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Rational Design and Preparation of Organic Semiconductors for use in Field Effect Transistors and Photovoltaic Cells

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# Rational Design and Preparation of Organic Semiconductors for use in Field Effect Transistors and Photovoltaic Cells

By

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A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Chemistry

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

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### Abstract

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Doctor of Philosophy in Chemistry

University of California, Berkeley

Professor Jean M. J. Fréchet, Chair

The goal of this research was to develop methods to control the material properties of organic semiconductors, like solubility, stability, charge mobility, and self-assembly, through structural design. Investigations of structure-property relationships were conducted to optimize the properties of organic semiconductors for applications in organic field effect transistors (OFETs) and organic photovoltaics (OPVs).

Chapter 1 gives an introduction to charge transport in organic semiconductors, and describes how the structure of conjugated molecules can affect their electrical performance and facilitate facile solution deposition. Furthermore, factors that can affect the stability of organic semiconductors to ambient conditions are discussed. Also, the device characteristics of OFETs and OPVs are summarized as a reference for subsequent chapters.

Chapter 2 discusses the investigation of the air stability of distyryl oligothiophenes in OFETs. This work made use of thermally labile solubilizing groups to facilitate solution deposition of the oligothiophenes. In addition to device characterization, an extensive analysis of the thin film morphology using AFM, NEXAFS and GIXD is presented. This work revealed the general stability of distyryl oligothiophenes to oxidative degradation, and the high degree of crystallinity in our thin films.

In Chapter 3, the charge transporting properties of pentathiophene monolayer islands is analyzed using current sensing AFM. The pentathiophenes were prepared with carboxylic acid moieties for self assembly, and the sub-monolayer films were transferred onto conductive substrates using the Langmuir-Blodgett technique. The morphology of the monolayers was observed to be sensitive to the alkyl substitution pattern of the pentathiophenes, which in turn affected charge transport.

Hierarchical supramolecular assemblies of oligothiophenes and block copolymers are studied in Chapter 4. The structure of the assemblies is studied by TEM and small angle X-ray scattering, confirming successful formation of supramolecular assemblies. Thin films are studied further by grazing incidence X-ray scattering, and their charge transporting properties are evaluated in OFETs. This work demonstrates that non-covalent self-assembly can be used to access nanostructured thin films of functional organic semiconductors.

Finally, Chapter 5 discusses the photophysical, morphological, and electronic properties of boron(subphthalocyanine)s with conjugated axial ligands. The tendency of these materials to form polycrystalline films instead of amorphous films was shown to be very sensitive to axial ligand structure and coordination geometry. The morphology of thin films was also shown to affect OPV device characteristics, with crystalline films supplying higher photocurrents.

For my parents, Chuck and Barbara Mauldin, for all of their support and encouragement of my pursuit of a career in the sciences.

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## Chapter 1 Introduction to Small Molecule Organic Semiconductors

### Abstract

In this chapter, a short introduction to charge transport in organic semiconductors will be presented that will lead into a discussion of structural factors that influence solubility and stability of small molecule organic semiconductors. Finally, an introduction to organic field-effect transistors (OFETs) and organic photovoltaics (OPVs) is presented, because they provide test structures for evaluation of our materials and represent their target application.

### **1. Introduction**

Organic semiconducting materials are of broad interest because of their potential use in low cost electronic devices such as organic field-effect transistors (OFETs),<sup>1-3</sup> photovoltaic cells,<sup>4-6</sup> sensors,<sup>7,8</sup> light-emitting diodes (OLEDs),<sup>9,10</sup> and radio frequency identification (RFID) tags.<sup>11-13</sup> The ability to deposit organic semiconductors from solution allows device fabrication via spin coating,<sup>3,14</sup> stamping,<sup>15,16</sup> or ink-jet printing.<sup>17,18</sup> Low temperature solution processing also extends the substrate compatibility of organics to include flexible plastics or fabrics. As a result, solubility is a critical parameter in the development of organic semiconductors for commercial applications in addition to environmental stability and overall performance in electronic applications.<sup>19,20</sup>

These bulk properties of organic semiconductors can be controlled at the molecular level, which makes them an interesting field of study at the interface of materials science and synthetic organic chemistry. Concepts from organic chemistry like molecular orbital theory, chemical reactivity and supramolecular chemistry are central to the design and development of these materials as semiconductors. Small molecule semiconductors in particular are discrete units with well defined molecular electronics and intermolecular interactions. Tuning of material properties therefore starts primarily with the rational variation of conjugated molecule structure.

The focus of our work has been to investigate structure property relationships in organic semiconductors, and to tailor their properties for specific applications. This chapter serves as an introduction to charge transport in organic semiconductors and the relevant physical and chemical properties of conjugated molecules that function as semiconductors in OFETs and OPVs.

#### 2. Charge Transport in Organic Semiconductors

Organic semiconductors are generally easily oxidized to radical cations (p-type) or reduced to radical anions (n-type) to yield stable species with charge delocalized over a conjugated system. A key figure of merit for organic semiconductors is charge mobility ( $\mu$ ), which is the average drift velocity of charge per unit electric field. Ideally, strong intermolecular electronic coupling would allow extensive charge delocalization within the crystal lattice of a conjugated molecule and high mobility charge transport. However, the accommodation of charge in a conjugated system results in a relaxation of the molecular structure and a distortion of the crystal lattice.<sup>21</sup> Transfer of charge from one molecule to another via electron transfer therefore results in a migration of this lattice distortion. As a result, charge in organic semiconductors is self-trapped and travels through localized states, which is in contrast to highly delocalized states in inorganic semiconductors is therefore modeled as thermally activated hopping,<sup>22,23</sup> and charge mobility values are typically an order of magnitude lower than those of inorganic semiconductors. In OFETs, charge mobilities of 1 – 0.1 cm<sup>2</sup>/Vs have become common, while OPV materials typically exhibit charge mobilities ranging from 10<sup>-4</sup> – 10<sup>-2</sup> cm<sup>2</sup>/Vs.

The rate at which charge migrates through an organic semiconductor crystal lattice depends on the intermolecular overlap of the highest occupied molecular orbital or lowest unoccupied molecular orbital for p-type or n-type semiconductors, respectively.<sup>22</sup> The reorganization energy associated with charge transfer also plays a role in charge mobility. These factors make rigid molecules that crystallize with extensive  $\pi$ -orbital overlap ideal.

Solution deposition of conjugated molecules is only a viable device fabrication technique when film morphology can be controlled to optimize electronic properties. Polycrystalline thin films are superior to amorphous films in terms of charge mobility, and values an order of magnitude higher are measured for single crystals.<sup>24,25</sup> This suggests that charge transport across grain boundaries is the limiting process in thin film measurements. Therefore, organic semiconductor deposition conditions should be optimized to maximize crystalline domain size to decrease resistance.

### 3. Solubility of Organic Semiconductors

Rigidity and stong intermolecular  $\pi$ - $\pi$  interactions combine to make organic semiconductors very insoluble. Solubility can be increased by introducing bulky and flexible groups onto conjugated molecules, but this method decreases the intermolecular electronic interactions that facilitate charge transport and yields a material with reduced crystallinity and electrical performance. As a result, alternative methods have been developed to allow solution deposition of polycrystalline high mobility organic semiconductors.

One method to generate films of a conjugated small molecule is to use thermal elimination of labile functional groups. In this process, a highly soluble precursor molecule is cast into a film and then annealed to afford the elimination product. A key aspect of this approach is that an initially amorphous film is transformed into a polycrystalline film with high charge mobility during the annealing step. This concept has been successfully applied to diverse conjugated small molecule structures, as can be seen in Figure 1. Retro-Diels-Alder reactions have been used to access films of pentacene and benzoporphyrin.<sup>26-29</sup> In addition, oligothiophenes with branched secondary esters have been developed that undergo thermolysis to yield polycrystalline oligothiophene thin films.<sup>30-32</sup> These materials have allowed solution processing of active layers with high charge mobility for OFETs and OPVs.<sup>32,33</sup>

Another approach used to increase the solubility of conjugated molecules is to block their normal packing mode with judicious substitution. Aromatic molecules without electronegative substituents are quadrupolar in character. The greatest electron density lies within the pi-cloud and the peripheral hydrogen atoms bear a partial positive charge. Therefore, electrostatic interactions dictate that edge-to-face packing is the most favorable arrangement of molecules in a crystal lattice. If this packing mode is blocked by sterically bulky groups, then the molecules may crystallize in a slip-stacked fashion.<sup>34</sup> Since this is usually a less energetically favorable alternative to edge-to-face packing, the solubility of the conjugated molecule improves dramatically. However, the conjugated molecules must still crystallize with extensive pi-orbital overlap in order to maintain high charge mobility.



**Figure 1.** Thermal treatment of soluble precursors leads to decomposition of Diels-Alder adducts and thermolysis of secondary esters. The conjugated molecule products are then free to self assemble into polycrystalline thin films.

