBTTT system. These materials were characterized as single crystals and further evaluated with computational chemistry for insight into observed crystal-packing conformations and charge transport. BTTT-1-H adopts the anti-anti confirmation, while BTTT-1-C₆ adopts a syn-syn conformation in the single crystal. Computations reveal that destabilizing S–S closed-shell repulsions and alkyl chain steric repulsions are responsible for the anti conformational preference. The syn-syn conformation is preferred for BTTT-1-C₆ because repulsions between Hₐlky and S outweigh S-S or Hₐlky-Hₐryl repulsions. However, both of these factors contribute to the substantial backbone distortion (SCCS dihedral angle = 38°). The BTTT-2-C₆ single-crystal structure shows a nearly planar backbone with both anti and syn terminal thiophenes. While the anti conformation is preferred in a planar alkylated system, we attribute the presence of a syn terminal thiophene in the BTTT-2-C₆ to enhanced backbone interaction between adjacent molecules.

Charge-transport characteristics were determined by BGBC thin-film OFETs. We determined the hole mobilities for the BTTT-1-H, BTTT-1-C₆ and BTTT-2-C₆ to be 3.4 x 10⁻⁴, 5.2 x 10⁻³, and 2.5 x 10⁻³ respectively. Computations of hole-mobilities for BTTT-1-H, BTTT-1-C₆ and BTTT-2-C₆ reproduce the observed values within an order of magnitude.[98] They confirm that the alkyl chains result in enhanced charge-transport properties because of the slip-stacked arrangement of BTTT-1-C₆ and BTTT-2-C₆. The hole mobility of BTTT-1-H is an order of magnitude lower because of substantially reduced electronic coupling in the herringbone arrangement.
This study highlights the strength of the role and interplay between sidechain and backbone enthalpic contributions in defining the crystal packing and conformation of the thiophene rings. Additionally, this work indicates substitution is an effective design tool for manipulating the backbone interactions and controlling registration and order. By familiarizing ourselves with the molecular system, we are now able to venture further in understanding the more subtle structure-property interactions and contributions from sidechain modification.

**Collaborators:** Stephen Lopez, Ilhan Yavuz, Lei Zhang, Kendall Houk, Sean Parkin
CHAPTER 3

EFFECTS OF ALKYL CHAIN LENGTH ON BTTT MONOMERS

![Molecular structure of BTTT-1-R and the side chains studied in this chapter.](image)

R = C\textsubscript{7}H\textsubscript{15}, C\textsubscript{8}H\textsubscript{17}, C\textsubscript{9}H\textsubscript{19}, C\textsubscript{10}H\textsubscript{21}, C\textsubscript{11}H\textsubscript{23}

3.1 Introduction

In the previous chapter, we focused on the impacts of side chains on intramolecular interactions and how they contribute to conformation and crystal packing. Working from this foundation, I now investigate the fundamental effects of alkyl side chain length with monomers of the PBTTT system (Figure 10). By using small molecule analogs of the benchmark polymer semiconductor, PBTTT, we can leverage the single crystal X-ray diffraction to elucidate the fine details of the structure property trends manifesting from side chain length. Monomers are much more crystalline than their polymeric counterparts allowing for large single crystals to be probed using X-ray analysis to reveal molecular packing details that could not be seen in polymer systems. We use a benchmark polymer’s monomer for this study, 2,5-bis-(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene (BTTT), as the polymer’s high crystallinity and mobility made it an ideal candidate for this study.
Although there are now various flexible side chains used, we focused on linear, alkyl side chains, as they remain ubiquitous among organic conjugated systems.[5, 9, 38, 99, 100] The side chain length was varied from heptyl to undecyl which encompass a large portion of the alkyl chain size range commonly reported in literature (C4 to C16).[2, 7] Unfortunately, our range was limited on both ends by the onset of a new crystal packing at C6 (reported in Chapter 1) and of packing frustrations observed in alkyl chains longer than C12. Nevertheless, the C7-C11 explores the heart of the materials-relevant chain lengths and insures that both even and odd length chains are included. We observe a clear even-odd side chain dependence was observed in crystal packing, thin film morphology, DSC, and charge transport. Additionally, I synthesized a variably substituted monomer, BTTT-1-7/12 which contains one C7 chain and one C12 chain. This system adopts yet another single crystal packing dominated by the side chain interactions. This study reveals the vast complexity and parameter/design space available to even the most basic side chain modifications and how it can be directed to alter crystal packing.

### 3.2 Synthesis of Substituted and Unsubstituted Oligothiophenes

![Scheme 3. Monomer synthesis with custom linear alkyl side chain lengths.](image)

BTTT monomers were synthesized by Stille coupling of 2,5-bis(trimethylstannyl)-theino[2,3-b]thiophene with 2-bromo-3-alky/thiophene. Alkylated thiophenes were synthesized via Kumada
coupling as reported in literature. [101] The material’s chemical structure can be seen in Scheme 3.

**General procedure for synthesis of 3-**alkyl**/thiophene**

n-bromo(heptane, octane, nonane, decane, and undecane) were purchased from Sigma Aldrich. Ni(II)Cl₂(dppp), Magnesium, and 3-bromothiophene were purchased from Alfa Aesar. THF was dried in a still with sodium / benzophenone. Glassware was thoroughly dried prior to use. Preparation of alkyl functionalized thiophene from 3-bromothiophene follows a Kumada coupling procedure adapted from reference [101]. n-bromoalkanes (1 eqv., ~10g) were added to a stirring flask of magnesium (1.05 eqv.) and anhydrous THF (~10ml/g thiophene) under nitrogen. Grignard formation took place over 2-4 hours of warm sonication. In some cases, crystalline iodine (~1-3 mg) was added to help speed up the reaction. Formation of Grignard was determined by the disappearance of magnesium and a grey solution color. Note, proper dilution is especially important for longer alkyl chains so they do not ‘solidify’ and clog the cannula or addition funnel in the subsequent steps. After complete formation of the Grignard, the reaction is cannula transferred into a dry addition funnel and added dropwise to a stirring mixture of 3-bromothiophene (0.85 eqv.), Ni(II)Cl₂(dppp) (0.02 eqv.), and anhydrous THF at 0 °C under nitrogen. The reaction turns dark brown after addition and is allowed to warm to RT and stir over night. All materials were purified via column chromatography (silica) with hexanes eluent yielding a colorless/light-yellow oil at 70-80% yield. ¹H NMRs are available in literature.

**General procedure for synthesis of 2-bromo-3-**alkyl**/thiophene**

NBS was purchased from Alfa Aesar and recrystallized from water. Chloroform and glacial acetic acid were purchased from Fischer Scientific.
Bromination of 3-alkyl thiophenes proceeds via electrophilic aromatic substitution directed by the alkyl group. 3-alkyl thiophene (1 eqv.) is added to stirring mixture of chloroform:glacial acetic acid (50:50 vol) at 0 °C. NBS is then added (1 eqv.) and the reaction is covered to prevent light from forming radical bromine species and is left in ice and covered to stir overnight. The reaction mixture is then extracted with hexanes/water and the organic layer is collected to dry in vacuo. Care must be taken to remove all the acetic acid, and may require additional extraction. The concentrated organic layer is then purified via column chromatography (silica, hexanes) to yield a colorless/light-yellow oil at 90-95% yield. 1H NMR is available in literature.

**General procedure for synthesis of BT TT monomer (BT TT-1-R)**

2-Bromo-3-hexyl thiophene and 2-bromo-3-dodecyl thiophene were purchased from Alfa Aesar. Anhydrous toluene was purchased from Sigma Aldrich. Tetrakis(triphenylphospheno) palladium(0) was purchase from Strem Chemicals. 2,5-bis(trimethyltin)-thieno[3,2-b]thiophene was synthesized according to reference [17]. Glassware was thoroughly dried prior to use.

**BT TT-1-R** synthesis follows a procedure previously reported by our group in reference [5, 20]. 2-bromo-3-alkyl thiophene (2.1 eqv), 2,5-bis(trimethyltin)-thieno[3,2-b]thiophene, Tetrakis(triphenylphospheno)palladium(0), and anhydrous toluene are combined in a dry round bottom flask under nitrogen. The reaction is degassed and heated to reflux overnight. After cooling, toluene is mostly removed in vacuo and hexanes is added forming a red precipitate. This mixture is heated, sonicated, and then gravity filtered and washed with hexanes. The red solid (used catalyst) is discarded. Skipping catalyst removal typically results in clogged column and material trapped in the solidified catalyst. The remaining solution is purified in column chromatography (silica, hexanes) and dried to yield a yellow solid (bright blue fluorescence on TLC); 70% yield.

1H NMR shifts of synthesized monomers:
BTNTT-1-7 $^1$H NMR (500 MHz, CDCl$_3$, $\delta$) 7.26 (s, 2H), 7.24 (d, 2H), 6.99 (d, 2H), 2.83 (t, 4H), 1.71 (m, 4H), 1.42-1.28 (m, 16H), 0.92 (t, 6H)

BTNTT-1-8 $^1$H NMR (500 MHz, CDCl$_3$, $\delta$) 7.26 (s, 2H), 7.24 (d, 2H), 6.99 (d, 2H), 2.83 (t, 4H), 1.71 (m, 4H), 1.42-1.28 (m, 20H), 0.92 (t, 6H)

BTNTT-1-9 $^1$H NMR (500 MHz, CDCl$_3$, $\delta$) 7.26 (s, 2H), 7.24 (d, 2H), 6.99 (d, 2H), 2.83 (t, 4H), 1.71 (m, 4H), 1.42-1.28 (m, 24H), 0.92 (t, 6H)

BTNTT-1-10 $^1$H NMR (500 MHz, CDCl$_3$, $\delta$) 7.26 (s, 2H), 7.24 (d, 2H), 6.99 (d, 2H), 2.83 (t, 4H), 1.71 (m, 4H), 1.42-1.28 (m, 28H), 0.92 (t, 6H)

BTNTT-1-11 $^1$H NMR (500 MHz, CDCl$_3$, $\delta$) 7.26 (s, 2H), 7.24 (d, 2H), 6.99 (d, 2H), 2.83 (t, 4H), 1.71 (m, 4H), 1.42-1.28 (m, 32H), 0.92 (t, 6H)

BTNTT-1-12 Reported in literature.[20]

Synthesis of BTNTT-1-7/12

2-bromo-3-heptyl-5-(triisopropyl)silylthiophene
Synthesis of the triisopropylsilyl (TIPS) protected thiophene is reported here. Briefly, 2-Bromo-3-heptylthiophene is added to a dry round bottom flask under nitrogen. The reaction is degassed, dry THF is added, and the reaction is cooled to -78 °C. Next, lithium diisopropylamide (1.1 eqv) is added dropwise to the stirring mixture. The reaction is warmed to RT and then cooled again. Triisopropylsilyl chloride (1.5 eqv) is then added at once to the reaction and the reaction is left to warm. The solution is purified in column chromatography (silica, hexanes) and dried to yield a
clear oil; 90% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\), δ) 6.93 (s, 1H), 2.57 (t, 2H), 1.60 (m, 2H), 1.38-1.30 (m, 8H), 0.92 (t, 3H), 0.31 (s, 9H)

**5-(trimethyl)stanyltieno[2,3-b]thiophene**

Synthesis is reported in ref [80]. Briefly, thieno[2,3-b]thiophene is added to a dry round bottom flask under nitrogen. The reaction is degassed, dry THF is added, and the reaction is cooled to -78 °C. Next, butyl lithium (1.1 eqv) is added dropwise to the stirring mixture. The reaction is warmed to RT and then cooled again. trimethyltin chloride (1.5 eqv) is then added at once to the reaction and the reaction is left to warm. The reaction was extracted with hexanes/water, concentrated under vacuum, and used without further purification. Note, this generates a significant amount of the di-stannylated product, however column chromatography is not possible due to the labile nature of the stannyl group.

**Tips-T7-TT synthesis:**

2-bromo-3-heptyl-5-(triisopropyl)silylthiophene (1.2 eqv) and 5-(trimethyl)stanyltieno [2,3-b]thiophene (1 eqv tin), Tetrakis(triphenylphospheno)palladium(0), and anhydrous toluene are combined in a dry round bottom flask under nitrogen. The reaction is degassed and heated to reflux overnight. After cooling, toluene is mostly removed in vacuo and hexanes is added forming a red precipitate. This mixture is heated, sonicated, and then gravity filtered and washed with hexanes. The dark red solid (used catalyst) is discarded. Skipping catalyst removal typically results in clogged column and material trapped in the solidified catalyst. The remaining solution is purified in column chromatography (silica, hexanes) and dried to yield a white solid; 35% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\), δ) 7.38 (d, 1H), 7.29 (d, 1H), 7.27 (d, 1H), 7.09 (s, 1H), 2.80 (t, 2H), 1.68 (m, 2H), 1.42-1.28 (m, 8H), 0.90 (t, 3H), 0.36 (s, 9H)

**BTTT-1-C7/12 synthesis:**
Tips-T7-TT is stannylation with the same procedure as 5-(trimethyl)stanylthieno[2,3-b]thiophene. The reaction was extracted with hexanes/water, concentrated under vacuum, and used without further purification. 2-bromo-3-heptylthiophene was synthesized as previously described.