Oligothiophenes with alkyl substitution in the 3 or 4 thiophene ring positions are highly soluble, but typically exhibit much lower charge mobilities than their unsubstituted counterparts.<sup>25</sup> This may be the result of a loss in planarity of the conjugated system or a decrease in crystalline domain size. A more successful application of this concept was realized with rigid acene derivatives. 6,13-Bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene) and 5,11-bis(triethylsilylethynyl)anthradithiophene, shown in Figure 2, are two examples of highly soluble acene derivatives that form polycrystalline thin films with high charge mobility in OFETs.<sup>35,36</sup>



Figure 2. Bulky substituents on the central benzene ring of acenes render the materials highly soluble, but allow the molecules to pack in a slip-stacked cofacial fashion.

### 4. Stability of Organic Semiconductors

Organic semiconductors are typically sensitive to air and light. For this reason, device fabrication and testing usually must be performed under inert atmosphere or vacuum, which complicates the low-cost device applications envisioned for organic semiconductors. Conjugated molecules that function as p-type semiconductors are easily oxidized, which explains their sensitivity to the oxygen in air. In devices, oxygen can act as a dopant in p-type organic semiconductors, <sup>37</sup> meaning oxygen accepts an electron to yield a mobile hole in the semiconductor. This is mainly an issue in OFETs where a semiconductor is ideally depleted of charge carriers when the device is in the off state. In OPVs and OFETs, organic semiconductors are usually intensely colored and can generate singlet oxygen when exposed to light.<sup>38</sup> Indeed, rapid photobleaching can make working with these materials difficult, especially in solution. On the other hand, n-type organic semiconductors are very stable towards oxidation as molecules, but in devices high energy electrons travelling through the LUMO of the materials are highly susceptible to trapping. Hydroxyl groups or adsorbed oxygen have been shown to be charge traps for mobile electrons, but increasing the electron affinity of n-type organic semiconductors has made materials more environmentally robust in device applications.<sup>39,40</sup>

Methods to improve the stability of p-type organic semiconductors have focused on increasing the oxidation potential, widening the HOMO-LUMO gap, and removing chemical reactivity pathways. Increasing the oxidation potential of conjugated molecules can be achieved by introducing electronegative substituents, and can reduce the effect of oxygen exposure on device performance.<sup>40,41</sup> The HOMO-LUMO gap can also be tuned to minimize light absorption and avoid singlet oxygen sensitization. Examples of these approaches are shown in Figure 3. Fluorene building blocks stabilized the HOMO and destabilized the LUMO of the conjugated oligomer so that the chromophore absorbed outside of the intense wavelengths of ambient light.<sup>42,43</sup>

The chemical reactivity of conjugated oligomers that adversely affects device performance can be difficult to elucidate because of the low solubility of the materials and the small amounts of material deposited in device thin films. Nevertheless, knowledge of the general degradation pathways of molecules can be applied to the development of materials with enhanced stability. For example, pentacene is known to oxidize in the 6 and 13 positions to pentacenequinone. Depending on its spin state, oxygen is believed to add either stepwise or in a 4+2 concerted fashion to the central ring of pentacene. Further decomposition of this adduct leads to a variety of oxidation products, and removal of these impurities led to large improvements in the performance of pentacene OFETs.<sup>44</sup> Substitution at the 6 and 13 positions, like in TIPS-pentacene, prevents this degradation pathway and has improved the air stability of the material.<sup>45</sup>

#### Depressed HOMO



Figure 3. Electron-withdrawing imine nitrogens and carbonyl groups can increase the oxidation potential of conjugated oligomers. Fluorene moieties decrease the extent of conjugation in the  $\pi$ -system and increase the HOMO-LUMO gap.

#### 5. Device applications of Organic Semiconductors

**5.1 Field-Effect Transistors.** Transistors are the basic logic element in integrated circuits that operate RFID tags and sensors and are used to drive individual pixels in active matrix displays. Laboratory test structures consist of many isolated FETs on a substrate coated with an organic semiconductor film. A diagram of FET test structures is shown in Figure 4. The device consists of a gate electrode, a dielectric insulating layer, and the organic semiconducting material that forms a channel between a source and drain electrode. In the most commonly used devices, low resistivity doped silicon is used as both the substrate and the gate electrode. Oxidation of the silicon surface forms an insulating SiO<sub>2</sub> layer, usually with thicknesses of ~100-300 nm thick. These silicon devices are used for standard comparisons, but plastic substrates,<sup>11,14,17,46</sup> polymeric insulators,<sup>47,48</sup> and conductive inks for use as the source and drain electrodes<sup>49,50</sup> are being developed for flexible electronic applications.

Two different test structure geometries are shown in Figure 4. In top contact geometry, the organic film is deposited on a uniform dielectric surface, then the source and drain electrodes are deposited on top by metal evaporation through a shadow mask. This allows a good contact to be made between the electrodes and the organic. However, shadowing effects can limit how small the channel dimensions can be (usually >5  $\mu$ m channels), and this process is not amenable to large-scale manufacturing. In bottom contact devices, the source drain electrodes are lithographically pre-patterned on the substrate and the organic layer is deposited last. Bottom

contact devices typically exhibit less than half the effective drive current of top contact devices due to contact resistance and the difficulty in preparing highly ordered films on an irregular surface.<sup>17,51,52</sup> Furthermore, metal electrode surfaces may not wet as well as the dielectric surface during solution deposition of the organic semiconductor. We have used top contact device structures in our work whenever possible to eliminate these issues and because small channel dimensions are unnecessary for our experiments.



Figure 4. OFET test structure geometries.

For OFETs, organic semiconductors ideally have very low intrinsic conductivity but high charge mobility. As a result, an insulating channel exists under zero gate bias, and the FET can be operated under accumulation mode to inject mobile charges into the organic semiconductor that then forms a conductive channel. This process is shown in Figure 5. Gate bias creates a large electric field at the semiconductor-dielectric interface, causing a shift in the HOMO and LUMO energy levels in the organic semiconductor. Depending on the polarity of the gate bias relative to the source electrode, electrons will either flow out of the HOMO into the electrodes (leaving behind holes) or will flow from the electrodes into the LUMO, forming a conducting channel between the source and drain. Current can then be driven through the device by applying a voltage between the source and drain.



Figure 5. Diagram depicting operation of a p-channel OFET.

The most important figures of merit for an organic semiconductor in an OFET are the charge mobility and the  $I_{on}/I_{off}$  ratio. The charge mobility can be calculated in the saturation regime using equation 1, where W = channel width, L = channel length, C<sub>i</sub> = capacitance of the insulator,  $\mu$  = field-effect mobility, V<sub>g</sub> = gate voltage and V<sub>T</sub> = the threshold voltage.<sup>53,54</sup>

(eq. 1) 
$$I_{DS} = (WC_i/2L)\mu(V_g - V_T)^2$$

This equation assumes that the mobility of the material is constant. However, mobility in organic semiconductors has been found to be dependent on the gate voltage, which suggests that charge mobility is dependent on charge density at the dielectric-semiconductor interface.<sup>55</sup> Equation 2 can be further derived from equation 1, and calculates mobility based on the transconductance ( $g_m$ ), defined as the derivative of  $I_d$  with respect to  $V_g$ . The use of this equation eliminates the mobility dependence on the ill-defined threshold voltage,<sup>56-59</sup> and is also valid for materials with gate-dependent mobilities. The  $I_{on}/I_{off}$  ratio is typically defined in OFETs as the maximum source-drain current modulation with gate bias.

(eq. 2) 
$$\mu = g_m^2 / 2I_D C_i (W/L)$$

In an ideal system, there is no barrier to charge injection from metal electrodes into the organic semiconductor, but this requires a perfect match of the Fermi level of the electrode with the HOMO (p-type) or LUMO (n-type) of the semiconductor. The majority of organic semiconductors are p-type materials (hole conductors), and have a HOMO level between 4.9 and 5.5 eV, and ohmic contacts can be obtained with high work-function metals such as gold (5.1 eV) and platinum (5.6 eV).<sup>60</sup> Contact resistance is typically smaller than the bulk resistance of the semiconductor, but in some cases contact resistance and barrier height can be significant, reducing on-currents appreciably.<sup>61</sup> N-type materials (electron conductors) typically have better contact with low work function metals like aluminum, but surprisingly gold electrodes have proven useful as well.<sup>62</sup>

**5.2 Organic Photovoltaics.** Organic solar cells are widely studied as an environmentally benign or "green" energy source. Because organic semiconductors can be deposited from solution on flexible plastic substrates, OPVs are hoped to offer a low-cost and lightweight alternative to silicon solar cells.<sup>63,64</sup> However, power conversion efficiencies still need improvement from roughly 5% to %10 for OPVs to become economically viable.

Photocurrent in an organic solar is generated at the interface of an electron donor, or p-type semiconductor, and an electron acceptor, or n-type semiconductor. Absorption of light in a donor or acceptor layer creates Coulombically bound electron-hole pairs, or excitons, and diffusion of excitons to the donor-acceptor interface must occur in order for them to be split into free electrons and holes that are extracted through the organics to the cathode and anode, respectively. The cathode material is a low work function metal like aluminum or silver, and the anode is usually transparent indium tin oxide (ITO), poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS), or ITO coated with PEDOT-PSS. Cathode and anode materials are chosen to make good electrical contacts with the HOMO of the acceptor and the LUMO of the donor, respectively. A diagram of a planar heterojunction or bilayer OPV is shown in Figure 6.