Stannylated Tips-C7-TT (1 eqv tin), 2-bromo-3-dodecylthiophene (1.2 eqv), Tetrakis(triphenylphospheno)palladium(0), and anhydrous toluene are combined in a dry round bottom flask under nitrogen. The reaction is degassed and heated to reflux overnight. After cooling, toluene is mostly removed in vacuo and hexanes is added forming a red precipitate. This mixture is heated, sonicated, and then gravity filtered and washed with hexanes. The red solid (used catalyst) is discarded. Skipping catalyst removal typically results in clogged column and material trapped in the solidified catalyst. The remaining solution is purified in column chromatography (silica, hexanes) and dried to yield a yellow solid (bright blue fluorescence on TLC); 70% yield.

$^1$H NMR (500 MHz, CDCl$_3$, $\delta$) 7.38 (d, 1H), 7.29 (s, 1H), 7.27 (d, 2H) 7.09 (s, 1H), 2.80 (t, 4H), 1.68 (m, 4H), 1.42-1.28 (m, 24H), 0.90 (t, 6H), 0.36 (s, 9H)

Finally, the TMS-BTTT-1-7/12 monomer is deprotected in a THF solution with the addition of TBAF (~5eqv) to yield BTTT-1-7/12 as a yellow solid; 95% yield. $^1$H NMR (500 MHz, CDCl$_3$, $\delta$) 7.26 (s, 2H), 7.24 (d, 2H), 6.99 (d, 2H), 2.83 (t, 4H), 1.71 (m, 4H), 1.42-1.28 (m, 24H), 0.92 (t, 6H) MALDI: M/Z 571, Calc 571
3.3 Opto-Electronic Properties

The computational analysis in Chapter 2 showed that only the first two methylene groups on the alkyl chain participate in intramolecular interactions with the core. As the series of oligomers studied here have an alkyl chain ranges from C7-C11, I expect no variation in the solution absorption spectra. Additionally, the solid state spectra also shows no variation in line shape or intensity also indicating that the chromophore alignment and orientation in the thin film is conserved across the range of side chain lengths.

![Graph](image1)

**Figure 11. UV-Vis spectroscopy of BTTT monomers in a) chloroform and b) thin film on glass.**

The UV-Vis absorption spectra of the BTTT monomers in chloroform solution and thin films are shown in Figure 11. The solution and thin film maximum absorption are ~ 350 nm. The solid state has an additional absorption shoulder at 425 nm for all monomers. Additionally, all the materials demonstrated similar onsets of oxidation as shown in Figure 12. Cyclic voltammetry was performed in dichloromethane with 0.1 M TBAPF6 as the electrolyte and a scan rate of 100 mV/s
to determine the ionization potentials (IP) of the oligomers as compared to ferrocene. IP of a BTTT monomer is -5.4 eV.

3.4 Thermal Properties of Oligomer Crystals

Differential scanning calorimetry (DSC) was used to investigate the effect of side chains on BTTT monomers thermal properties. [36, 58, 102, 103] Samples were prepared from single crystals loaded into hermetically sealed aluminum pans using heating/cooling ramps ranging from 0°C to 150°C at 10°C/min. Figure 13 shows the first heating and cooling curves of the BTTT monomers. A melting and crystallization point alternation is present with increased alkyl side chain length as shown in Figure 3b. This odd-even melting point alternation is well documented for n-alkanes:
even-numbered alkanes melt at higher temperatures than odd-numbered alkanes.[104] However, in the case of the BTTT monomers, this alternation is reversed, with odd-numbered BTTTs showing higher melting points than the even-numbered (Figure 13).

Melting transitions occur when the thermal energy available in the system overcomes the intermolecular packing forces that bind together these Van der Waals solids.[104] For this system to show an alternating melting trend corresponding with even and odd sidechains, we understood this transition likely arises from the different intermolecular interactions mediated by the side chain.[104] To further explore this hypothesis, we employed single crystal XRD.

Figure 13. Differential scanning thermograms (left) and transition onsets (right) of the series of BTTT monomers. Method: HCH, 10 °C/min

to show an alternating melting trend corresponding with even and odd sidechains, we understood this transition likely arises from the different intermolecular interactions mediated by the side chain.[104] To further explore this hypothesis, we employed single crystal XRD.

3.5 Substitution Effects on Crystal Packing and Morphology

To investigate how the chain length affects the solid-state structures of the BTTT monomers, single crystals were obtained from a slow evaporation of a hexane solution and analyzed by X-ray diffraction. Crystals of all BTTT monomers with alkyl side chains of length 7-11 form as very
thin, easily deformed plates/flakes. All the structures consist of stacked single layers of BTTT molecules. Figure 14 shows the BTTT monomers arranged in a molecular layer. The refined structures of all the monomer crystals exhibit two distinct conformations for the central fused thiophene pair relative to the distal alkylated thiophenes. Although disorder was present in the series of crystals, all unit cells could be indexed as primitive monoclinic, with two short (\(~5\text{Å}\)) and one long (\(~46\text{Å} — 59\text{Å}\)) cell axis, though the convention of defining the monoclinic (i.e., non \(90^\circ\)) angle as \(\beta\) leads to two distinct packing types. Additionally, the refined crystal structure models all have the two BTTT conformers (blue and red molecules in Figure 14) superimposed (i.e., disordered), whereas the centered model has the two BTTT orientations alternating within each layer. Likely, on a sub-microscopic scale there exist domains in which the two conformers alternate, but that for diffraction from macroscopic crystals this alternation is scrambled, leading to disorder.

![Figure 14. Crystal orientation of BTTT-1-9 Oligomers within a molecular layer. Left and Right panels are rotated 90° about the c-axis. All other monomers (1-7 to 1-11) adopt this same packing within a layer of the crystal.](image-url)
The similar layer structure and visual similarities of all C7–C11 monomer crystals notwithstanding, the underlying crystal packing falls into two distinct types that vary in the relative orientation of adjacent layers as shown in Figure 15. We identify the two packings as even-type and odd-type. In even-type packing, crystals of the C8, C10, and C12 (C12 reported in ref. [20]) monomers crystallize with alternate BTTT layers rotated by 180° by virtue of the 2₁ screw axis (of space groups P2₁/n for C8, C10, and P2₁ for C12). In contrast, C7, C9, and C11 demonstrate odd-type packing where the layers are related by the c-glide operation (space group P2₁/c). Of note, we found exceptions for crystals of the C8 which exhibited both even and odd type packings in different crystal samples, however, multiple types were not found in any of the other chain length variants.

Figure 15. Crystal packing of BTTT monomers highlighting the alternating layers with odd-type (a, c, d) and even-type (b, d) orientations. C7 – C11 is a-e respectively.
In both layer stacking types, the interlayer interactions are very weak and is analogous to a van der Waals heterostructure. Interlayer interaction consists solely of contacts between the end-methyl groups of the alkyl chains as is shown in Figure 16. To understand the driving force for layer alternation, we sought to understand the surface topography of the alkyl chains and how the terminal methyl groups effected the registration of the adjoining layer. Due to the relatively strong intermolecular interactions between the backbones, the intralayer packing between the two different packing types is the same. However, this allows for a strongly expressed even-odd effect in the interaction between layers which is facilitated by the terminal methyl groups on the alkyl chains. Figure 16a,b shows how a single chain orients relative to four interacting chains from

![Figure 16. Top: zoom in of interlayer interaction between the alkyl chains of alternate layers in odd-type C9 (a) and even type C10 (b) crystal packings. Bottom: Van derwaals surface of the alkyl chain interface for odd and even type crystals (C9 and C10 respectively. Generated using Chimera and van der Waals interaction values from ref [1]](image-url)
another layer. Clearly, the terminal bond vector is different in between the even and odd packing types and presents a different interacting surface and topology. Figure 16c,d shows a van der Waals interaction surface created from a monomer layer of 4x4 molecules and has been oriented to show the topology of the alkyl chain surface. Using this qualitative approach, we observe a difference in the interaction surface in the alkyl chains which is highlighted by the red ovals/circles. In the odd-type packing (Figure 16c) the terminal bond vector is ~80° from the surface normal allowing both the terminal and penultimate methyl groups to interact. The two methyl groups require more of an elongated space to register on the surface which is highlighted by the red ovals. Interestingly, the templating surface shows a pocket for the terminal ethyl group to occupy and the orientation of that pocket is commensurate with the adjoining layer’s twisted orientation. In the even type packing, the terminal bond vector is nearly parallel to the surface normal. The surface formed from an array of even numbered alkyl chains resembles a ‘peg board’ and is more symmetric relative to the odd-type surface. The even type surface can facilitate registration of adjacent layers without a need to rotate to maximize the surface interaction.

We contend that the terminal methyl groups and their orientation result in the observed even and odd-type packing. It should be stated that these crystals/diffraction patterns were all exceedingly difficult to handle/measure, so the possibility exists that both polymorph types exist for all C9—C12 variants. It is also possible that some crystals are composites that include domains with both types of layer stacking. Indeed, many crystals with uninterpretable composite diffraction patterns were encountered during the crystallographic analyses.
3.6 Effects of Alkylation on Charge Transport

To see if this packing trend has an effect on the monomers electronic properties, organic field-effect transistors (OFETs) were fabricated by spin coating monomer solutions onto Si(n++)/SiO2 substrates with photolithographically prepatterned Au as source/drain electrodes in a bottom-gate/bottom-contact (BG-BC) geometry with channel dimensions of length = 100 µm and width = 3000 µm. Bottom-gate/Top-contact architecture devices were also fabricated by spin coating monomer solution onto bare Si(n++)/SiO2 substrates then thermally depositing Au source/drain electrodes through a shadow mask using the same dimensions as the BG-BC devices. Transistor device characteristics were then measured at room temperature under ambient conditions as shown in Figure 17.

![Figure 17. OTFT hole mobilities of BTTT monomer thin films in bottom-gate, bottom-contact (BG-BC) and bottom-gate, top-contact (BG-TC) devices.](image)

Mobility in the monomer series also shows an even odd trend. Admittedly, the deviation between the even and odd mobilities is almost within error of the measurement, there is a small deviation between them. This trend is also conserved between two device architectures (both top and bottom contact).
To correlate the even and odd type packing trend to the thin film mobility even/odd trend, we employed GIXD to understand the thin film morphology. GIXD of the thin films is shown in Figure 19. Using the diffraction spectra and the single crystal structures, our collaborator Stephan Mannsfield was able to determine a molecular model of the monomer packing in the thin film (Figure 18). Thin films of even molecules appear to organize similar to the single crystal packing with layers of slip-stacked backbones and no twist between layers. The odd type molecules, while also very similar to the original packing, adopt a herring bone edge – face interaction among the

![GIXD diffractograms of the monomer series.](image)

![Molecular packing in the thin film of (a) even length side chains BTTT monomers relative to the substrate and (b) odd length side chain BTTTs. The top view of (c) even and (d) odd BTTT monomer packing in the thin film.](image)
backbones and the alternating twist between layers observed in the single crystal is no longer present. The slight difference in thin film packing between the two molecule types (even vs odd) directly motivates the observed variation in charge transport. Note, the crystal packing and thin film packing both show even odd trends, however they are separate behaviors.

3.7 Odd-Even Monomer BTTT-1-7/12

Naturally, we were curious how an asymmetric molecule with both even and odd side chains would pack. So BTTT-1-7/12, a monomer with one odd (C7) and one even (C12) sidechain was synthesized. Crystals were very challenging to grow, but were formed in a dilute solution of monomer in isopropanol and left to crystalized in a refrigerator ~30 °C. The resulting crystals were analyzed by single crystal x-ray diffraction. Figure 20 shows the structure which at first glance does not appear to have resolved clearly. Since the alkyl chains on each molecule are uneven in

Figure 20. BTTT-1-C7/12 single crystal packing (left) and zoom-in of alkyl chain interdigitation/registration.
length, and the BTTT rings are on inversion centers, that means that both of the two half-molecules in the asymmetric unit each get half a C12 chain and half a C7 chain, and these chains are superimposed because the X-rays ’see’ an average of all the contents of the crystal. In the crystal, any C12 chain must butt up to a C7 chain on an adjacent molecule, and vice versa as shown in Figure 20 right. I contend that the orientation of the molecules with respect to the C12 and C7 chains is random, aside from the criterion that C12 and C7 chains always match end-to-end. The lack of diffraction peaks indicating a larger (C12) or smaller (C7) spacing corroborate this unique packing.

Compared to other BTTT monomers, the backbone orientations are again nearly identical to the arrangement of the backbones in BTTT-1-7 to BTTT-1-12. However, the interlayer arrangement is different from either the even, odd, or thin film packings previously identified. The ‘pitted’ alkyl chain surface generated by the randomly packed long and short sidechains act like a peg-board and forces the sidechains in adjacent layers to orient parallel as seen in Figure 20.

3.8 Conclusion

To understand the fundamental effects of side chain length, I synthesized and characterized a systematic series of BTTT monomers with linear alkyl sidechains C8 to C11 and an asymmetric monomer, BTTT-1-7/12. We observed even-odd effects in the thermal properties, crystal structure, and thin film mobilities. The C12 monomer (previously reported [20], although not included in this study) also follows the single crystal packing trend observed in this series. However, BTTT-1-6 does not follow the packing trend (Figure 4). The smaller sidechains do not seem to provide enough interaction to replicate the packing in -C7 to -C12.
Of particular interest in this study are the concepts of interlayer registration and the role of sidechains in defining crystal packing. These concepts are not new; many even-odd studies [36, 58, 102, 103] as well as side chain interdigitations[18] have been reported in literature, however, this system is unique in that it exhibits 3 different interlayer registrations with relatively small changes in the side chains. To understand how the side chains motivate crystal packing we must to describe the very special situation provided by the BTTT monomer system. Based on the packings determined from the monomer study, we can say that the cores maintain the highest enthalpic contributions for crystallization and the contributions from the sidechains are much less. Secondly, the BTTT monomer system provides a ‘ridged’ array of cores sandwiched in between a densely packed array of alkyl chains. Within the crystal, the cores do not directly interact with adjacent layers, but instead the side chains define that interface. Additionally, the sidechains are not allowed much entropic freedom as their density is too high to accommodate much movement. This confines the surface of the crystals to a fairly well defined topographical interface which we observe to be extraordinarily sensitive to any slight variation in side chain length. This alkyl chain surface is a weakly interacting Van der Waals structure dominated by the topology of surface. However, the observation of crystals with composite (both even and odd type) diffractions are a clear indication of the truly delicate attractive forces at play.

On the other hand, the BTTT-1-C7/12 asymmetric monomer provides another approach to well-defined interlayer registration. The interpenetration of side chains into adjacent alkyl layers is undoubtedly a type of interdigitation. Among organic semiconductors, interdigitation is often observed in polymeric systems where the substitution pattern of the side chains allows enough space to accommodate side chains from an adjacent polymer.[17] However, in this study, the asymmetric substitution of long (C12) and short (C7) side chains on a single monomer and the
random accretion of monomers to a growing crystal provides the ‘peg-board’ template for further layers to orient. This peg-board registration confines both the orientation of the side chain and backbones to be co-linear among layers. I would predict the stability of this type of crystal packing to be slight higher than what is observed in the symmetric monomers and would be confirmed by a higher melting point of the crystalline material.

As a final note, the symmetry is also an important consideration in the crystal formation. Compared with the symmetric monomer systems, the asymmetric monomer is very difficult to grow. The asymmetric monomer is very challenging to crystalize and needs very specific situation to allow the growing layers to properly form and interdigitate. Likely, BTTT-1-7/12 would not form well-a defined interdigitated morphology in the thin film where rapid solvent evaporation would kinetically trap the molecules before they can access their equilibrium bulk packing. This study provides a very compelling example of the correlation between molecular symmetry/complexity and how it influences the kinetics of self-assembly.

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CHAPTER 4

UNDERSTANDING FULLERENE INTERCALATION IN BTIT DIMER BLENDS

![Molecular structure of BTIT-2-12 and PC61BM. Molecules are arranged in an intercalated co-crystal.](image)

4.1 Introduction

The bimolecular crystal microstructure found in some PBTTT:fullerene systems is rare among OSC systems. Fullerene intercalated systems benefit from highly crystalline, intimately mixed, and well characterized morphology which does not substantial disrupt the donor’s microstructure, often improving order.[3, 40, 55] Recently, we observed fullerene intercalation into PBTTT oligomers (Figure 21).[20] To the best of our knowledge, no other small molecule system is capable of PCBM intercalation and this system presents a unique opportunity to explore the impacts of intercalated microstructure in an all-small-molecule donor-acceptor system. To better understand fullerene intercalation, how morphology evolves with blend composition, and the ramifications to device performance, we extensively characterized the BTIT(dimer):PC61BM system. We combine TEM, GIXD, and device characterization (OPV and OFET) to elucidate subtle differences as compared to the polymer system through the full range of blend fractions.
4.2 Morphology (GIXD, NEXAFS, TEM)

4.2.1 Grazing-Incidence X-Ray Diffraction

Figure 22. Diffractograms (left) and Qz linecuts (right) of BTTT:PCBM blends. Percentages indicate BTTT wt%. dotted lines indicate the 100 diffraction peak of neat BTTT (right most, 2.9 nm⁻¹) and the Co-crystal (left most, 2.1 nm⁻¹).

To accurately correlate the performance trends observed in devices and understand the nuances in photophysical spectra, a detail picture of the morphology through the full range of blend compositions must be well understood for the BTTT-2-12 / PC₆₁BM system. To explore the morphology evolution as a function of film composition in intercalated oligomer:PCBM blends, we used grazing incidence X-ray diffraction (GIXD), transmission electron microscopy (TEM), and Near Edge X-ray Absorbtion Fine Spectroscopy (NEXAFS). Figure 22 shows diffraction patterns (left) of BTTT:PC₆₁BM blends and out-of-plane diffraction plots (right) of the full range of BTTT:PC₆₁BM blends. We have previously reported on the structural information of both the neat and intercalated system.[20] Briefly, the unit cell of the pure BTTT-2-12 is a = 4.9 Å, b = 17.3 Å, c = 41.6 Å, α = 90.0, β = 91.2, and γ = 90.0 and the intercalated unit cell is a = 7.6 Å, b = 7.6 Å, c = 33.0 Å, α = 85.7°, β = 83.6°, and γ = 97.2°.
Upon addition of PCBM, a new set of peaks appears corresponding to a shift in the (h00) lamellar spacing when the fullerene is intercalated as seen in Figure 22. These new peaks show less azimuthal misorientation (less arcing). In the oligomer system with C12 sidechains, fullerene blending shifts the (100) peak from 2.9 Å⁻¹ to 2.1 Å⁻¹, indicating an increase in lamellar spacing from 22 Å (half of the neat BTTT unit cell) to 33 Å.

Figure 23. Relative peak intensities at Qz = 11 (PCBM, black triangles), 2.9 (co-crystal, blue circles), and 2.1 (BTTT, red squares). Relative peak areas are normalized independently.

Figure 23 shows the morphology evolution using relative peak areas. We identify three unique spectral signatures that we attribute to i) pure BTTT, 2.9 Å⁻¹, ii) intercalated/co-crystal, 2.1 Å⁻¹, and iii) pure PCBM, 11 Å⁻¹. In 100 - 60 BTTT wt% blends, the pure BTTT signal decreases monotonically to zero indicating loss of pure BTTT crystalline domains at 60wt%. In this region,
the cocrysal signal increases with increasing PCBM content. Interestingly, the co-crystal signal is apparent even at very low PCBM loading ratios. We attribute this ‘early’ increase in intercalated signal to incomplete PCBM intercalation. The intercalated model established in ref [20] and [3] shows a fullerene channel consists of a pair of 1-D collimated fullerenes oriented with their solubilizing groups facing one another. In incomplete intercalation, likely only one fullerene of the pair is present but is sufficient to increase the backbone spacing. The 50:50 wt% blend is the ideal co-crystal ratio. We identify this ratio as the fully intercalated blend based on the sharpness and intensity of peaks from GIXD as well as data from TEM, DSC, and PL, OFETs. We have previously detailed the intercalated diffractogram with full indexing and reconstruction of the co-crystal unit cell.[20] In low BTTT wt% blends, GIXD shows the co-crystal signal diminishes quickly by the 20 wt% blend. This contrasts with polymer studies where scattering from the intercalated polymer is still present at the 20 wt% blend.[50] This indicates that the BTTT dimers do not phase separate like their polymer analogues and are likely dispersed through the sample. Additionally, the PCBM signal does not recover as quickly as expected in the low BTTT wt% films, indicating the scattering from the PCBM domains is disrupted by the distributed BTTT and corroborating the dispersed BTTT model.

4.2.2 Transmission Electron Microscopy

Energy filter transmission electron microscopy (EF-TEM) of selected BTTT:PCBM blends yields further insight into the thin film morphology (Error! Reference source not found.). In zero-loss images, brighter regions correspond to thinner or non-diffracting regions, whereas in the sulfur and carbon elemental maps, brighter regions correspond to sulfur- and carbon-rich domains, respectively. The 80 wt% BTTT blend shows a unique mesoscale morphology of visible crystal
shards. These shards are approximately 50 - 200 nm wide and can be 1 μm in length. Comparison with GIXD, DSC, and PL (Figure 29) results suggests that the films have pure BTTT domains which we attribute to the observed shards. This image also indicates crystals of pure BTTT can form even in the presence of 20 wt% PCBM, which appears to sequester large crystal formation in the 50 wt% blend. Most surprisingly, the 50 wt% blend shows a network-like morphology, where BTTT (sulfur-rich) forms a more defined network and PCBM (carbon-rich) surrounds it more loosely. Despite many efforts, we could not directly image the co-crystal by TEM due to the lack of visual order at the nanometer scale. GIXD indicates we should have pronounced co-crystalline domains with a high degree of order. However, we found instead a network-like structure of fullerene and co-crystalline domains. It is possible processing conditions do not allow large co-crystals to form. In the 20 wt% blend, little structure is visible, in contrast to polymer
studies where PBTTT forms plate-like domains.\textsuperscript{[105]} This corroborates the GIXD data, which suggests that no co-crystal exists in the 20 wt% blend and that the BTTT oligomers are dispersed throughout the film.

4.2.3 Near-Edge X-Ray Absorption Fine Spectroscopy

![Graph showing surface composition analysis of PCBM](image)

**Figure 24.** NEXAFS Surface composition analysis of PCBM. The red dotted line indicates the 1 to 1 surface composition assuming perfect mixing and negligible surface interactions.

We also performed NEXAFS of the thin film blends to probe the film/air interface and gain insight on the relative surface composition (Figure 24). The red dotted line indicates the expected intensity profile if the materials had no enthalpic drive to accumulate at an interface, i.e., perfect mixing. As expected, PCBM intensity increases as BTTT wt% decreases. However, NEXAFS reveals that
PCBM signal significantly deviates from perfect mixing values at the 30, 40, and 50 BTTT wt% blends. In these blends, the PCBM surface composition is roughly half of the pure PCBM film and maintains the value of the ~50:50 co-crystal film. This strongly indicates that the intercalated co-crystal preferentially accumulates at the air interface.

4.3 Thermal Characterization (DSC)

![Differential Scanning Calorimetry of BTTT:PCBM Blends](image)

Figure 25. Differential Scanning Calorimetry of BTTT:PCBM Blends. Red squares indicate BTTT melting endotherms. Blue circles indicate co-crystalline melting endotherms. Black triangles are PCBM melting endotherms. Dotted lines indicate phase boundaries determined in part by GIXD.
We employed DSC to evaluate the impact of intercalation on the thermal properties of the blended system. Figure 25 shows the phase diagram constructed from first-heating thermograms of casted films and GIXD. Pure BTTT (red square) shows a melting transition at 104 °C. As fullerene is blended into the film, that melting point decreases slightly and reaches a eutectic point ~ 75wt% BTTT, ~100 °C. At from 70-50 wt% BTTT another melting transition appears at ~ 104-106 °C which is attributed to the melting of the bimolecular crystal (blue circle) and agrees well with GIXD. When additional fullerene was added beyond the ideal 50:50 co-crystal ratio, the blends did not show any significant melting endotherms. In films composed of 20% or less BTTT, new melting transitions from PCBM are observed. This indicates fullerene can phase segregate away from BTTT to form pure domains only in low BTTT wt% blends. These PCBM melting transitions also exhibit melting point depression from BTTT ‘impurities’. This is consistent with our conclusion the BTTT dimers are dispersed through the sample in low BTTT wt% blends.

4.4 Devices (OFET, OPV)

To evaluate the impact of blend ratio on charge transport we made bottom gate bottom contact (BGBC) transistors. BGBC OFETs were dropcast from warm chlorobenzene at 10 mg/mL. Channel length 100 μm and width was 3000 μm. Figure 26 shows hole and electron mobilies of the best devices of the BTTT:PCBM blended films. A similar figure can be found for the polymer system in ref [48]. Hole transport (red, square) in the dimer system shows stable mobility (~0.01 cm²/Vs) in blends with majority BTTT (100% to 50%). Below 50 wt%, hole mobility drops > 3 orders and continues to drop with decreasing BTTT content. Hole transport in the dimer & co-crystal is 2 dimensional within a sheet of pi-stacked dimers. We conclude that excess PCBM disrupts these sheets and destroys connectivity. GIXD shows the presence of PCBM scattering in
blends of 40% and lower BTTT. Clearly, the presence of any excess PCBM (beyond that of the ideal cocrystal) is not conducive to efficient hole transport.

Electron transport in the dimer system shows an immediate drop in mobility from pure PCBM with addition of 20% BTTT. This initial drop is caused by the BTTT disrupting the PCBM phase purity also observed in the polymer system. This is supported by GIXD scattering (Figure 22) and DSC (Figure 25) which show a significant drop in PCBM scattering intensity and melting point depression, respectively. As the BTTT content is increased from 30% to 50%, the mobility plateaus at \(1\times10^{-5}\, \text{cm}^2/\text{Vs}\). We attribute this behavior to the 1-D limited transport of PCBM in the

Figure 26. BGBC ambipolar transistors of BTTT:PCBM blended films. Red squares correspond to hole mobility and black circles correspond to electron mobility values.
co-crystal channels. In 30%-50% blends, we argue a percolating network of pure PCBM does not exist and the transport of electrons will be limited by the mobility in the 1-D co-crystal channels. GIXD (Figure 22) of these films show the presence of co-crystal domains which supports this hypothesis. When BTTT content is increased beyond 50% the electron mobility suffers a steep drop in mobility. This is not surprising; if there is not sufficient PCBM to maintain connectivity within the channel, the 1-D electron transport pathways will be disrupted by vacancies.