Acceptor Donor	
Donor	2
	り
Anode	

OPV

Figure 6. Diagram of the diode structure of an OPV.

For exciton splitting to occur, there must be an offset in the energy levels of the donor and the acceptor that is greater than the exciton binding energy, so the energy difference between the LUMOs of the donor and the acceptor is at least 0.3 eV.<sup>65,66</sup> The charge separation process is shown in Figure 7. Typical donors are polythiophenes and phthalocyanines and commonly used acceptors are C<sub>60</sub> and its soluble derivative [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM). Small molecule OPVs are usually prepared via vapor deposition in a bilayer device geometry (see Figure 6), while the best results in polymer OPVs have been obtained for donor-acceptor blends deposited in a single layer from solution. Single layer blends, or bulk heterojunctions, benefit from a greater interfacial area, because exciton formation must take place in the vicinity of the heterojunction in order for electron transfer to occur. Indeed, much research has been directed towards optimizing heterojunction morphology.<sup>67</sup>



**Figure 7.** Excitons in OPVs are split into free electrons and holes at the donor acceptor interface. (1) The process shown is for excited states formed in the donor layer. (2) The exciton must diffuse to the heterojunction in order for an electron transfer to occur from the LUMO of the donor to the LUMO of the acceptor. (3) Free electrons and holes are formed in the acceptor and donor layers, respectively.

The magnitude of the photocurrent generated in OPVs is determined by the efficiency of exciton generation through light absorption, exciton harvesting at the heterojunction, and photogenerated charge extraction. However, the power conversion efficiency (PCE) of a cell is determined by the current density (J) supplied at a specific voltage (V). To examine the relationship between these quantities, JV curves are obtained by sweeping the diode voltage of a cell under calibrated illumination ( $P_{in}$ ) and the maximum power point ( $J_mV_m$ ) allows calculation of PCE (equation 3).

(eq. 3) 
$$PCE = \frac{P_{out}}{P_{in}} = \frac{J_m V_m}{P_{in}}$$
  
(eq. 4) 
$$PCE = FF\left(\frac{J_{sc} V_{oc}}{P_{in}}\right)$$
  
(eq. 5) 
$$FF = \frac{J_m V_m}{J_{sc} V_{oc}}$$

Important diagnostic values are introduced in equations 4 and 5. The short circuit current density ( $J_{SC}$ ) is simply the current flowing through the device at zero applied voltage, and the open circuit voltage ( $V_{OC}$ ) is the voltage required to yield zero net current in the device. The maximum theoretical power produced by the cell is the product of  $J_{SC}$  and  $V_{OC}$ , and the ratio of the experimental maximum power of the cell to  $J_{SC}V_{OC}$  is given by the fill factor (FF), as shown in equation 5. The magnitude of  $J_{SC}$  is useful for estimating the efficiency of photocurrent generation and extraction. The  $V_{OC}$  is related to the energy difference of the acceptor LUMO and the donor HOMO and the morphology of the heterojunction(ref).<sup>68,69</sup> Finally, the FF is primarily related to the series resistance of the cell.<sup>70</sup>

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## Chapter 2

# Development of Solution Processed Air-Stable Organic Field-Effect Transistors with α,ω-Distyryl Oligothiophene Semiconductors

### Abstract

We describe the rational design of oligothiophene semiconductors to facilitate solution-based fabrication of environmentally stable organic field-effect transistors (OFETs). Films of  $\alpha, \omega$ distyryl quaterthiophene (DS4T), pentathiophene (DS5T), and sexithiophene (DS6T) were prepared via solution processing to probe the effect of styryl end-groups, oligomer length, and thin film structure on air-stability. Films were prepared via solution deposition and thermal annealing of precursors featuring thermally labile ester solubilizing groups. Soluble quaterthiophene thermolysis products are analyzed by MALDI-TOF mass spectrometry, UV-Vis and NMR spectroscopy. A detailed study of the thin film structure was performed using atomic force microscopy (AFM), near-edge x-ray absorption fine structure (NEXAFS) spectroscopy, and grazing incidence x-ray diffraction (GIXD). Functional OFETs were obtained for DS5T and DS6T and have, respectively, hole mobilities of 0.051 and 0.043  $\text{cm}^2/\text{Vs}$  and on/off ratios of 10<sup>5</sup> - 10<sup>6</sup>, while DS4T OFETs failed to function due to poor film continuity. The effect of both shortterm and long-term exposure to air is tracked in OFETs revealing remarkable stability for both DS5T and DS6T. This stability is attributed to the elimination of reactive sites in  $\alpha,\omega$ -distyryl oligothiophenes and suggests that careful choice of end-group structure can stabilize these molecules against oxidative degradation.

#### **1. Introduction**

Conjugated small molecules and polymers that show promise as organic semiconductors are typically limited by their sensitivity to ambient conditions. In particular, positive hole-transporting materials are believed to be susceptible to oxidation by molecular oxygen that decreases the charge mobility ( $\mu$ ) of the materials and degrades on/off ratios by increasing the off-currents in organic field-effect transistors (OFETs).<sup>1-3</sup> As a result, much work has focused on improving the stability of these materials, typically by increasing the oxidation potential of the molecules to preserve high on/off ratios.<sup>4-6</sup> While this strategy has proven to be successful, theoretically it can adversely affect charge injection by pushing the HOMO energy of the molecules away from the Fermi level of commonly used gold electrodes.<sup>6-8</sup> Alternatively, the molecular structure of these conjugated materials can be rationally designed to minimize sensitivity to common degradation pathways under ambient conditions. However, further elucidation and validation of these degradation pathways is necessary for this method to be effective.

One such approach is suggested by the exceptional stability of  $\alpha, \omega$ -distyryl quarterthiophene (**DS4T**) to ambient conditions.<sup>9</sup> This material formed the active layer in OFETs that provided stable operation under ambient conditions for a period of 17 months, which greatly exceeds the stability of unfunctionalized oligothiophenes. The stabilizing effect of terminal styryl groups appears unrelated to the oxidation potential of the material because styryl end-groups actually increase the HOMO level of the molecules relative to the parent oligothiophenes. Therefore, the origin of the stability of **DS4T** to ambient conditions and oxygen in particular is unclear. Specifically, the aforementioned results suggest that the styryl end-groups may somehow have a stabilizing effect on the delocalized  $\pi$ -system so that the stability of **DS4T** is a unique property of that structure as a whole. Nevertheless, a better understanding of this stability is relevant for the structural design of oligothiophenes, which are synthetically versatile and therefore widely utilized organic semiconductors.<sup>10-19</sup>

In order to gain further insight into the stabilizing effect of styryl end-groups on oligothiophenes, we prepared thermal precursors to  $\alpha,\omega$ -distyryl quarterthiophene (**DS4T**), pentathiophene (**DS5T**), and sexithiophene (**DS6T**). These thermal precursors feature bulky esters that inhibit crystallization of the oligomers and render them readily soluble. Upon thermal annealing, elimination of the esters initiates a reorganization of an initially amorphous film into a polycrystalline film<sup>20,21</sup> of  $\alpha,\omega$ -distyryl oligothiophenes. This structural transformation is shown in Figure 1.



Figure 1. Thermolysis of ester solubilizing groups generates a,  $\omega$ -distyryl oligothiophenes.

We chose to prepare films of these  $\alpha, \omega$ -distyryl oligothiophenes through thermal removal of ester solubilizing groups as the high solubility of the precursor oligothiophenes allows facile material purification. Numerous strategies exist for solubilizing conjugated small molecules,<sup>22,23</sup> but importantly, this method allows simple deposition of ultra-thin films via spin-coating and thermal annealing. As a result, the first few monolayers of conjugated oligomers responsible for charge transport in OFETs are directly exposed to ambient conditions with little of the self-encapsulation that could play a role in the stability of thicker films.

In this chapter, we present the synthesis and thermal characterization of precursors to  $\alpha,\omega$ distyryl oligothiophenes (**preDS4T**, **preDS5T**, and **preDS6T**). Analysis of thermally prepared **DS4T** by matrix-assisted laser desorption ionization -time of flight mass spectrometry (MALDI-TOF) reveals the clean thermal conversion of **preDS4T** to the desired styryl terminated product, which corresponds to a red-shift in the visible light absorption spectrum of the material. Structural and morphological characterization by atomic force microscopy (AFM), grazing incidence x-ray diffraction (GIXD), and near edge x-ray absorption fine structure (NEXAFS) spectroscopy of solution-processed films of the series of oligomers is presented. The materials are used as the active layer in field effect transistor devices demonstrating the enhanced stability to ambient conditions attributable to the terminal styryl groups appended to the oligothiophene core.

#### 2. Results

Scheme 1.