Figure 27 shows OPV characteristics for the best device of each BTTT/PCBM blend. Devices were only operational at < 50 wt% BTTT and the 0 wt% BTTT represents an all-PCBM device for reference. The 50 wt% blend has no significant photocurrent which parallels previous studies with polyBTTT where the 1:1 co-crystal morphology facilitates extensive loss of charges to germinate recombination.[24, 25, 43, 46] By decreasing film compositions to 15 wt% BTTT, all OPV parameters improve. The low BTTT content allows for formation of pure fullerene phases as is characterized by GIXD and DSC. We observe an increase in Voc with decreasing BTTT content which is also reported in the polyBTTT system.[45] Voc derives from the interfacial area, carrier recombination rates, and energy of the charge transfer state. As the blend morphology increases in PCBM content crystallinity interfacial area, and recombination, are reduced; likely all contributing to the ~100 mV shift in Voc.[106]

Additionally, the fullerene rich domains provide an energetic sink to help separate coulombically bound charges and dramatically improves the Jsc by reducing recombination. Despite a significant loss the main light absorbing material and hole mobilities, Jsc improves due to the reduction in recombination. This illustrates the critical importance of limiting recombination through proper microstructure control as is a common theme in OPVs.[41, 50, 52, 106, 107]
Figure 27. Voc (black squares), Jsc (red circles), FF (blue diamonds), and PCE (green triangles) of solar cells of low BTTT wt% blends. Device architecture: ITO/PSMB/A/BTTT:PC_{61}BM/MoO_{3}/Al.

BTTT optimizes at even lower (1:6) BTTT:PCBM ratio compared to polymer systems (1:4).[45] Monte carlo simulations for polyBTTT indicate that the 1:4 ration gives equal volumes of co-crystalline and PCBM phases.[48] In the dimer system, however, pure PCBM phases are more disrupted by donor impurities as the dimer cannot localize itself like polyBTTT.[50] This supported by DSC and GIXD. Previous reports[50] of polyBTTT shows coherent scattering even at 20 wt% polymer (localized co-crystal domains) and PCBM melting transitions (with relatively...
small melting point depressions) in films as high as 55 wt% polyBTTT. To compensate for the more distributed BTTT donors, the blend ratio must be further increased to optimum performance.

### 4.5 UV-Vis

![UV-Vis spectra for BTTT:PCBM blends](image)

**Figure 28.** UV-Vis absorption spectra for blends of BTTT:PCBM. Each film was normalized to a film thickness of 100 nm.

Figure 28 shows UV-Vis spectra for BTTT / PCBM blended films on glass. Films were spin coated from a 10mg/ml chloroform solution and their thickness was measured. The films intensity was then normalized to a 100nm thick film for comparison. Interestingly, the maximum absorption blue shifts slightly with increasing PCBM content until the cocrystal breaks around 50 wt% BTTT.
4.6 Photoluminescence

Figure 29. Bulk photoluminescence of blended BTIT dimer: PCBM thin films. BTIT was selectively excited at 450 nm and PL response was measured between 480nm and 750nm. The inset on the left panel enhances low intensity films. Right panel shows the quenching as a function of blend ratio for two different peak values and as an integrated sum.

Figure 29 shows rapid photoluminescence quenching of the BTIT excitons as PCBM wt% increases in the blended films. This exceptionally rapid quenching indicates that PCBM is distributed throughout the sample. To our surprise, both the GIXD co-crystal signal and the PL quenching do not reach unity until the 50% threshold. The 60 BTIT wt% film (light blue line) shows a very faint PL signal indicating that some pure domains of BTIT still exist.

4.5 Conclusion

We have characterized the morphology, charge transport, thermal behavior, and opto-electronic processes for the full range of BTIT:PC_{61}BM blend compositions.
• **BTTT>PCBM:**

High BTTT wt% blends of BTTT contain a two-phase morphology of crystalline BTTT and intercalated domains as revealed by TEM. As fullerene is added, co-crystal formation sequesters large crystal growth as observed in TEM despite indications of improved order in GIXD. Hole transport through the BTTT is not effected by blend composition in this high wt% regime. However, electron transport is severely hindered at these ratios due to lack of fullerene percolation. OPVs in this region do not function due to lack of pure fullerene domains and percolation. These blends do not yield any photo current due to the inability to form free charges. Behavior of these high BTTT wt% blends parallels that of the reported polymer system.[48]

• **BTTT=PCBM:**

The 1:1 blend is the ideal co-crystal ratio that gives molar stoichiometry of ~ 1 fullerene for every 1 BTTT backbone. DSC shows a single co-crystal melting endotherm. OFETs indicate that the 2-D ‘lamella’ of the BTTT are not disrupted as hole transport does not deviate substantially from the neat BTTT mobility. Electron mobility is about 1E-5 cm²/Vs which we attribute the mobility of the 1-D channel architecture formed by the co-crystal.

• **BTTT<PCBM:**

Low BTTT wt% blends have a mixed microstructure of co-crystalline and PCBM, as well as vitrified (distributed) BTTT. GIXD shows scattering from co-crystal regions at 30-40 BTTT wt% blends and PCBM scattering in 0-40 wt% BTTT blends. Most interestingly, we observe a morphology where the BTTT donor is distributed and vitrified in a matrix of PCBM. This morphology is distinguished by the reduced PCBM scattering intensity in GIXD, melting point depression in DSC, and TEM imaging. Additionally, in these blends, hole transport is substantially reduced as excess PCBM disrupts the connectivity of BTTT domains. Electron mobility is similar
to the value in the ideal co-crystal in the 40 and 30 BTTT wt% blends; even though the PCBM content is increasing, mobility is still limited by the 1-D transport through the co-crystal regions. The formation of PCBM domains explains the optimized OPV performance at the 1:6 blend ratio (~14 wt% BTTT). As with other fullerene intercalated systems, charge recombination can be suppressed in a blend with high fullerene loading.[48] However, unlike other polymer systems, these dimers are miscible with fullerene and distribute themselves throughout a fullerene matrix to form a new amorphous mixed phase which explain device optimization at lower BTTT:PCBM ratios.

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CHAPTER 5
INTERCALATION IN BTTT DIMERS WITH A SYSTEMATIC SERIES OF SIDE CHAIN LENGTHS

5.1 Introduction

Fullerene intercalation has been observed to form both amorphous[39] and crystalline phases[40, 48]; intercalated crystalline phases are defined as bimolecular crystals. While intimate mixing of donors and acceptors is detrimental to OPV performance, polymer/fullerene intercalated systems have provided valuable insight into fundamental OPV processes.[24, 41, 51, 107] Recently, Banerji and coworkers used PBTTT and fullerene bimolecular crystals to better understand charge separation and recombination physics at the donor-acceptor interface.[43] In general, intercalation provides a powerful approach for the inclusion of small molecules without disrupting microstructure, and has shown promise in doped polymer systems.[108]

Reports investigating the design rules for bimolecular crystal formation reveal that fullerene chemistry and side chain type and spacing influence intercalation.[40, 109, 110] Fullerenes with or without solubilizing groups are observed to intercalate with compatible polymers. With additional substitutions, the fullerene becomes too bulky to intercalate and phase separation is
observed instead. Steric limitations can also be imposed by side chains. For all intercalating polymers, the side chain substitution pattern along the backbone must offer sufficient space to accommodate a fullerene. This space, called the “pocket”, has been modulated by varying the substitution position, density, and side chain branching. Yet, the effect of the pocket height (modulated by side chain length) has not been explored due to solubility limitations in polymers with decreasing side chain length. Oligomers, which exhibit shared properties of the corresponding polymer, provide a versatile experimental platform unhindered by the solubility issues that limit systematic polymer studies. The benchmark polymer, PBTTT, is known to intercalate with fullerenes, and we previously demonstrated PBTTT-oligomers also form a bimolecular crystal with fullerenes. To systematically study the effect of side chain length on bimolecular crystal formation, we synthesized BTITT dimers with linear alkyl side chains from butyl (C4) to tetradecyl (C14) and blend them with three fullerenes derivatives varying in size and substitution (Figure 30A). Grazing-incidence X-ray diffraction (GIXD) reveals a transition from a bimolecular crystal to an intimately-mixed amorphous blend upon decreasing side chain length. We further characterize these oligomer/fullerene blends using differential scanning calorimetry (DSC) and photoluminescence spectroscopy (PL) to understand this transition and probe the newly-observed intercalated amorphous phase.

5.2 Synthesis of BTITT

Detailed synthesis is described below and the general procedure has been previously reported. n-bromo(butane, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, and tetradecane) were purchased from Sigma Aldrich. Ni(II)Cl₂(dppp), Magnesium, and 3-bromothiophene were purchased from Alfa Aesar. THF was dried in a still with sodium / benzophenone. Glassware was thoroughly dried prior to use. 3-alkylthiophene and 2-br-3-
alkylthiophenes are synthesized according to the general procedure in Chapter 3. NMR shifts available in literature.


**General procedure for synthesis of 3-alkylthiophene**

n-bromo(butane, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, and tetradecane) were purchased from Sigma Aldrich. Ni(II)Cl₂(dppp), Magnesium, and 3-bromothiophene were purchased from Alfa Aesar. THF was dried in a still with sodium / benzophenone. Glassware was thoroughly dried prior to use.

**General procedure for synthesis of monobromo-BTTT monomer (BTTT-1-R-Br)**

Bromination of BTTT-1-R monomer proceeds via electrophilic aromatic substitution of the thiophene α-hydrogen. Note, since both terminal-thiophene α-hydrogens have the same reactivity this reaction will result in significant yields of starting material, mono-brominated (desired product), and di-brominated products. BTTT-1-R (1 eqv.) is added to a stirring mixture of chloroform:glacial acetic acid (50:50 vol) at room temperature. NBS is then added (1.2 eqv.) and the reaction is covered to prevent light from forming radical bromine species. The reaction is left covered to stir overnight. The reaction mixture is then extracted with hexanes/water and the organic layer is collected to dry in vacuo. Care must be taken to remove all the acetic acid, and may require additional extraction. The concentrated organic layer is then purified via column chromatography (silica, hexanes) to yield a bright-yellow solid at 60-75% yield. Note, this can be
challenging to separate as the mono-brominated material elutes in between the starting material and di-brominated biproduct.

**General procedure for synthesis of the BTTT dimer (BTTT-2-R)**

Hexamethylditin was purchased from Alfa Aesar. Glassware was thoroughly dried prior to use. Dimers (BTTT-2-R) are synthesized through Stille coupling of BTTT-1-R-Br. Hexamethylditin (0.5 eqv.), tetrakis(triphenylphosphine) palladium (0) (0.1 eqv.), anhydrous toluene, and BTTT-1-R-Br are added to a dry round bottom flask with a reflux condenser. The reaction is degassed and heated to reflux overnight. After cooling, toluene is mostly removed in vacuo and hexanes is added forming a red precipitate. This mixture is heated, sonicated, and then gravity filtered and washed with hexanes. The red solid (used catalyst) is discarded. Skipping catalyst removal typically results in clogged column and material trapped in the solidified catalyst. The remaining solution is purified in column chromatography (silica, hexanes) and dried to yield an orange solid (yellow fluorescence on TLC); 60% yield. Note, low side chain lengths (C4 for example) are not very soluble in hexanes and may require alternate catalyst removal techniques. C4 and C5 materials are purified in chromatography with hot hexanes.

Characterization: NMR, Bruker 500 MHz.

**BTTT-4** $^1$H NMR (500 MHz, CDCl$_3$, δ) 7.25 (s, 4H), 7.22 (d, 2H), 7.04 (s, 2H), 6.96 (d, 2H), 2.82 (t, 8H), 1.68 (m, 8H), 1.42 (m, 8H), 0.95 (t, 12H)

**BTTT-5** $^1$H NMR (500 MHz, CDCl$_3$, δ) 7.27 (s, 4H), 7.25 (d, 2H), 7.06 (s, 2H), 7.00 (d, 2H), 2.80 (m, 8H), 1.71 (m, 8H), 1.39 (m, 16H), 0.95 (t, 12H)

**BTTT-6** $^1$H NMR (500 MHz, CDCl$_3$, δ) 7.27 (s, 4H), 7.25 (d, 2H), 7.06 (s, 2H), 7.00 (d, 2H), 2.84 (m, 8H), 1.71 (m, 8H), 1.42-1.30 (m, 24H), 0.95 (t, 12H)

**BTTT-7** $^1$H NMR (500 MHz, CDCl$_3$, δ) 7.25 (s, 4H), 7.23 (d, 2H), 7.04 (s, 2H), 6.97 (d, 2H), 2.80 (m, 8H), 1.68 (m, 8H), 1.42-1.25 (m, 32H), 0.88 (t, 12H)

**BTTT-8** $^1$H NMR (500 MHz, CDCl$_3$, δ) 7.25 (s, 4H), 7.23 (d, 2H), 7.04 (s, 2H), 6.97 (d, 2H), 2.80 (m, 8H), 1.68 (m, 8H), 1.42-1.25 (m, 40H), 0.88 (t, 12H)
**BTTT-9** $^1$H NMR (500 MHz, CDCl$_3$, $\delta$) 7.25 (s, 4H), 7.23 (d, 2H), 7.04 (s, 2H), 6.97 (d, 2H), 2.80 (m, 8H), 1.68 (m, 8H), 1.42-1.25 (m, 48H), 0.88 (t, 12H)

**BTTT-10** $^1$H NMR (500 MHz, CDCl$_3$, $\delta$) 7.25 (s, 4H), 7.23 (d, 2H), 7.04 (s, 2H), 6.97 (d, 2H), 2.80 (m, 8H), 1.68 (m, 8H), 1.42-1.25 (m, 56H), 0.88 (t, 12H)

**BTTT-11** $^1$H NMR (500 MHz, CDCl$_3$, $\delta$) 7.25 (s, 4H), 7.23 (d, 2H), 7.04 (s, 2H), 6.97 (d, 2H), 2.80 (m, 8H), 1.68 (m, 8H), 1.42-1.25 (m, 64H), 0.88 (t, 12H)

**BTTT-12** $^1$H NMR (500 MHz, CDCl$_3$, $\delta$) 7.25 (s, 4H), 7.23 (d, 2H), 7.04 (s, 2H), 6.97 (d, 2H), 2.80 (m, 8H), 1.68 (m, 8H), 1.42-1.25 (m, 72H), 0.88 (t, 12H)

**BTTT-14** $^1$H NMR (500 MHz, CDCl$_3$, $\delta$) 7.27 (s, 4H), 7.25 (d, 2H), 7.06 (s, 2H), 7.00 (d, 2H), 2.84 (m, 8H), 1.71 (m, 8H), 1.42-1.28 (m, 88H), 0.88 (t, 12H)

**BTTT-14** $^{13}$C NMR (500MHz, CDCl$_3$, $\delta$) 140.97, 140.32, 139.27, 139.12, 137.89, 137.24, 135.33, 130.71, 130.10, 129.92, 126.67, 124.41, 118.01, 117.82, 31.94, 30.81, 30.63, 29.72, 29.68, 29.61, 29.56, 29.49, 29.38, 29.25, 22.71, 14.14

5.3 **Experimental Design**

Chemical structures of BTTT dimers, side chains, fullerenes, as well as interdigitated and intercalated lamellar packings are shown in Figure 30 at the onset of this chapter. We selected [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM), its C$_{70}$ analogue (PC$_{71}$BM), and indene-C$_{60}$-bisadduct (ICBA) fullerenes to explore variations in fullerene size and substitution.

5.4 **Grazing-Incidence X-ray Diffraction**

Intercalation of fullerenes causes an increase in the lamellar spacing of a BTTT dimer, visualized in Figure 30 B, C, thus GIXD was employed to measure the lamellar spacing of the neat and blended BTTT/fullerene films to determine if bimolecular crystal formation occurs. Samples were prepared by mixing 50:50 wt% BTTT with PC$_{61}$BM, PC$_{71}$BM, and ICBA in a heated chloroform solution and spin coating onto silicon substrates. In the neat films, the BTTT dimers pack in a similar manner to PBTPTT, with the lamellar stacking axis oriented out-of-plane with side chain
interdigitation.[111] Out-of-plane line cuts of the neat and blended films for all side chain lengths are shown in Figure 31A. BTTT lamellar spacing increases linearly from BTTT-2-7 (14.9 Å) to BTTT-2-14 (24.5 Å) similar to PBTHTT films with varied side chains lengths.[17] Upon blending with PC_{61}BM, a shift in the peak positions along q_{z} ~ 0 indicates an increase in lamellar spacing consistent with bimolecular crystal formation for BTTT-2-7/PC_{61}BM (25.8 Å) through BTTT-2-
14/PC$_{61}$BM (31.4 Å). Figure 31B shows the d-spacing vs side chain length in the neat and blended films.

BTTT with hexyl (C6) and shorter side chains (C5, C4) do not follow the linear lamellar spacing trend observed for longer side chains due to a different thin-film molecular packing. Interestingly, blends of BTTT-2-C6 and shorter with fullerenes do not show an increase in d-spacing, instead the BTTT scattering intensity is completely suppressed and replaced by broad powder rings corresponding to PC$_{61}$BM, indicating the formation of an amorphous blend. However, we contend that even at decreased pocket height, fullerenes can still occupy the space between the side chains and intercalate, disrupting aggregation and crystallization of the dimer. In separate studies, polyterthiophene (PTT) also exhibited similar side chain mediated behavior. McGehee and coworkers report bimolecular crystal formation in fullerene blends with PTT-C14 containing long tetradecyl side chains.[48] Yet, McCulloch and coworkers reported fullerene blends with shorter hexyl side chains, PTT-C6, show crystallization suppression also observed in our study and attributed this to fullerene intercalation.[100] These studies support our claim that BTTT dimer-fullerene blends transition from crystalline to amorphous with decreasing side chain lengths while maintaining an intercalated morphology.

Additional experiments varying fullerene size (PC$_{61}$BM vs PC$_{71}$BM) showed no significant differences in lamellar spacing of the bimolecular crystal or transition to the amorphous blend. We do note a small deviation in lamellar spacing at side chains C7 and C8 with PC$_{71}$BM. ICBA, an alternate di-substituted fullerene known to intercalate with PBTTT, was also investigated. ICBA blends demonstrated only partial intercalation into BTTT dimers $\geq$ C11. Additionally, blends with BTTT-2-11, -12, and -14 exhibit lamellar spacing corresponding to domains of both pure dimer and bimolecular crystal. Films of ICBA with BTTT-10 and shorter show suppression of all
crystalline microstructure, similar to the PCBM blends with smaller side chains. Interestingly, the lamellar spacing of the ICBA bimolecular crystal was very similar to the PCBM blends, differing from what has been previously reported with blends of PBTTT/ICBA, which exhibited a smaller expansion of the side chains upon the introduction of ICBA compared to PCBM derivatives.\[110\] This could be due to the ICBA arranging in a differing manner in which the side groups are not perpendicular to the BTTT side chains and thus contribute to the lamellar spacing of the bimolecular crystal.

Figure 32. d-spacing values from PBTTT and BT TT intercalated blends with various fullerenes. Neat PBTTT values from ref [2] and PC71BM intercalated values from ref [3].

from what has been previously reported with blends of PBTTT/ICBA, which exhibited a smaller expansion of the side chains upon the introduction of ICBA compared to PCBM derivatives.\[110\] This could be due to the ICBA arranging in a differing manner in which the side groups are not perpendicular to the BT TT side chains and thus contribute to the lamellar spacing of the bimolecular crystal.
To further evaluate trends in the Intercalated BTTT oligomers, Figure 32 shows linear regressions based on collected and literature[2, 3] data. Polymer data by Kline et al. shows PBTTT backbone spacing as a function of alkyl chain length (C10, C12, C14, C16, and C18, green line).[2] A linear regression of the neat PBTTT polymers (green line) shows a smaller lamellar d-spacing and smaller side chain dependence relative the neat BTTT oligomers (black line). The regressions have the from:

\[
\text{backbone } d \text{ spacing (Å)} = \text{slope } \times \# \text{ side chain carbons} + \text{intercept(Å)}
\]

For PBTTT, the equation is \(y_{\text{poly}}(\text{Å}) = 1.05x + 6.46\) and for the BTTT oligomers, the equation is \(y_{\text{oligo}}(\text{Å}) = 1.39x + 5.22\). In comparing the slopes, the polymer has a smaller slope relative to the oligomers. The compression of the polymer backbone spacing arises from alkyl chain orientation off of the backbone normal as previously reported by Kline.[2]. Put another way, the sidechains do not orient straight out from the polymer and instead tilt at some angle < 90°.

![Figure 33. Single crystal packing of the BTTT-2-C9 dimer along the a-axis (left) and a top down view (right) to highlight the skewed layered stacking.](image)

On the other hand, single crystals x-ray analysis of the oligomer series reveals the side chains on oligomer molecules project directly away from the backbone (90°, Figure 33). The bond length and angle of the oligomer C-C alkyl chain bonds to be \(\sim 1.51\text{Å}\) and 114.3° respectively. The theoretical increase in backbone spacing as a function of alkyl chain length for the oligomers is
1.51 Å * \( \sin(114.3^\circ) \) = 1.38 Å which corresponds well with the slope observed in the oligomers, 1.39. This indicates that the chains of the oligomers in the thin film orient in a similar way to the single crystal which are essentially orthogonal to the backbone. Interestingly, GIXD indexing of the BTTT-2-12 oligomer thin films from ref [20] does not support the skewed interdigitated layered packing allows for efficient reduction in free volume observed in these single crystal. Likely, a mix of slip stacking and compression is present in the thin film as the kinetics of film drying do no give the dimers enough time to order the side chains more efficiently.

Using the bond values obtained from single crystal analysis, we can calculate the polymer alkyl chain angle relative to the backbone using:

\[
\theta_{\text{sidechain}} = \cos^{-1}\left(\frac{\text{slope}_{\text{polymer}}}{\text{slope}_{\text{oligomer}}}\right) = \cos^{-1}\left(\frac{1.05}{1.39}\right) = 50^\circ
\]

Kline reported a value of 45 degrees by vector analysis based on a simplistic packing model.[2]

The method and value we report provides a more accurate analysis of the alkyl chain interdigitation and orientation in the polymer system. Finally, we also observe a discrepancy in the y-intercept between the polymer and oligomer, 6.46 Å and 5.22 Å respectively. Kline reports this value arises from the space needed for the backbone to reside as well as some non-interdigitated portions of the sidechains. In the oligomer system, X-ray analysis reveals the dimers pairs interact with one another to effectively span the majority of the 5.22 Å.

After blending with fullerene, the BTTT oligomers show a significant change in the effect of the side chains on the lamellar spacing. Since we did not observe a clear trend in lamellar spacing as a function of fullerene type, each alkyl chain length spacing for all fullerene loadings (when applicable) was averaged and a linear regression was calculated to quantitatively evaluate the alkyl chain dependence on the backbone spacing, Figure 32 yellow dotted line. A linear regression of the intercalated oligomers takes the form, \( y_{\text{oligo}}(\text{Å}) = 1x + 17(\text{Å}) \). Curiously, the slope of the
intercalated co-crystals is much slower than the neat oligomers and compares much more closely to the neat polymer (slope_{polymer} = 1.05). Previous reports characterizing the co-crystal of PBTTT-C14 indicate that the backbone conformation is twisted in order to accommodate more backbone interaction with the fullerene. I speculate a similar interaction is at play in the oligomer system which drives the entire BTTT dimer to orient 50 degrees relative to the substrate as depicted in Figure 34. This could account for the slower side chain dependence of the backbone spacing. However, this packing does raise concerns about the C7 intercalated co-crystal. With side chain length of ~10 Å, a 50 degree tilt lowers the available pocket height to ~7.5 Å. The fullerene core is 7 angstroms in diameter and accounting for some appropriate separation between the BTTT backbone and the fullerene core necessitates exposure of the fullerene out of the top of the pocket. This brings into question the underlying driving force which forms the co-crystal in the first place. Fullerene co-crystal formation is only present in oligomers in C7 and greater. Interestingly, the thin film crystal packing changes in the neat dimers at sidechains C6, C5 and C4. It is possible that the loss in co-crystal formation is linked to the preferred conformation of the small-sidechain dimers. However, I believe this is unlikely due to the complete disruption in the thin film crystallization described previously. Clearly, fullerenes and dimers are strongly interacting as their molecular mixing is still favorable. Other reports on the driving force for intercalation claim the backbone interaction is essential to spontaneous co-crystal formation.[3, 40, 48, 53] By this logic, a co-crystal with a single fullerene channel should be
possible. Assuming the same packing geometry and 50 degree side chain tilt, the pocket height would be half a fullerene ~5Å. Working backwards, this equates to a theoretical alkyl chain length of 4.5 carbons. Additionally, the fullerene would need to be carefully selected in order to accommodate backbone-fullerene interactions on both sides of the molecule. I believe ICBA is an excellent candidate for this experiment as it has already been shown to lay down in the fullerene channel with the side groups co-aligned with the fullerene channel as reported in ref [110].

5.5 Differential Scanning Calorimetry

![Figure 35. Differential scanning calorimetry first heating curves of neat dimers (black) and 50:50 wt% blends with PC61BM (red) of A) BTTT-2-4, B) BTTT-2-6, C) BTTT-2-9, and D) BTTT-2-12. Exo up.](image)

To probe the order to disorder transition observed in GIXD, we characterized the thermal behavior of both neat and blended films of BTTT-2-12, -9, -6, and -4 with DSC. Figure 35 shows the first heating thermograms of the neat dimer and PC61BM blends. To emulate the thin film processing conditions, 5 mg/mL chloroform solutions were drop cast directly into aluminum hermetic pans, or dried in glass vials, scraped, then loaded. All neat materials exhibit strong melting endotherms. BTTT-2-6, BTTT-2-9, and BTTT-2-12 melt around 100 °C, whereas BTTT-2-4 melts at 155 °C. Upon blending, BTTT-2-12 and BTTT-2-9 show a melting point shift, indicating a new crystalline phase which we attribute to the bimolecular crystal. In the blended samples of BTTT-2-6 and
BTTT-2-4, the melting transition is suppressed. The absence of a strong melting endotherm in BTTT-2-6 and BTTT-2-4 support the featureless diffraction patterns and the proposed order to disorder transition at side chain lengths ≤ C6.