**2.1 Synthesis.** The symmetry of the target molecules allowed formation of each oligothiophene from a single coupling partner. Preparation of coupling partner **4** shown in Scheme 1 began with

a Friedel-Crafts acylation of 2,2'-bithiophene with phenylacetyl chloride to yield ketone 1. The ketone 1 is then converted to the corresponding alcohol 2 by reduction with lithium aluminum hydride. The alcohol 2 is then esterified to compound 3 using trimethylacetyl chloride with dimethylaminopyridine as the catalyst. The final step in the synthesis of the coupling partner is bromination with N-bromosuccinimide to generate 4.

Each precursor oligomer was prepared by varying the linking strategy as shown in Scheme 1. Treatment of **4** with bis(pinacolato)diboron along with catalytic Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and excess potassium acetate led to formation of **preDS4T**. Treatment of **4** with 2,5-bis(trimethylstannyl)thiophene and catalytic Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> provided a precursor oligomer to  $\alpha,\omega$ -distyryl pentathiophene (**preDS5T**), and an analogous cross-coupling utilizing 5,5'-bis(tributylstannyl)-[2,2']bithiophene provided a precursor oligomer to  $\alpha,\omega$ -distyryl sexithiophene (**preDS6T**).

**2.2 Thermogravimetric Analysis.** In order to generate  $\alpha, \omega$ -distyryl oligothiophenes from the precursor oligomers, loss of the ester solubilizing groups (Fig. 1) must occur during thermal annealing. Thermogravimetric analysis (TGA) shows the weight loss corresponding to cleavage of the solubilizing groups for the series of precursor oligomers (**preDS4T**, **preDS5T** and **preDS6T**). The TGA data shown in Figure 2 for **preDS4T** and **preDS5T** demonstrates that thermal removal of the solubilizing groups is complete at 200 °C, while a higher temperature (225 °C) is required to effect removal of the ester solubilizing groups of **preDS6T**. Since the TGA data show a clear step pattern with a flat region from about 200-225 °C to 350-400 °C, thermal annealing of films within this temperature range results in removal of ester solubilizing groups without further degradation of the material.



**Figure 2.** Thermogravimetric analysis conducted at 5 C°/min. Thermolysis of esters results in an expected weight loss of 28 % for **preDS4T**, 25 % for **preDS5T**, and 23 % for **preDS4T**.



Figure 3. Absorption spectra of preDS4T, preDS5T, and preDS5T obtained in chloroform.

**2.3 UV-vis and MALDI-TOF Characterization.** UV-vis absorption spectra of the precursor oligomers (**preDS4T**, **preDS5T**, and **preDS6T**) exhibit characteristic absorption patterns of the oligothiophene cores, as shown in Figure 3. Peak absorbance values within the series of oligothiophenes increase with conjugation length: 400 nm for **preDS4T**, 424 nm for **preDS5T**, and 436 nm for **preDS6T**. Conversion of **preDS4T** to **DS4T** results in a red-shift of 40nm, as

shown in Figure 4, and the wavelength of maximum absorption corresponds to that of **DS4T** prepared via an alternate route.<sup>9</sup>





**Figure 4.** Thermal conversion of **preDS4T** to **DS4T** results in a red-shift of 40 nm and a loss of solubility. Additional peaks in the absorption spectrum of **DS4T** are likely associated with the phenyl end-groups.

Figure 5. MALDI-TOF of DS4T prepared by heating preDS4T to 200 °C for 20 minutes (MW calculated for DS4T = 534.8 g/mol).

Analysis of the thermally prepared **DS4T** by MALDI-TOF mass spectrometry reveals a single signal that corresponds to the mass of **DS4T**, as shown in Figure 5. Higher mass signals that would result from polymerization of the styryl groups were not observed.

**2.4 Analysis of Alkene Stereochemistry.** Use of thermally removable solubilizing groups to prepare films of distyryl oligothiophenes requires that thermolysis be stereoselective for a *trans* double bond. In past studies, thermolysis was not relied upon to extend the conjugation of the system, so stereochemistry of a resulting alkene was not critical.<sup>20,21</sup> Stereochemistry of alkenes is easily investigated by <sup>1</sup>H NMR, however it was impossible to obtain <sup>1</sup>H NMR spectra of  $\alpha, \omega$ -distyryl oligothiophenes because of their limited solubility. Therefore, an asymmetric quarterthiophene was prepared which upon thermolysis yields a product more soluble than **DS4T** by virtue of the alkyl chain that remains after heating to impart solubility, as shown in Figure 6. The oligomer shown can be heated to generate a terminal styryl group in conditions analogous to that used for distyryl oligothiophenes so that selectivity, analyzed by NMR spectroscopy, for a *trans* double bond can be assumed to extend to DSnTs.



Figure 6. Heating an asymmetric quarterthiophene approximates the thermolysis conditions used for generating distyryl oligothiophenes.

To prepare oligomer 5, coupling partner 4 was treated with (5'-decyl-[2,2']bithiophen-5-yl)-trimethylstannane and catalytic Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> to yield the cross-coupled product. In order to obtain an NMR sample of the thermolyzed product, a sample of 5 was heated to 200 °C under

nitrogen in a TGA instrument and held at that temperature for 40 minutes. The resulting sample was only sparingly soluble in deuterated chloroform, but heating the sample resulted in disappearance of the precipitate. Therefore, a <sup>1</sup>H NMR spectrum of the sample was obtained at 50 °C in CDCl<sub>3</sub>, as shown in Figure 7.



Figure 7. <sup>1</sup>H NMR spectrum obtained on a 500 MHz instrument at 50 °C in CDCl<sub>3</sub>.

The NMR spectrum shows a pair of alkene signals in the aromatic region that exhibit *trans* splitting exclusively as evidenced by a large coupling constant,  $J_{ab} = 16.0$  Hz. Furthermore, a MALDI-TOF mass spectrum, shown in Figure 8, of the thermolyzed asymmetric quarterthiophene shows a single signal corresponding to the molecular weight of the desired product.



**Figure 8.** MALDI-TOF mass spectrometry analysis of the thermolyzed product shows a single signal (574 amu) that closely corresponds to the calculated value (573 amu) for the molecular weight of 5'''-decyl-5styrylquarterthiophene.



**Figure 9.** Thermolysis to yield 5<sup>\*\*\*</sup>-decyl-5styrylquarterthiophene leads to a bathochromic shift of 30 nm. Spectra obtained in chloroform.

The UV-vis spectrum of the thermolyzed product shows the bathochromic shift resulting from addition of one styryl group (Fig. 9) to a quarterthiophene chromophore is less than from addition of two styryl groups (Fig. 4). This data suggests that our original design involving the thermal conversion of the precursor oligomers to  $\alpha, \omega$ -distyryl oligothiophenes is indeed valid. However, the practical application of this approach to prepare semiconducting films depends critically on the morphology of the resulting films.

**2.5 Film Morphology and Structural Characterization.** Using a previously developed procedure,<sup>24</sup> films of each precursor-oligomer were spun-cast from 2-3 mg/mL solutions in chloroform onto freshly oxidized silicon wafers with 100 nm of thermally grown oxide. The substrates were thermally annealed under nitrogen at 200-225 °C for 20 minutes to convert the precursor oligomers into  $\alpha, \omega$ -distyryl oligothiophenes. The morphology of the ultra-thin films was examined using AFM and a detailed structural characterization of the molecular packing and alignment was conducted using NEXAFS spectroscopy and GIXD.

AFM reveals that films of **DS4T** exhibit poor surface coverage after thermal conversion as shown in Figure 10a. The majority of the surface shown appears bare and only isolated islands are seen with most of the material clumped into large islands, such as the one shown in the upper left of the image. This finding is supported further by the following NEXAFS data (vide infra), and is consistent with previous studies involving oligothiophenes with thermally labile solubilizing groups in which quarterthiophene films failed to maintain surface coverage after thermal annealing.<sup>21</sup> In that work, increasing the length of oligothiophene cores of thermal precursors from 4T to 7T allowed films to be treated at progressively higher temperatures to yield continuous films. The temperature required for ester thermolysis imparts enough energy for **DS4T** to overcome the substrate surface energy and form islands. In contrast, thermal conversion of the precursor oligomers of **DS5T** and **DS6T** generates thin films with excellent surface coverage and a terraced multilayer morphology, which is characteristic of highly ordered films, as seen in Figure 10b and c. A trend of increasing step-heights consistent with the lengths of the molecules is observed, which suggests that the films are composed of stacked monolayers of

nearly vertically-aligned oligomers. Note that in both cases the resulting films are only a few nanometers thick.



Figure 10. AFM images of thermally treated films of DS4T (a), DS5T (b), and DS6T (c). Island formation is suppressed and layer growth encouraged by lengthening the oligothiophene backbone, as seen in (a), (b), and (c).

A systematic shift in the morphology of the three films is observed from a predominantly island growth mode to a more layer-island growth mode.<sup>25,26</sup> While **DS4T** shows a strong tendency for island growth only, **DS5T** appears to form a couple of continuous layers before additional layers grow as islands. In contrast, films of **DS6T** show an even stronger tendency for a layer by layer growth. However, both the **DS5T** and **DS6T** form continuous films as seen in the following X-ray diffraction and NEXAFS data. Since film continuity is essential for the fabrication of the OFETs, only the **DS5T** and **DS6T** films are of interest for structural and electrical characterization.

**2.6 NEXAFS Spectroscopy**. We have previously shown that NEXAFS spectroscopy can be an effective tool to study the conversion, orientation, and surface coverage of solution-processed organic semiconductors formed by a thermolysis strategy.<sup>27,28</sup> A series of films of each oligomer (**DS4T**, **DS5T**, and **DS6T**) were prepared for NEXAFS analysis by spin casting and thermal treatment up to 250 °C followed by quenching to room temperature. NEXAFS spectroscopy is based on the resonant excitation of core electrons – which for low-z elements are in the K shell – to unfilled molecular orbitals, which are typically of antibonding character. The technique is therefore element-specific by selection of the soft X-ray energy range to match a particular core shell, and bond-specific by the energy of the final state accessed.<sup>29</sup> Both carbon K-edge and oxygen K-edge NEXAFS spectra reveal details of the transformation from **preDSnT** to **DSnT**.

The carbon edge spectra reveal the chemical transformation of the material as well as the molecular orientation, while the oxygen edge spectra reveal chemistry associated with carbonyl removal as well as coverage via the exposure of the underlying silicon oxide substrate.

The carbon K-edge NEXAFS spectra shown in Figure 11 follow the chemical conversion of the preDS5T to DS5T. Conversion is most readily observed by changes in the position of the carbon-carbon  $1s \rightarrow \pi^*$  resonance near 285 eV and the carbonyl  $1s \rightarrow \pi^*$  resonance near 288.5 eV; the intensity of the carbon-hydrogen  $1s \rightarrow \sigma^*$  resonance at  $\approx 287.4$  eV changes with the amount of carbon-hydrogen bonds relative to the overall carbon content. The preDS5T film as-cast and after heat treatment to 100 °C exhibits a narrow C=C  $\pi^*$  peak located at 285.3 eV. After the film is exposed to temperatures of 150°C and above, the peak location shifts to 285.0 eV and the peak broadens substantially. This change in C=C  $\pi^*$  character can be related to the conversion of preDS5T to DS5T. The styryl group resulting from the thermolysis process adds an alkenyl carbon-carbon double bond to the core 5T molecule extending its conjugation. The newly formed alkene bond is not part of a ring, and is expected to have a somewhat greater length than the other  $\pi$  bonds. Since longer  $\pi^*$  bonds typically exhibit lower-energy NEXAFS resonances, the shift in the C=C  $\pi^*$  peak location after exposure to temperatures >150°C can be attributed to the convolution of the lower-energy alkene resonance with the aromatic resonances of the core 5T. It is of course possible that changes in the other bonds due to resonance could also shift the peak character. Due to energy resolution limitations, and the expected peak broadening which occurs in solid state samples, we cannot discriminate the individual resonances. The C=C  $\pi^*$  peak shape and location are nominally identical for exposure to 150°C and above. These data therefore show that **preDS5T** is converted to **DS5T** between 100°C and 150°C. By a similar analysis, **preDS4T** was found to convert between 100°C and 150°, while preDS6T was found to convert between 150°C and 200°C.

While the C=C  $\pi^*$  trend indicates that conversion is completed by 150°C, the carbonyl  $\pi^*$  trend reveals that the pivalic acid is not removed until the film is exposed to much higher temperatures. In the **preDS5T** film as-cast and after heat treatment to 100°C, the carbonyl  $\pi^*$  peak is located at  $\approx 288.7$  eV. After the film is exposed to temperatures of 150°C and 200°C, the carbonyl peak location shifts to 288.3 eV. Because the C=C  $\pi^*$  trend indicates that the conversion is completed by 150°C, it is reasonable to attribute this shift in carbonyl character to the conversion of the ester to pivalate. The molar density of pivalate carbonyl present at 150°C appears to be of the same order as the precursor carbonyl density. The intensity of the pivalate  $\pi^*$  peak is significantly decreased by 200°C, but it is only removed after heating to 250°C. We note that these NEXAFS spectra were collected in partial electron yield (PEY) mode at a grid bias of -50 V, so that the spectra reflect the chemistry within  $\approx 4$  nm of the top surface of the film. We therefore cannot determine whether the residual pivalic acid is evenly distributed throughout the film or only present at the top interface. However, it is clear that significant residual pivalic acid is present in films exposed to temperatures below 250°C.



Figure 11. NEXAFS carbon K-edge spectra following the conversion of the preDS5T to DS5T.

NEXAFS spectroscopy can also be employed to follow changes in molecular orientation throughout the conversion process. The substrate-relative orientation of molecular resonances can be determined by changing the orientation of the electric field vector with respect to the substrate, which is typically accomplished by changing the angle of beam incidence. Spectra of **preDS5T** and **DS5T** are shown in Figure 12a and b. The variation of C=C  $\pi^*$  intensity with incident angle reveals strong molecular orientations relative to the substrate both before and after conversion. In **preDS5T**, the intensity of the C=C  $\pi^*$  resonance is greatest at 20° incidence, where the electric field vector is tilted 20° away from surface normal, indicating that the molecular  $\pi^*$  vector is preferentially tilted away from the substrate plane. In contrast, **DS5T** has the greatest C=C  $\pi^*$  intensity where the electric field vector is tilted >80° away from surface normal, indicating that the  $\pi^*$  vector is preferentially tilted parallel to the substrate plane.

The orientation of the  $\pi^*$  vector with respect to the molecule can be understood from the illustration shown in Figure 12d. A  $\pi^*$  resonance has a transition dipole that is perpendicular to a double bond; in ring systems, the sum of the  $\pi^*$  resonances is a vector perpendicular to the ring plane. In **DS5T**, and all  $\alpha, \omega$ -distyryl oligothiophenes for which the rings are expected to be coplanar, the molecule is expected to exhibit a single  $\pi^*$  orientation normal to the coplanar rings. Because the **preDS5T**  $\pi^*$  vector is preferentially aligned away from the substrate plane, the substrate plane and the molecular conjugated plane are more parallel in a "plane on" arrangement. In contrast, the **DS5T**  $\pi^*$  vector is preferentially aligned parallel to the substrate plane, so the substrate plane and molecular conjugated plane are more perpendicular in a preferentially "edge on" arrangement. We previously observed a qualitatively similar precursor / product orientation shift in thin films of thermally convertible thiophene semiconductors with pendant alkylene substitution rather than styrene substitution.<sup>27,28</sup>

Although the  $\pi^*$  vector orientation describes the orientation of the molecular conjugated plane, it does not describe the orientation of the molecular long axis. The AFM images shown previously suggest a roughly vertical long axis orientation for the converted **DS5T**, based on the similarity of layer thickness to long axis length, as does the X-ray diffraction (vide infra). This vertical long axis orientation is consistent with the edge-on **DS5T** conjugated plane. A vertical long axis orientation is further supported by the NEXAFS carbon-hydrogen  $\sigma^*$  resonance orientation of **DS5T**, which is roughly parallel to the surface plane, because  $\sigma^*$  transitions are parallel to the bond, and the net carbon-hydrogen bond orientation of **DS5T** is more perpendicular to the long axis than it is parallel. The vertical long axis orientation is also supported by the slight vertical preference of the carbon-carbon  $\sigma^*$  resonance at  $\approx 298 \text{ eV}$ , because the carbon-carbon bonds are more parallel to the long axis than perpendicular to it. While these two resonance trends support the vertical long axis assignment, we note that neither provides sufficient information to quantify the long axis orientation.

The  $\pi^*$  vector orientation can be quantified using a dichroic ratio, R, which we have previously defined.<sup>27,28</sup> The quantity R varies from -1.0 for a perfect plane-on orientation such as that exhibited by highly oriented pyrolytic graphite, to 0.7 for a perfectly edge-on orientation. An R value of 0, which occurs when the resonance intensity does not vary with incident angle, indicates either an isotropic system or one in which the resonance is tilted 54.7° (the "magic angle") away from surface normal. The R-values are determined by a simultaneous fit of  $\pi^*$ intensity to the squared sine of incident angle, as shown in Figure 12c. The quantified plane-on and edge-on preferences of **preDS5T** (R = -0.38) and **DS5T** (R = 0.36), respectively, are significant (e.g. far from R=0), but not absolute (e.g. not -1.0 and not 0.7, respectively). If the samples were well-described by a single  $\pi^*$  vector orientation, the  $\pi^*$  vector of **preDS5T** would tilt  $\approx 41^{\circ}$  from surface normal while that of **DS5T** would tilt  $\approx 67^{\circ}$ . However, this assumption is likely to be incorrect as we believe that the  $\pi^*$  orientation distribution is broadened by molecular disorder and may also be bimodal if the molecules are in a herringbone-packed, 2-molecule unit cell (as suggested by the GIXD) with inequivalent surface-relative molecular tilts. The average  $\pi^*$  vector tilt provides important constrains on possible long axis orientations. The average **preDS5T** long axis tilt from substrate normal cannot be less than  $90^{\circ}-41^{\circ}=49^{\circ}$ , whereas the average **DS5T** long axis tilt cannot be less than  $90^{\circ}-67^{\circ}=23^{\circ}$ .