5.6 Photoluminescence

Figure 36. Photoluminescence of neat (black) and 50:50 wt% BTTT/PC61BM (red) films of (a) BTTT-2-4, (b) BTTT-2-5, (c) BTTT-2-6, (d) BTTT-2-7, (e) BTTT-2-9, and (f) BTTT-2-12. Excitation wave-length: 450 nm.

PL quenching is an indicator of how efficiently excitons can diffuse to a donor-acceptor interface.[112, 113] In intercalated systems, excitons are formed in immediate proximity of a fullerene, allowing for near quantitative PL quenching.[39, 109] Conversely, in phase separated systems, some population of excitons formed in the donor phase do not reach an interface and
recombine emissively.[39, 41, 51, 107, 109] To gain insight into the distribution of donor and acceptor molecules within the amorphous blends, we compare the PL quenching behavior of the co-crystalline and amorphous blends. Figure 36 shows the PL signal for both neat and blended systems. Upon fullerene blending, both co-crystalline and amorphous systems demonstrated complete quenching. Based on PL spectra of the crystalline and amorphous blends, we conclude that the amorphous blends must also be mixed at the molecular level.

5.7 Conclusion

We investigated the effect of side chain length on the formation of BTTT/fullerene bimolecular crystals. BTTT dimers with alkyl side chain lengths ranging from C4 to C14 were blended with PC_{61}BM, PC_{71}BM, and ICBA to explore fullerene intercalation previously inaccessible with polymer systems. In both PC_{61}BM and PC_{71}BM blended films, we observe two regimes. BTTT-2-14 to BTTT-2-7 show spontaneous bimolecular crystal formation while BTTT-2-6 to BTTT-2-4 exhibit a lack of thin film microstructural order as demonstrated by GIXD and DSC. However, complete PL quenching of the amorphous blends indicate that the fullerene and dimer are also molecularly mixed. We contend that the small-side chain BTTTs still intercalate fullerenes, however do not form bimolecular crystal. This work highlights the growing list of side chain related phenomena and rational molecular design considerations essential to morphologic control of organic semiconductors.

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CHAPTER 6
SYNTHESIS AND CHARACTERIZATION OF VARIABLY-SUBSTITUTED BTTT DIMERS

6.1 Introduction

Building on work in Chapter 5, I sought to explore how patterning of long and short chain substitution on the BTTT would affect the crystal packing, thin film morphology, and intercalation of fullerene. BTTT-2-4 shows a different packing in the neat thin film as compared to the larger members of the ‘standard’ dimers series described in the previous chapter. Additionally, when mixed with fullerene, BTTT-2-4 forms an intercalated amorphous blend. To further explore the solid state interactions and self-assembly in the BTTT system, I synthesized dimers with varying substitution patterns of short C4 (butyl) and long C12 (dodecyl) alkyl chains. Figure 37 shows the structures of all iterations of two long and two short chains; BTTT-4-4-12-12, BTTT-12-4-4-12, BTTT-4-12-12-4, and BTTT-4-12-4-12. Unfortunately, BTTT-4-12-4-12 could not be successfully synthesized and purified due to inseparable impurities in the precursors. However, I have included a failure analysis for the synthetic pathway and identified key road blocks in the synthesis. Still, the rest of the molecules yielded a wealth of information on the influence of variable chain substitution on this small molecule system. Compared with the BTTT-2-4 and
BTTT-2-12 ‘standard’ dimers, the variable-substitution dimers exhibit a broad array of thin film crystallization and blending behaviors which we are still working to rationalize. Most notably, BTTT-4-12-12-4 when blended with fullerene forms bimolecular crystals with unprecedented order and fidelity.

6.2 Synthesis of Variably-Substituted Oligothiophenes

Scheme 5 Synthesis of selected variable-substituted BTTT dimers. Molecule 9 could not be synthesized with the attempted pathway.

General Synthesis of Synthesis of 1, 2, 3, 4, 5, and 6 are previously described in chapter 3. 1H NMR, Maldi, reported here:

(3) **TIPS-T4-TT:** 1H NMR (500 MHz, CDCl3, δ) 7.38 (d, 1H), 7.32 (d, 1H), 7.27 (d, 1H), 7.09 (s, 1H), 2.80 (t, 2H), 1.68 (m, 2H), 1.42 (m, 2H), 1.34 (m, 3H) 1.15 (d,18H), 0.96 (t, 3H)
(4) **TIPS-T12-TT**: $^1$H NMR (500 MHz, CDCl$_3$, $\delta$) 7.38 (d, 1H), 7.32 (d, 1H), 7.27 (d, 1H), 7.09 (s, 1H), 2.80 (t, 2H), 1.68 (m, 2H), 1.42-1.25 (m, 21H), 1.15 (d, 18H), 0.96 (t, 3H)

(5) **TIPS-T4-TT-T12**: $^1$H NMR (500 MHz, CDCl$_3$, $\delta$) 7.29 (s, 1H), 7.26 (s, 1H) 7.24 (d, 1H), 7.09 (s, 1H), 6.99 (d, 1H), 2.82 (dt, 4H), 1.68 (m, 4H), 1.5-1.22 (m, 26H), 1.15 (d, 18H), 0.97 (t, 3H), 0.90 (t, 3H) MALDI: M/Z 684, Calc 684 g/mol

(6) **TIPS-T12-TT-T4**: $^1$H NMR (500 MHz, CDCl$_3$, $\delta$) 7.29 (s, 1H), 7.26 (s, 1H) 7.24 (d, 1H), 7.09 (s, 1H), 6.99 (d, 1H), 2.82 (m, 4H), 1.68 (m, 4H), 1.5-1.22 (m, 26H), 1.15 (d, 18H), 0.97 (t, 3H), 0.90 (t, 3H) MALDI: M/Z 684, Calc 684 g/mol

**Purification challenges of 5**

Note, despite several columns (silica gel, hexanes), purification of 5 could not be accomplished. The starting material (3) could not be separated from the desired product. After several columns without good separation, the material was moved to the next reactions where either bromination or deprotection would hopefully provide an acceptable separation of the starting material impurity. As is described below, this did not provide the necessary separation needed to purify 5 or its derivatives. 6 was easily separated and purified away from the starting materials.

**General procedure for synthesis of 7 and 8 (BTTT-4-12-12-4 and BTTT-12-4-4-12, respectively).**

The monoprotected asymmetric monomer (5 or 6) is brominated with NBS via electrophilic aromatic substitution of the thiophene $\alpha$-hydrogen. 5 or 6 (1 eqv.) is added to a stirring mixture of chloroform:glacial acetic acid (50:50 vol) at room temperature. NBS is then added (1.05 eqv.) and the reaction is covered to prevent light from forming radical bromine species. The reaction is left covered to stir overnight. The reaction mixture is then extracted with hexanes/water and the organic layer is collected to dry in vacuo. Care must be taken to remove all the acetic acid, and may require additional extraction. The concentrated organic layer is then purified via column
chromatography (silica, hexanes) to yield a bright-yellow solid at 90% yield. Note, despite bromination of 5, the starting material (now brominated as well, 3-Br) was still inseparable. 5-Br was purified as much as possible with column chromatography and collected for the to the next reaction. Stille coupling of impure materials is particular detrimental to final product purification; coupling can occur between the various active species generating multiple impurities in significant yield as illustrated in Scheme 6. Thus, starting material purity is of particular importance for Stille coupling reactions.

(5-Br) TIPS-T4-TT-T12-Br: \(^1\)H NMR (500 MHz, CDCl\(_3\), \(\delta\)) 7.28 (s, 1H), 7.21 (s, 1H), 7.09 (s, 1H), 6.94 (s, 1H), 2.86 (t, 2H), 2.75 (t, 2H), 1.65 (m, 4H), 1.5-1.22 (m, 26H), 1.15 (d, 18H), 0.97 (t, 3H), 0.90 (t, 3H) MALDI: M/Z 764, Calc 764 g/mol

(6-Br) TIPS-T12-TT-T4-Br: \(^1\)H NMR (500 MHz, CDCl\(_3\), \(\delta\)) 7.28 (s, 1H), 7.21 (s, 1H), 7.09 (s, 1H), 6.94 (s, 1H), 2.86 (t, 2H), 2.75 (t, 2H), 1.65 (m, 4H), 1.5-1.22 (m, 26H), 1.15 (d, 18H), 0.97 (t, 3H), 0.90 (t, 3H)

After bromination, 5-Br or 6-Br is homocoupled with hexamethylditin by Stille coupling in the same manner reported in Chapters 2, 3 and 5. Purification by column chromatography (silica gel, hexanes) yielded the TIPS-protected dimers 7-Tips and 8-Tips, respectively. Finally, dimers 7 and 8 were synthesized by deprotection of 7-Tips and 8-Tips (1 eqv.) in a stirring THF solution with tetra-n-butylammonium floride (TBAF, 1 M in THF) (~8 eqv.) for 4 hours. Final product was extracted with hexanes/water and purified in a short column (silica gel, hexanes). Note, the final product 7-Tips was separable despite a dirty stille coupling from impure 5-Br and any other cross coupling impurities as illustrated in part by Scheme 6. I also attempted deprotection of 5-Br prior to dimerization to see if this improve separation however, the deprotected 5-Br and 3-Br were also inseparable.

(7-Tips) TIPS-T4-TT-T12-T12-TT-T4-TIPS: \(^1\)H NMR (500 MHz, CDCl\(_3\), \(\delta\)) 7.30 (s, 2H), 7.28 (s, 2H), 7.10 (s, 2H), 7.06 (s, 2H), 2.84 (m, 8H), 1.71 (m, 8H), 1.45 (m, 4H), 1.45-1.22 (m, 48H), 1.17 (d, 32H), 0.99 (t, 6H), 0.90 (t, 6H)
(8-Tips) TIPS-T12-TT-T4-T4-TT-T12-TIPS: $^1$H NMR (500 MHz, CDCl$_3$, δ) 7.30 (s, 2H), 7.28 (s, 2H), 7.10 (s, 2H), 7.06 (s, 2H), 2.84 (m, 8H), 1.71 (m, 8H), 1.5-1.22 (m, 52H), 1.17 (d, 32H), 0.99 (t, 6H), 0.90 (t, 6H) MALDI: M/z 1366, Actual 1368 g/mol

(7) T4-TT-T12-T12-TT-T4: $^1$H NMR (500 MHz, CDCl$_3$, δ) 7.28 (s, 2H), 7.27 (s, 2H), 7.25 (s, 2H), 7.06 (s, 2H), 7.00 (s, 2H), 2.82 (m, 8H), 1.70 (m, 8H), 1.43 (m, 8H), 1.4-1.22 (m, 28H), 0.99 (t, 6H), 0.90 (t, 6H) MALDI: M/z 1055, Actual 1056 g/mol

(8) T12-TT-T4-T4-TT-T12: $^1$H NMR (500 MHz, CDCl$_3$, δ) 7.28 (s, 2H), 7.27 (s, 2H), 7.25 (s, 2H), 7.06 (s, 2H), 7.00 (s, 2H), 2.82 (m, 8H), 1.70 (m, 8H), 1.43 (m, 8H), 1.4-1.22 (m, 28H), 0.99 (t, 6H), 0.90 (t, 6H) MALDI: M/z 1055, Actual 1056 g/mol

Failed synthesis of 9 (BTTT-4-12-4-12), shown in Scheme 6.

The general strategy for synthesis of the asymmetric dimers is shown below in Scheme 6. Synthesis of the protected and brominated asymmetric BTTT monomers (5 and 6) enabled the best chance at adapting the synthetic scheme to difficulties encountered in purification. Through this method, I could leverage bromination, deprotection, or lithiation/stannylation to gain additional separation and purification enhancement. Additionally, the protected and brominated 5-Br and 6-Br molecules were required for synthesis of 7 (BTTT-4-12-12-4) and 8 (BTTT-12-4-4-12), so this synthetic approach provided the best flexibility and fewest synthetic steps to produce molecules 7, 8, and 9. As previously mentioned, the starting material, 3 and its brominated or deprotected derivatives were impossible to separate from 5 and its brominated or deprotected derivatives as
illustrated in Scheme 6. Due to this difficulty, and the array of possible side products, 9 could not be purified.

![Scheme 6: Strategy for synthesis of molecule 9 (BTTT-4-12-4-12) and failure analysis.](image)
Synthesis of BTTT-4-4-12-12

Synthesis of remaining dimer is described here. BTTT-4-4-12-12 was synthesized through stille coupling of monobromo BTTT-1-C4 and monobromo BTTT-1-C12 with hexamethylditin. Hexamethylditin (1 eqv.), tetrakis(triphenylphosphine) palladium (0) (0.1 eqv.), anhydrous toluene, BTTT-1-C12-Br (1 eqv.) and BTTT-1-C4-Br (1 eqv.) are added to a dry round bottom flask with a reflux condenser. The reaction is degassed and heated to reflux overnight. After cooling, toluene is mostly removed in vacuo and hexanes is added forming a red precipitate. This mixture is heated, sonicated, and then gravity filtered and washed with hexanes. The red solid (used catalyst) is discarded. Skipping catalyst removal typically results in clogged column and material trapped in the solidified catalyst. The remaining solution is purified in column chromatography (silica, hexanes) and dried to yield an orange solid (bright yellow fluorescence on TLC); 60% yield. Note, homocoupled biproducts BTTT-2-12 and BTTT-2-4 are easily separable from the desired BTTT-4-4-12-12 (middle fraction) in column chromatography.