Figure 12. Orientation analysis of preDS5T and DS5T, including spectra of a) preDS5T and b) DS5T (250°C) each collected at 5 incident angles, c) fits of the C=C  $\pi^*$  intensity to incident angle, and d) an illustration of the primary  $\pi^*$  and  $\sigma^*$  resonance orientations for DS5T.

Changes in molecular orientation throughout the conversion from **preDSnT** to **DSnT** may be followed by the  $\pi^*$  vector **R** of samples exposed to heat treatment, as shown in Figure 13. All three precursors exhibit plane-on orientation until full chemical conversion is achieved, which occurs above 100°C for **preDS4T** and **preDS5T**, and above 150°C for **preDS6T**. After conversion, all molecules exhibit an edge-on orientation preference. Notably, the presence of excess pivalate does not appear to disturb or alter the molecular orientation. The greatest edge-on preference is exhibited by **DS6T** at 200°C. At temperatures exceeding that required for conversion, the edge-on orientation appears to decrease. This effect is most significant for **DS4T**, which loses most of its orientation preference above 150°C, with a trend towards the disorder condition (R=0). We believe that this loss of orientation is related to a reduction in surface coverage (i.e. formation of more islands), leading to poor intermolecular packing and substantial disorder. More modest losses of edge-on orientation are observed for both **DS5T** and **DS6T** at 250°C. The loss in surface coverage at higher temperatures is supported by oxygen K-edge NEXAFS data showing an increase in the contribution of the underlying silicon oxide substrate as temperature increases. Because the partial electron yield signal is surface-sensitive, the increasing substrate contribution can only be attributed to thinning or discontinuity in the organic layer. The series of NEXAFS spectra shown in Figure 14a illustrate the loss of surface coverage for **DS4T**. Above 100°C, the spectrum shape and intensity rapidly approaches that of silicon oxide. This loss in coverage is consistent with our AFM observations showing that the films rapidly lose surface coverage at temperatures greater than 100 °C. The organic fraction can be quantified by the fraction of the spectrum which does not resemble silicon oxide, as shown in Figure 14b. The **DS5T** and **DS6T** films exhibit greater persistence of film surface coverage at higher temperatures.



Figure 13. Changes in molecular orientation over the conversion of pre-DSnT to DSnT.



Figure 14. a) NEXAFS data for a thermally prepared DS4T film. Above 100 °C, the spectrum rapidly approaches that of bare silicon oxide. B) organic fraction coverage trend for the three precursors.

**2.7 GIXD Analysis.** While NEXAFS spectroscopy is an excellent technique for monitoring the chemical and morphological changes that take place during thermal treatment of films, it does not provide information on the film crystallinity or on the detailed crystal structure. This can be obtained from X-ray diffraction, but to date an explicit diffraction study of the crystallinity of these films has not been performed. An analysis of the packing mode of the oligothiophenes and the degree of crystallinity in these films is valuable as it would provide a comparison of the crystal structure of thermally converted oligothiophene films to films grown via vapor-deposition. Therefore, we used both synchrotron based X-ray diffraction and NEXAFS spectroscopy to elucidate the structure and molecular packing of these ultra-thin films.



Figure 15. Grazing incidence X-ray diffraction (GIXD) areal plots of (A) **DS5T** and (B) **DS6T** respectively, showing the different peaks in  $Q_{xy}$  and  $Q_z$  directions. The  $Q_{xy}$  and  $Q_z$  values are accurate to approximately 0.005 and 0.01 Å<sup>-1</sup>, respectively.

The in-plane and out-of-plane crystalline order in the films was probed with GIXD (small incidence angles) and specular diffraction, respectively. For the GIXD experiments the substrates are Si wafer pieces with a 10 nm thick SiO<sub>2</sub> film. Figures 15a and 15b show the grazing incidence X-ray diffraction data obtained on a 2D image plate, which records intensity (I) as a function of  $q_{xy}$ ,  $q_z$ , which are the in-plane and out-of-plane components of the scattering vector, respectively. Individual peak positions, shown in Table 1, are obtained after an appropriate background correction and Gaussian fits to the data.<sup>30</sup> As the AFM data show, these films consist of a continuous monolayer in contact with the substrate and discontinuous layers atop this monolayer. This heterogeneous morphology makes it nearly impossible to quantitatively analyze the film structure. The diffraction from a monolayer consists of Bragg rods - diffraction that is sharp along of  $q_{xy}$  but extended along  $q_z$  - while that from a 3D crystal has Bragg spots – sharp along both  $q_{xy}$  and  $q_z$ . For a multilayer, the diffraction is intermediate between these as there is interference between the diffraction from each layer leading to a modulation in the intensity of the Bragg rods. The diffraction from these films consists of all above and hence we cannot unambiguously index the  $q_z$  components of the spots/rods, although we accurately determine the in-plane lattice. Hence, in the discussion that follows we label the peaks as (hkL), where hk are determined, but L is not identified.

Table 1. Peak positions in the GIXD data

	DS5T	
Peak	$Q_{xy}(A^{-1})$	$Q_z(Å^{-1})$
(11L)	1.362	0.18
(11L)	-	0.40
(02L)	1.579	0
(02L)	-	0.39
(12L)	1.931	0.23
(12L)	-	0.40

DS6T
------

Peak	Q <sub>xy</sub>	Qz
(11L)	1.360	0.18
(02L)	1.580	0
(02L)	-	0.44
(12L)	1.928	0.44

The absence of (10L) and (01L) peaks/rods shows the molecules adopt a herring-bone edge-toface packing, which is commonly observed in oligothiophene molecules. The in-plane lattice parameters a, b and  $\gamma$  are calculated using the  $q_{xy}$  positions of the peaks. For the **DS5T** system, the peaks are indexed to a rectangular unit-cell with dimensions  $a = 5.659 \pm 0.005$  Å,  $b = 7.955 \pm$ 0.005 Å, and  $\gamma = 90^{\circ}$ . Given the similar molecular structure for the two systems it is not surprising that the **DS6T** systems also shows a rectangular unit-cell with dimensions almost identical to **DS5T** systems;  $a = 5.675 \pm 0.005$  Å,  $b = 7.957 \pm 0.005$  Å, and  $\gamma = 90^{\circ}$ . In principle, the  $q_{xy}$  and  $q_z$  data from GIXD can be used to determine the 3D lattice parameters of the thin film unit cell.<sup>30,31</sup> However, as mentioned above, the poorly defined morphology obviates such an analysis. The rationale for using such ultra-films for the GIXD analysis was to study the crystallinity in the films with the same morphology as that in the OFETs. These GIXD experiments show that there is good in-plane crystallinity in such films.

In addition to the GIXD data, specular X-ray diffraction measurements of these ultra-thin films can be used to estimate the interlayer spacing for both of the films. This data shows fairly weak peaks due to the ultra-thin nature of the films, which are only  $\sim 2-4$  layers thick, with not more than two continuous layers. Nonetheless, we were able to model the data in both cases, as shown in Figure 16.


Figure 16. Specular measurements on DST5 and DST6 films in (A) and (B) respectively, with similar morphology as the AFM images in Fig. 5. The dashed lines show the model fit to the raw data.

A reasonable fit to the **DS5T** film data is obtained by modeling the film as consisting of up to 4 layers with decreasing coverage for successive layers. Specifically, 1st layer: 100% coverage and thickness of 4 nm; 2nd layer: 83% coverage and thickness of 3.65 nm; 3rd layer: 33% coverage and thickness of 3.6 nm; 4th layer: 6% coverage and thickness of 3.6 nm. Using these parameters, the average interlayer spacing is calculated to be d = 3.8 nm. Note that the layer closest to the SiO<sub>2</sub> is thicker than the other three layers. Similarly, a model fit to the **DST6** film data is obtained by modeling only 2 layers with decreasing coverage for successive layers. (i.e. 1st layer: 100% coverage and thickness of 4.25 nm; 2nd layer: 60% coverage and thickness of 3.95 nm.) Using this model, the average interlayer spacing is then calculated to be d = 4.14 nm, while the decrease in thickness for the second layer is also noted. The choice of the number of layers as well coverage of each layer is validated by looking at the AFM images of the films. Using DFT calculations, the molecular lengths for the DS5T and DS6T are estimated to be 32.7 Å and 37.0 Å, respectively. (This is the H-H distance measured from the 4-position hydrogen nuclei on the terminal phenyl groups.) At this time, we are unable to explain the variation in layer thickness definitively. We hypothesize that the larger thickness of the first layer located next to the SiO<sub>2</sub> surface results from the presence of some adventitiously adsorbed hydrocarbons or water (a few Angstroms) on the SiO<sub>2</sub>. Furthermore, the decrease in the interlayer spacing with increasing thickness may be due to some material that remains within the successive layers after the thermolysis process. Given that the NEXAFS data shows trace amounts of pivalic acid byproduct present in the films after thermolysis, it is possible that this impurity affects the layer thickness. It is also likely that substrate effects dominate the crystallization of the bottom layers so that the ultra-thin films do not grow in a layer-by-layer fashion.<sup>31</sup>

This diffraction data, the first obtained for an ultra-thin thermolysis based oligothiophene film, demonstrates that the same intermolecular packing observed in vapor deposited films is preserved in these solution deposited films. The presence of good in-plane crystallinity, critical for charge transport in OFET device geometry, shows that the thermolysis process, which has been introduced to allow solution deposition, does not compromise the eventual quality of the organic semiconductor thin-films. More importantly, the intermolecular packing of **DS5T** and

**DS6T** in the present study is consistent so that any differences in air-stability observed for the materials result from structural variations at the molecular level.

**2.8 OFET Performance.** OFET devices were fabricated on low resistivity n-type silicon wafers, using 1000 Å of thermally grown SiO<sub>2</sub> as the dielectric, in top contact geometry. The active semiconducting layer was applied by spin-casting 2-3 mg/mL solutions of the oligomers in chloroform, and the films were then annealed at 200 °C for **DS5T** and 225 °C for **DS6T** in a nitrogen atmosphere. Gold contacts were patterned on top of the films using various shadow masks giving channel lengths from (5 to 40) µm and widths from (200 to 400) µm. All devices were tested as p-type OFETs in the accumulation regime and saturation mobilities were calculated using the equation,  $\mu = g_m^2 / 2I_DC_{ox}(W/L)$ , where  $g_m =$  transconductance,  $I_D =$  current measured at the drain electrode,  $C_{ox} =$  capacitance of the insulator, W = width of the electrodes, and L = channel length.

Functional OFETs were obtained for thermally converted films of **DS5T** and **DS6T**, but not for **DS4T** because of its poor film morphology as discussed above. Devices fabricated with **DS5T** and **DS6T** were initially tested under nitrogen to minimize the effects of oxygen. The average mobility values and on/off ratios for a set of six devices are summarized in Table 3. Representative output and transfer IV curves are shown in Figure 17 for **DS5T** and Figure 18 for **DS6T**.



Figure 17. Transfer (A) and output (B) IV plots for a top-contact DS5T device with  $W = 400 \mu m$  and  $L = 40 \mu m$ . The current levels measured at  $V_G = (2.5 \text{ and } -10) \text{ V}$  are too low to distinguish in the plot.



**Figure 18.** Transfer (A) and output (B) IV plots for a top-contact **DS6T** device with  $W = 400 \mu m$  and  $L = 40 \mu m$ . **Table 3.** Average saturation mobilities and on/off ratios for a set of six devices.

	$\mu$ (cm <sup>2</sup> /Vs)	on/off
DS5T	$0.051\pm0.007$	10 <sup>6</sup>
DS6T	$0.043\pm0.006$	$10^{5}$

**2.9 Short-Term Air Exposure.** In order to monitor the short-term effects of exposure to ambient conditions on the electrical properties of **DS5T** and **DS6T**, films were prepared on patterned silicon substrates to yield bottom contact OFETs with  $W = 500 \mu m$  and  $L = 20 \mu m$ . The substrates were placed inside a custom-built automated probe station capable of testing four devices simultaneously. The devices were then tested in the dark under ambient conditions once every hour for 3 d. In order to derive threshold voltage and mobility values from I<sub>D</sub>, the devices were biased at  $V_D = -20$  V with a short  $V_G$  sweep from (-17 to -20) V. The saturation current and mobility measured for each device is plotted as a function of time in Figure 19.

The data show different behavior for **DS5T** and **DS6T** initially, but both sets of devices exhibit a stabilization in  $I_D$  after the first day of testing. The calculated mobility values are an order of magnitude lower than those values obtained in top-contact devices, which is likely the result of poor contacts with the patterned electrodes and the relatively lower  $V_G$  and  $V_D$  values accessible in the automated probe station. For each device, the evolution of saturation mobility tracks the trend seen in  $I_D$ . The saturation current shows a significant increase upon exposure to air for both **DS5T** devices, while both **DS6T** devices exhibit a slight decrease in current. This effect is the result of  $V_T$  shifting to negative values for **DS6T** devices while remaining close to zero for **DS5T** devices, as shown in Figure 20. Neither set of devices show a trend of decreasing mobility over the trial period.



Figure 19. Short-term evolution of device performance for a set of four bottom-contact devices as a function of hours exposed to air. Trends in  $I_D$  (solid symbols) match trends in  $\mu$  (outlined symbols).



Figure 20. A plot of threshold voltage for four bottom-contact devices as a function of hours exposed to air.

**2.10 Long-Term Device Testing**. In order to track the effect of ambient conditions on the performance of **DS5T** and **DS6T**, top-contact device substrates were stored in air protected from light and the transistor performance was tested periodically. Long-term testing of the devices revealed that both **DS5T** and **DS6T** are highly resistant to degradation due to ambient conditions for at least 130 days. Saturation mobilities measured for **DS5T** and **DS6T** as a function of days stored in air are shown in Figure 21.



Figure 21. A plot of  $\mu$  as a function of days stored in air for a pair of top-contact devices. The variation in the observed  $\mu$  correlates with the variation observed in initial device testing (Table 3). No trend toward lower saturation currents is observed.

High on/off ratios were initially obtained as mentioned previously and maintained over the time period shown in Figure 21 through the application of positive gate bias. This characteristic of the devices is probably due to the oxidative doping of **DS5T** and **DS6T** as a result of exposure to atmospheric oxygen. Since initial testing of the devices revealed a positive turn-on voltage, it is likely that **DS5T** and **DS6T** rapidly dope even upon slight exposure to oxygen. This characteristic of the materials is not surprising given that the oligomers contain no electron-withdrawing substituents, which are known to render materials resistant to oxidative doping. However, both materials seem to rapidly reach a stable level of doping that does not result in oxidative degradation of the material, as evidenced by the high mobility values maintained over the entire period of the study (see Fig. 14). This is important, since the resulting devices therefore have predictable and well-controlled threshold voltage levels and on-off ratios. Furthermore, devices utilizing **DST5** and **DST6** still provide high saturation currents and low off currents even after storage in air for 130 days as shown in Figures 22A and B respectively.



Figure 22. (A) DS5T transistor after storage in air for 130 days, device dimensions L = 20, W = 400. (B) DS6T transistor after storage in air for 130 days, device dimensions L = 20, W = 200.

### **3. Discussion**

Structural analysis of **DS4T**, **DS5T** and **DS6T** films by AFM reveals a trend of island growth evolving into a more layer-by-layer growth mode as the oligothiophene backbone is lengthened. As a result, **DS4T** fails to form a continuous film and a direct comparison between ultra-thin films deposited using our methods and previously published vapor-deposited films is impossible.<sup>9</sup> Fortunately, **DS5T** and **DS6T** both formed continuous films that exhibit high levels of surface molecular orientation in NEXAFS and high levels of crystallinity in GIXD.

Previous studies on oligothiophenes with thermally labile solubilizing groups demonstrated the tendency of these materials to orient on silicon oxide surfaces and showed a monolayer provided ideal electrostatics in OFET channels.<sup>32</sup> Given the GIXD data presented here, this result can be rationalized to arise from the lack of layer-by-layer growth in the crystalline films. Each layer boundary may then exist as a probable site for impurities and charge traps. Due to the ultra-thin nature of the films, neither **DS5T** nor **DS6T** transition into a bulk 3D crystalline phase. In fact, only the very bottom layer of either oligomer is completely continuous and therefore conducts the majority of charge in OFET channels. Nevertheless, GIXD data shows that edge-to-face intermolecular packing, predominant in vapor-deposited organic semiconductor films,<sup>33-35</sup> is preserved in solution processed films of **DS5T** and **DS6T** after thermal annealing.

A direct consequence of the ultra-thin nature of these films is that no barrier exists between the active layer of **DS5T** or **DS6T** and atmospheric oxygen. Therefore, tracking the performance of **DS5T** and **DS6T** in OFETs exposed to air provides a sensitive probe of the stability of the materials towards oxidative degradation. In a 72 h trial of bottom-contact devices, neither **DS5T** nor **DS6T** showed signs of degradation in terms of hole mobility. Instead, **DS5T** exhibited an increase in hole mobility and the threshold voltage of **DS6T** devices shifted to negative values. Both sets of devices displayed stable operation after 24 h. The difference in the behavior of **DS5T** and **DS6T** in this experiment is not easily rationalized, as the two oligomers provide more consistent performance in top-contact devices. It may be that the transitional phase of the device performance that was observed by testing the bottom-contact devices once every hour went unnoticed in the long-term testing of top-contact OFETs. However, both **DS5T** and **DS6T** of **DS6T** of the seniconductor interface for these materials, although the reason why only **DS6T** in bottom-contact OFETs exhibits a threshold voltage shift is not clear.