Characterization: \(^1\)H NMR, Bruker 500 MHz:

(8) T4-TT-T4-T12-TT-T12: \(^1\)H NMR (500 MHz, CDCl\textsubscript{3}, \(\delta\)) 7.28 (s, 2H), 7.27 (s, 2H), 7.25 (s, 2H), 7.06 (s, 2H), 7.00 (s, 2H), 2.82 (m, 8H), 1.70 (m, 8H), 1.43 (m, 8H), 1.4-1.22 (m, 28H), 0.99 (t, 6H), 0.90 (t, 6H) MALDI: M/z 1055, Actual 1056 g/mol
Figure 38. Crystal packing of BTTT-4-12-12-4. Green colored molecules to highlight orientation difference in the crystal structure.

6.3 Substitution Effects on Crystal Packing and Morphology

Only the BTTT-4-12-12-4 molecule was able to form single crystals suitable for single crystal X-ray diffraction (Figure 38). Interestingly, the terminal C4-thiophene is oriented cis relative to the internal C12 thiophene. This conformation allows for increased backbone interaction (3 exposed sulfurs) as seen in Figure 38, left. This behavior is not observed in the majority of the standard dimers, BTTT-2-7 to BTTT-2-12 (only 2 exposed sulfurs) however is observed in the BTTT-2-6 molecule described in Chapter 2. Sufficiently short alkyl chains do not provide enough Van der Waals interactions to outweigh an increase in favorable backbone interactions. By orienting in the cis confirmation, the rotation of the terminal thiophene allows for increase backbone interactions with neighboring dimers depicted in shown in Figure 38, left. This is also exemplified in the peculiar conformation of the butyl alkyl groups shown in Figure 38. The butyl groups adopt a curled conformation with the 2\textsuperscript{nd} and 3\textsuperscript{rd} methylenes assuming cis conformations. This compressed chain
allows for butyl chains in nearby molecules to fit near one another but does not facilitate efficient dispersion interactions with neighboring chains.

The first clue as to the impact of substitution location of short and long chains the BTTT oligomers was that only one dimer was capable of forming single crystals suitable for analysis. The other molecules, BTTT-4-4-12-12 and BTTT-12-4-4-12 suffer packing frustrations to prohibit efficient crystal formation. As previously described for the monomer system in Chapter 3, the backbone interactions are the largest enthalpic contributions to crystallization. In all BTTT oligomers, the backbone provides a favorable template to align neighboring dimers through edge-to-edge, edge-to-face, and face-to-face interactions. Therefore I expect the ability for the backbone interactions to form and align properly is essential to efficient crystallization. In the 4-4-12-12 substitution pattern, the arrangement of the butyl and dodecyl chains are asymmetric and the dimer loses an inversion center present in all other synthesized dimers. I hypothesize the lack of symmetry is especially detrimental to crystallization. From an entropic viewpoint, the broken symmetry greatly increases number of non-degenerate conformations and thus increases the molecular entropy. Likely, the molecule has trouble distinguishing between the butyl and dodecyl ends during the crystal formation process and prevents efficient alignment and registration of the of the molecules. I expect the backbone-backbone interaction to be much greater than the difference in interaction energy between the side chains and cannot effectively distinguish between them in a growing crystal. Because of this, growing large single crystals is challenging and may be impossible. Further evidence of the misorientation in BTTT-4-4-12-12 seen later in the DSC and GIXD of the neat material.

In the BTTT-12-4-4-12 molecule, the inversion center is preserved by the symmetric arrangement of the alkyl chains (like most of the BTTT dimers). However, the crystallization is still impeded.
I hypothesize the large dodecyl chains on the terminal thiophenes prevent other molecules from coming into close contact. Additionally, the short chains on the interior of the molecule lack the proper length to provide a driving force for registration with neighboring dimers and are likely sterically screened by the long terminal chains. Combined, these effects inhibit efficient registration and alignment from neighboring dimers and manifests as an inability to form large single crystals.

6.4 Thermal Analysis

![Differential scanning calorimetry of selected BTTT dimers. The second heating cycle is lowered for clarity. Method Heat/Cool/Heat, -20 to 200, 10 °C/min.](image)

A comparison of the thermal properties between selected dimers is shown in Figure 39 and reveals the dramatic effect of side chain substitution pattern on the melting and crystallization properties of the BTTT dimer system. BTTT-2-4 shows the highest melting transition around 155 °C and two
cold crystallization peaks in the second heating at 110 °C and 135 °C. The lack of crystallization on the cooling ramp and the subsequent cold crystallization indicates that the material has kinetic difficulties self-assembling into crystalline domains. This is somewhat surprising due to the small size of the alkyl side chains. However, likely, this molecule adopts symmetry-broken confirmations like that observed in BTTT-2-6 in Chapter 2. This would explain the hindered crystallization and higher melting transition. BTTT-2-12 thermal properties are described in ref [20]; briefly, the first smaller melting transition at 93 °C is attributed to the side chain melting and the larger melting transition is attributed to the true melting transition at 105 °C. BTTT-2-12 shows a strong crystallization peak on the cooling ramp at 40 °C. Curiously, the side chain melting peak is not present in the second heating ramp. In BTTT-4-4-12-12 and BTTT-12-4-4-12 the melting peaks are broad and weak indicating a large distribution in crystal size and quality and the possibility of polymorphism. Additionally, an absence of any crystallization peak or melting during the second heating ramp for both materials indicates that they are severely kinetically limited in their ability to form crystalline domains. Surprisingly, the symmetric molecule BTTT-12-4-4-12 has a lower melting transition than the asymmetric BTTT-4-4-12-12. This suggests that the long terminal dodecyl groups in preventing strong backbone interactions and when paired with interior butyl chains, the crystallized material has a relatively weak intramolecular interactions. Only when the butyl groups are on the ends of the molecule can they rotate out of the way and provide improved backbone interactions as seen in Figure 38. I hypothesize that the steric screening of the long alkyl chains in BTTT-12-4-4-12 contributes to its lower melting point as compared BTTT-4-4-12-12 which still has a terminal butyl group. Finally, BTTT-4-12-12-4 with its superior crystallization properties shows a single reproducible melting endotherm at 103 °C. Curiously, the melting transition is slightly lower than BTTT-2-12 despite the increased backbone
interactions afforded by the butyl chains. Likely the different backbone orientation (edge-to-face, Figure 38) and fewer alkyl chain interactions contribute to the slightly lower melting transition. On the other hand, this molecule crystalized at much higher temperatures than the BTTT-2-12. This highlights the difference of the, sterics, temperature dependent kinetics, and intermolecular contributions from the terminal side chains between the butyl and dodecyl end groups.

6.5 Grazing-Incidence X-ray Diffraction

The degree efficient self-assembly registration and order in the variable substitution dimers is also apparent in the thin film morphologies as characterized by GIXD. Figure 40 shows the structures and diffractions patterns for both neat and PC$_{61}$BM blended molecules. BTTT-2-4 is shown for reference although in the thin film does not pack in the same manner as the other dimers. We have not determined the thin film packing for BTTT-2-4. Nearly all other dimers (including the variable substitution dimers) adopt slight variations to a 2-D lamellar packing where sheets of pi-stacked dimers are separated by alkyl chains as shown in Figure 33, Figure 30, Figure 34, Figure 38 and
represented schematically by Figure 41. A thin film packing model for BTTT-2-12 has been calculated from the diffraction pattern and single crystal analysis in ref [20] which has lamellar spacing of 22 Å. Based on the BTTT-2-12 characterization and the diffraction pattern comparison with variable-substitution dimers, we are confident they have similar crystal habits in the thin film; namely an interdigitated 2-D lamellar morphology where the pi-stacking backbones form 2-D lamellar sheets as represented generally in Figure 41. The finer aspects of the interdigitation and registration of the side chains must be interpreted from GIXD out of plane reflections and are a work in progress.

![General Interdigitated 2-D Lamellar morphology](image)

Figure 41. Cartoon representing a general packing model illustrating the 2-D lamellar packing representative of many of the BTTT dimers.

Qualitatively, however the trend of order and registration can still be understood from the diffraction patterns shown in Figure 40. BTTT-2-12 shows diffraction similar to the polymer where crystalline domains have a moderate amount of azimuthal misorientation (denoted by arching of the peaks) relative to the substrate.[50] Surprisingly, BTTT-12-4-4-12 show less azimuthal misorientation and the appearance of bragg rods not observed in the C12 dimer. The
presence of multiple chain lengths should not improve alignment of the side chains and prohibit new bragg rods from forming. Despite this, we observe a more crystalline diffractogram than the C12 dimer which indicates that order in the crystalline domains of the 12-4-4-12 system is possibly higher. It is possible that the crystalline regions of BTTT-12-4-4-12 are more ordered but since GIXD only probes crystalline regions of a film, this material could overall be less crystalline than BTTT-2-12. This hypothesis is supported by DSC which shows a much lower and broader melting endotherm in in BTTT-12-4-4-12 as compared to BTTT-2-12 indicating a less homogeneously crystalline material.

The diffractogram for BTTT-4-4-12-12 shows the largest amount of azimuthal misorientation and lowest order among the group. This is not surprising as film forming is rapid as the solvent evaporates leaving little time for the already entropically frustrated dimers to pack in an ordered manner. Still, the presence of a lamellar morphology is clearly shown in the diffraction indicating that the molecules still conform to the general packing model suggested in Figure 41. However, the large lamellar spacing (~31.5 Å) indicates that this material likely does not have interdigitated side chains. We are continuing to look into this system for future study. Also in line with the observed trends in crystallinity, BTTT-4-12-12-4 show high degrees of order and orientation with sharp peaks, little azimuthal misorientation, and strong high order bragg rods. The diffraction indicates 2 packing morphologies in the thin film. We are continuing to analyze this system and indexing both polymorphs will be future work.

6.6 Blends of PC61BM with Variable-Substitution BTTT Dimers

Figure 40 (bottom row) also shows the diffractograms of 50:50 wt% blends of BTTT dimers and PC61BM. The selection of dimers in Figure 40 provides an excellent summary of previous work
described in other chapters (BTTT-2-4, Chapter 5, and BTTT-2-12, Chapter 4) as well as
diffractograms from the new variable-substitution dimers, BTTT-12-4-4-12, BTTT-4-4-12-12,
and BTTT-4-12-12-4. Upon blending with PCBM, BTTT-2-4 intimately mixes to create an
amorphous blend as described in Chapter 5 where as BTTT-2-12 forms a bimolecular crystal as
described in Chapters 4, and 5. The presence of variable substitution side chains that illicit different
types of behavior when mixed with fullerene begets the following questions: how will the variably
substituted dimers behave when blended with PCBM? Will they form bimolecular crystals? will
they reject fullerene and phase separate? Will they form an amorphous blend? Will they partially
intercalate?

Figure 40 reveals that each side chains substitution pattern interacts differently with fullerene. The
BTTT-12-4-4-12 does not intercalate in any capacity. The diffraction pattern shown no obvious
changes aside from an overall decrease in intensity and loss of some of the bragg rods. We believe
this system is phase separated and can maintain pure BTTT crystalline regions. On the other hand,
in the 4-4-12-12 blended film, fullerene readily intercalates to form a co-crystal. This is denoted
by a decrease in the lamellar spacing from 31 Å in the neat film to 25.5 Å in bimolecular crystal.
Interestingly, the lamellar spacing in the bimolecular crystal also correspond well to the
intercalated BTTT-2-8 spacing. We find this particularly surprising in such a disordered system
and instead would expect a spacing dominated by the longer C12 chains. However, C8 is the
average chain length between the C4 and C12 components and suggests the chains are registering
long-to-short in the crystal much alike BTTT-1-7/12 in Chapter 3. We are continuing to explore
the BTTT-4-4-12-12 system in future work.

Finally, the most interesting diffraction came from the blended BTTT-4-12-12-4:fullerene thin
films. GIXD reveals these materials readily form bimolecular crystals in higher fidelity and
crystallinity than observed in any other dimer/fullerene blend. We are currently working with collaborators to index the bimolecular crystal’s unit cell. Based on preliminary date, the molecular model is shown in Figure 42. The co-crystal is similar to the packing observed in BTTT-2-12 where a fullerene occupies the space between the sidechains and forms 1-D columnated rows. However, the lamellar spacing is 25 Å which corresponds closely to the BTTT-2-8 co-crystal spacing. This strongly supports that long and short chains butt-up to one another in the crystal. Along with fullerene intercalation, the side chain registration also affords interdigitation of the dodecyl side chains as shown in Figure 42. The interpenetration of dodecyl chains from adjacent dimer layers greatly reduces disorder in the intercalated system and allows for the unprecedented crystallinity observed in GIXD. To date this molecule has the best chance of forming a solution grown bimolecular crystal, which will be attempted in future work.

![Figure 42. Packing model for the BTTT-4-12-12-4 and PC$_{61}$BM bimolecular crystal.](image-url)
6.7 Conclusion

I described new synthesis for BTTT dimers with substitution patterns of two short C4 (n-butyl) and two long C12 (n-dodecyl) side chains. While 3 of the 4 possible patterns were synthesized, the last could not be purified due to inseparable impurities in the reagents prior to the final Stille coupling. Still, the successfully synthesized dimers provided a wealth of information and research direction. I observed neat films of BTTT-4-4-12-12 to pack in poorly ordered lamellar with a spacing that suggests no interdigitation. Blends of BTTT-4-4-12-12 a fullerene do however clearly show an increase in order and intercalation. BTTT-12-4-4-12 appears to interdigitate, however do not seem to intercalate PC61BM. BTTT-4-12-12-4 showed amazing degrees of crystallinity in both the neat and blended thin films. Most intriguingly, BTTT-4-12-12-4 formed co-crystals with PCBM in very high fidelity and at a lamellar spacing distance equivalent to the BTTT-2-8. This spacing indicates that the long and short alkyl chains register end-to-end with one another which allows the dodecyl chains to interdigitate with themselves while simultaneously intercalating PCBM.

A key component to the observed order and crystallinity in BTTT-4-12-12-4 is the interdigitation of the side chains. In neat films, PBTTT and many of its oligomers are known to efficiently interdigitate.[17, 18, 20] however what has not been observed is effective interdigitation in the co-crystal. Previous report indicate that alkyl chains can still interact when intercalated[3], yet we observe for the first time efficient and effective interlayer interdigitation with in a fullerene-intercalated cocystal. Just as interdigitation is responsible for PBTTT’s improved order relative to other thiophenes, the interdigitated co-crystal also in much improved in order and crystallinity.
The broader concept of variable chains to enable interdigitation is not limited to oligomers. Furthermore, it’s not limited to the PBTTT system. I predict that P3HT with varying alkyl chains could also benefit from improved crystallinity and registration with a variable substitution platform. Additionally, the interdigitated cocrystal could also be implemented in PBTTT to possibly allow for some of the highest levels of crystallinity every observed in a polymer system. This oligomer study, while not yet translated to polymer systems, will continue to excel as an exciting model for exploring structure properties relations and new molecular design directions for the much broader class of OCS (both polymer and small molecules alike).

This chapter invokes many of the themes inherent in the previous chapters. Dimers with varying substitution are observed to have a broad range of self-assembly behavior directly related to the substitution pattern of their side chains. The concept of smart self-assembly, where molecules are designed to adopt more and more complicated self-assemblies will continue to grow as applications demand more and more efficient solutions. Still, as observed here, the ability to imbue a material with spontaneous assembly information is inherently limited. More complexity in a molecular system often requires an increase in the entropy. This is exemplified by the 4-4-12-12 substitution pattern which is missing an inversion symmetry element as compared to the other dimers. In neat films, we see this manifest as both disorder and large, non-interdigitated, lamellar spacings indicating this molecule does not efficiently pack in the solid state. Still, if implemented correctly, more complex self-assemblies can be achieved as seen in the BTNT-4-12-12-4 system, which very efficiently packs in the neat film, and even more so in blends with fullerene.

Collaborators: Edmund Burnett, Detlef Smilgies, Sean Parkin
CHAPTER 7

CONCLUSION

7.1 Summary

The major underlying theme of this dissertation is:

*The implementation of side chains to drive self-assemble in semiconducting small molecules.*

To accomplish this, we first needed to characterize the intrinsic conformational preferences of the BTTT molecule. Chapter 2 focuses on this concept. After understanding the molecule at an atomistic scale, we can begin to piece together the intermolecular driving forces which work in tandem with the molecular design and intramolecular interactions to drive self-assembly. This fundamental work, presented largely in Chapter 2, establishes a baseline for future alternations to the molecular structure.

Chapter 3 and 5 leverage the fundamental baseline to generate powerful structure property conclusions through a systematic study of side chain length. Although both the systematic monomer and dimer studies are simple experiments in both chemistry and concept, this sort of deep exploration into the influence of side chains is largely underrepresented in the field. In the monomer system, we learned that alkyl chains are exclusively responsible in determining the registration between layers of molecules. Additionally, we also observe the ability for side chains to interdigitate in a variable-substitution monomer, which provided an exciting concept for the work in the final chapter. In the systematic dimer study (Chapter 5), we predicted a sufficiently short alkyl chain would prevent intercalation. However, we observed instead an order to disorder transition at small side chains where dimers and fullerene are still intercalated, but strangely not crystalline. Much of the preliminary work for this the systematic dimer study was supported by Chapter 4 where we extensively characterize BTTT-2-12:PC$_{61}$BM blended thin films at a variety
of blend ratios. Careful microstructure characterization of fullerene blends in Chapter 4 was well worth the effort as it provided an excellent comparative platform for the structure-property relations observed in systematic dimer series and variable-substitution dimers studied in Chapter 5 and 6, respectively.

Finally, in a beautiful combination of fundamental work in Chapters 2 and 4, and the structure property-exploration in Chapters 3 and 5, we apply our knowledge of the BTTT system to synthesize and characterize variable-substitution dimers. These molecules have varying patterns of short and long chains which display a myriad of assembly behaviors as neat films, and as blends with PC$_{61}$BM.

### 7.2 Outlook

In a broader sense, this dissertation also builds a compelling molecular design guide for future side chain engineering. In OSCs improvements in electronic properties can be gained by reducing disorder and improving crystallinity. This dissertation provides new approaches for improving the crystallinity and order in both small molecule and polymer systems. In BTTT dimers, the most crystalline systems which still adopt a favorable crystal packing is the BTTT-4-12-12-4 which has side chains of varying lengths. This molecule shows improve crystallinity in the thin film as well as unprecedented order in the intercalated co-crystal. Translating this to a polymer system would not require new chemistries or challenging synthesis and could yield a interdigitated and intercalated system like that observed in BTTT-4-12-12-4.

Additionally, the extensive study in intercalated systems is also relevant to new directions in the field of OSCs. Recently, OPVs have been surpassed by other solution based technologies and the research teams in these areas are already beginning to pivot to new OCS applications. One of the most promising fields is doped OSC. Doped OSCs currently are poorly understood although their
potential for application in Thermoelectrics and/or Organic Electrochemical Transistors is well recognized. Essential to both of these new technologies is the interaction of the OSC with a secondary dopant molecule however multicomponent blending almost always results in disruption of the microstructure, molecular packing, and charge transport properties. Although doping can be accomplished with many OSC systems, device performance leaves much to be desired. One strategy covered in detail in this dissertation is intercalation and specifically, co-crystal formation. The benefit realized by intercalation is intimate and multicomponent mixing required for the field of doping can be accomplished without disrupting the crystallinity, microstructure, or connectivity of the OCS. Building a more complete understanding of the packing forces which allow co-crystal formation will undoubted lead to new, more intelligent and flexible, molecular design to address the challenges presented in both new and old areas of OCS research.

Finally, future work in these systems includes, new side chain chemistries, ternary blends, self-assembly and templating through blending or thermal cycling, and implementation of new side chain patterns into polymer systems. A new class of side chains that are particularly interesting is the ethylene glycol based chains. These chains are more water, ion, and biologically compatible and will likely be a popular choice for new interdisciplinary work between OCS and biology. In future work, we also would like to blend multiple dimers together and compare the solid-state behavior in films of variable side chain dimers with blends of BTTT-2-4 molecules and BTTT-2-12. This concept could be expanded to explore the blending behavior of any binary, ternary, or quaternary blend of dimers and/or fullerenes. Finally, the lessons already learned from the variable-substitution in Chapter 6 already provide a tantalizing direction for improving polymer crystallinity through side chain patterning.
APPENDIX A

CHAPTER 2 SPECTRA

Spectra 1. BTTT-1-6, $^1$H NMR, CDCl$_3$, 500 MHz

Spectra 2. BTTT-1-6-Br, $^1$H NMR, CDCl$_3$, 500 MHz
Spectra 3. BTTT-2-6, $^1$H NMR, CDCl$_3$, 500 MHz

Spectra 4. BTTT-2-H and BTTT-2-H-TIPS, MALDI-TOF
Spectra 5. TIPS-T-TT, H\textsuperscript{1} NMR, CDCl\textsubscript{3}, 500 MHz

Spectra 6. TIPS-T-TT-Br, H\textsuperscript{1} NMR, CDCl\textsubscript{3}, 500 MHz
Spectra 7. BTTT-1-7, H\textsuperscript{1} NMR, CDCl\textsubscript{3}, 500 MHz

Spectra 8. BTTT-1-8, H\textsuperscript{1} NMR, CDCl\textsubscript{3}, 500 MHz
Spectra 9. BTTT-1-9, H\textsuperscript{1} NMR, CDCl\textsubscript{3}, 500 MHz

Spectra 10. BTTT-1-10, H\textsuperscript{1} NMR, CDCl\textsubscript{3}, 500 MHz
Spectra 11. BTTT-1-10, H\textsuperscript{1} NMR, CDCl\textsubscript{3}, 500 MHz

Spectra 12. 2-Bromo-3-Heptylthiophene, H\textsuperscript{1} NMR, CDCl\textsubscript{3}, 500 MHz
Spectra 13. 2-Bromo-3-Heptyl-5-(trimethyl)silylthiophene, H\textsuperscript{1} NMR, CDCl\textsubscript{3}, 500 MHz

Spectra 14. 2-thienothiophene-3-heptyl-5-(trimethyl)silylthiophene, H\textsuperscript{1} NMR, CDCl\textsubscript{3}, 500 MHz
Spectra 15. TMS-T7-TT-T12, H$^1$ NMR, CDCl$_3$, 500 MHz

Spectra 16. BTTT-1-7/12, H$^1$ NMR, CDCl$_3$, 500 MHz
Spectra 17. BTTT-1-7/12, 571 M/Z, MALDI-TOF
APPENDIX C

CHAPTER 5 SPECTRA

Spectra 18. BTTT-2-4, H$^1$ NMR, CDCl$_3$, 500 MHz

Spectra 19. BTTT-2-5, H$^1$ NMR, CDCl$_3$, 500 MHz
Spectra 20. BTT-2-6, H\textsuperscript{1} NMR, CDCl\textsubscript{3}, 500 MHz

Spectra 21. BTTT-2-7, H\textsuperscript{1} NMR, CDCl\textsubscript{3}, 500 MHz
Spectra 22. BTTT-2-8, H$^1$ NMR, CDCl$_3$, 500 MHz

Spectra 23. BTTT-2-9, H$^1$ NMR, CDCl$_3$, 500 MHz
Spectra 24. BTTT-2-10, $^1$H NMR, CDCl$_3$, 500 MHz

Spectra 25. BTTT-2-11, $^1$H NMR, CDCl$_3$, 500 MHz
Spectra 26. BTTT-2-12, H\textsuperscript{1} NMR, CDCl\textsubscript{3}, 500 MHz

Spectra 27. BTTT-2-14, C\textsuperscript{13} NMR, CDCl\textsubscript{3}, 500 MHz
Spectra 28. BTTT-2-14, $^1$H NMR, CDCl3, 500 MHz
APPENDIX D

CHAPTER 6 SPECTRA

Spectra 29. TIPS-T4-TT, H$^1$ NMR, CDCl$_3$, 500 MHz

Spectra 30. TIPS-T4-TT-T12, H$^1$ NMR, CDCl$_3$, 500 MHz
Spectra 31. TIPS-T4-TT-T12-Br, H\textsuperscript{1}NMR, CDCl\textsubscript{3}, 500 MHz

Spectra 32. BT TT-4-12-12-4-TIPS, H\textsuperscript{1}NMR, CDCl\textsubscript{3}, 500 MHz
Spectra 33. TIPS-T12-TT, H\(^1\) NMR, CDCl\(_3\), 500 MHz

Spectra 34. TIPS-T12-TT-T12, H\(^1\) NMR, CDCl\(_3\), 500 MHz
Spectra 35. TIPS-T12-TT-T12-Br, H¹ NMR, CDCl³, 500 MHz

Spectra 36. BTTT-12-4-4-12-TIPS, H¹ NMR, CDCl³, 500 MHz
Spectra 37. BTTT-12-4-4-12, $^1$H NMR, CDCl$_3$, 500 MHz

Spectra 38. BTTT-4-12-12-4, $^1$H NMR, CDCl$_3$, 500 MHz
Spectra 39. BTTT-4-4-12-12, H\textsuperscript{1} NMR, CDCl\textsubscript{3}, 500 MHz

Spectra 40 BTTT-4-4-12-12, BTTT-12-4-4-12, and BTTT-4-12-12-4, 1055 M/Z, MALDI-TOF
Spectra 41. TIPS-T4-TT-T12 and TIPS-T12-TT-T4, 684 M/Z, MALDI-TOF

Spectra 42. TIPS-12-4-4-12-TIPS, 1366 M/Z, MALDI-TOF
Spectra 43. TIPS-T4-TT-T12-Br, 764 M/Z, MALDI-TOF
BIBLIOGRAPHY