In top-contact devices, **DS5T** and **DS6T** have, respectively, hole mobilities of 0.05 and 0.04 cm<sup>2</sup>/Vs and on/off ratios greater than 10<sup>5</sup>. These values remained virtually unchanged over the course of 130 days of storage in air. These stability tests were conducted in the dark to allow a comparison to published stability data for oligothiophenes.<sup>9,20</sup> The stability of these devices implies that the structures of the molecules are especially resistant to the irreversible oxidation reactions that lead to a loss of conductivity in OFET channels. For example, the mobility of octathiophene (8T) in OFETs exposed to air is known to decrease by 70% after 100 days.<sup>9</sup> Oligothiophenes are known to be reactive at the  $\alpha$ -carbon of the terminal thiophene rings, especially in the oxidized state.<sup>36</sup> This may render unsubstituted oligothiophene OFETs relatively unstable to operation in air. In a previous study with oligothiophene films prepared via thermolysis of ester solubilizing groups, a decrease of 20% was reported to occur in a shelf-life test of one week and long-term sustainability of high mobility was not observed.<sup>20</sup> Those

oligothiophenes were substituted with propylene end-groups and differ from  $\alpha,\omega$ -distyryl oligothiophenes studied here only in the replacement of a methyl for a phenyl group, as shown in Figure 23.



Figure 23. The effect of end-group structure on stability is likely tied to the presence of moieties susceptible to autooxidation.

The conspicuous structural difference between these molecules is the presence of allylic carbon-hydrogen bonds in the propylene end-groups and the absence of any correspondingly weak bonds in the styryl end-groups. Given the well-known susceptibility of electron-rich olefins to oxidation at the allylic position,<sup>37</sup> the oxidative modification of oligothiophenes with propylene end-groups likely proceeds via this pathway.

Since styryl end-groups have a stabilizing effect on quaterthiophene, pentathiophene, and sexithiophene, the originally reported stability of **DS4T** is likely not a special property of that conjugated molecule but instead appears to be an end-group effect. This effect appears to arise from the ability of styryl end-groups to block the reactive sites in oligothiophenes without introducing structures susceptible to auto-oxidation.

### 4. Conclusions

We have reported the synthesis of new highly soluble oligothiophenes with thermally labile solubilizing groups and utilized ester thermolysis not only to afford a thin film morphological transformation but also to extend the conjugation of oligothiophene cores to include styryl endgroups. Analysis of the films by NEXAFS and GIXD revealed their edge-on orientation and high in-plane crystallinity. The stability of  $\alpha, \omega$ -distyryl oligothiophenes appears to be tied to the elimination of reactive sites in the conjugated molecule, which suggests that oligothiophenes can be rendered highly resistant to oxidative degradation through judicious choice of end-group structures. This improvement in structural design allows the favorable combination of solution deposition facilitated by thermally labile solubilizing groups and air stability offered by  $\alpha, \omega$ -distyryl oligothiophenes, which greatly simplifies processing conditions for organic electronics.

### 5. Methods

**5.1 Materials.** All chemicals were purchased from Aldrich and used without further purification unless otherwise noted. N-bromosuccinimide was recrystallized from 1:1 acetic acid /water prior to use. All reactions were performed under dry  $N_2$  unless otherwise noted. All extracts were dried over MgSO<sub>4</sub> and solvents were removed by rotary evaporation with aspirator pressure. Flash chromatography was performed using Merck Kieselgel 60 (230-400 mesh) silica. Methylene chloride, THF, toluene, pyridine, DMF, and triethylamine were purchased from Fisher and

vigorously purged with nitrogen for 1h. The solvents were further purified by passing them under nitrogen pressure through two packed columns (Glass Contour) of neutral alumina (for THF and methylene chloride), neutral alumina and copper(II) oxide (for toluene), or activated molecular sieves (for DMF).

**5.2 Characterization.** UV-Vis data were measured with a Varian Cary 50 spectrophotometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded with Bruker AV-300, AVQ 400, or DRX-500 instruments using CDCl<sub>3</sub> as the solvent. Matrix Assisted Laser Desorption Ionization -Time Of Flight (MALDI-TOF) mass spectrometry was performed on a Perseptive Biosystems Voyager-DE instrument in positive ion mode using  $\alpha$ -cyano-4-hydroxycinnamic acid as the matrix. High Resolution Mass Spectometry (HRMS) using Fast Atom Bombardment (FAB) was done with a Micromass ZAB2-EZ double focusing mass spectrometer (BE geometry). Elemental analyses were performed at the UC Berkeley Microanalysis Laboratory. TGA was performed using a Seiko instruments SSC 5200 TG/DTA 220. The electrical measurements were performed in a nitrogen atmosphere or in air using an Agilent 4156C Precision Semiconductor Parameter Analyzer.

**5.3 Transistor Fabrication.** OTFTs were fabricated using n-doped silicon wafers as the gate, and thermally oxidizing the surface to form a 1000 Å silicon dioxide dielectric layer. The semiconducting material was deposited by spin coating 2-3 mg/mL solutions in anhydrous CHCl<sub>3</sub> filtered through 0.2  $\mu$ m PTFE syringe filters at 2000 rpm. Samples were thermolyzed on a hot plate in a dry nitrogen glovebox at temperatures of 200-225 °C. For top contact devices, gold electrodes were evaporated in a thermionic evaporator at 5 Å/s through a shadow mask on top of the semiconducting material to a thickness of 500 Å. The channels tested in this geometry had widths of 200 or 400  $\mu$ m and lengths from 5 to 40  $\mu$ m.

## **5.4 Synthetic Details**

**1-[2,2']-Bithiophen-5-yl-2-phenylethanone (1).** A solution of 1.0 g (6 mmol) 2,2'-bithiophene in 10 mL dry CH<sub>2</sub>Cl<sub>2</sub> was cooled to 0 °C and 0.78 mL (6 mmol) phenyl acetyl chloride was added, followed by dropwise addition of 6 mL (6 mmol) 1.0 M SnCl<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> via syringe. The mixture was stirred for 1 hour at 0 °C and then stirred overnight at room temperature. The resulting mixture was poured into an aqueous 1.0 M HCl/ice slurry. The organic products were extracted with 200 mL CH<sub>2</sub>Cl<sub>2</sub> and washed once with 1.0 M HCl, once with saturated NaHCO<sub>3</sub>, and once with brine. The organic layer was dried and the solvent evaporated. The resulting solid was purified by flash chromatography though silica using 50% chloroform in hexanes as the eluent. The solvent was evaporated and the product was dried *in vacuo* to afford 0.98 g (57%) of a yellow solid. <sup>1</sup>H NMR (400 MHz):  $\delta$  4.18 (s, 2H), 7.06 (t, *J* = 4.2 Hz, 1H), 7.17 (d, *J* = 3.6 Hz, 1H), 7.27-7.37 (m, 7H), 7.66 (d, *J* = 4.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz):  $\delta$  46.00, 124.20, 125.69, 126.55, 127.04, 128.23, 128.71, 129.33, 133.52, 134.38, 136.25, 141.69, 146.01, 190.09. HRMS (FAB) *m*/z calc for (C<sub>16</sub>H<sub>12</sub>OS<sub>2</sub>) 284.0329; found 285.0407. Anal. Calcd for C<sub>16</sub>H<sub>12</sub>OS<sub>2</sub>: C, 67.57; H, 4.25; S, 22.55. Found C, 67.90; H, 4.33; S, 22.74.

**1-[2,2']-Bithiophen-5-yl-2-phenylethanol (2).** A solution containing 0.75 g (2.6 mmol) **1** dissolved in 10 mL dry THF was added dropwise via syringe to a flask containing 0.3 g (7.8 mmol) LAH in 50 mL dry THF. The mixture was stirred at room temperature for 2 hours. The reaction was quenched with Baekstrom's reagent and the resulting mixture was filtered through celite. The filtered solids were washed with ethyl acetate and chloroform. The solvent was

evaporated and the product was dried *in vacuo* to afford 0.65 g (88%) of a light brown solid. <sup>1</sup>H NMR (300 MHz):  $\delta$  2.22 (s, 1H), 3.07-3.21 (m, 2H), 5.09 (dd, J = 5.6 and 7.6 Hz, 1H), 6.82 (d, J = 3.6 Hz, 1H), 7.15-7.23 (m, 7H). <sup>13</sup>C NMR (75 MHz):  $\delta$  46.18, 71.67, 123.46, 123.92, 124.64, 124.84, 127.15, 128.10, 128.74, 128.90, 129.80, 136.94, 137.62, 137.77, 146.88. HRMS (FAB) *m*/*z* calc for (C<sub>16</sub>H<sub>14</sub>OS<sub>2</sub>) 286.0486; found 286.0482. Anal. Calcd for C<sub>16</sub>H<sub>14</sub>OS<sub>2</sub>: C, 67.10; H, 4.93; S, 22.39. Found C, 67.40; H, 5.00; S, 22.70.

**2,2-Dimethylpropionic acid 1-[2,2']bithiophen-5-yl-2-phenylethyl ester (3).** A mixture of 0.57g (2.0 mmol) **2** and 12 mg (5 mol %) DMAP were combined in 10 mL dry pyridine. The mixture was stirred under nitrogen and 0.24 mL (2 mmol) trimethyl acetyl chloride was added slowly via syringe. The mixture was stirred overnight and then diluted with 100 mL ethyl acetate and washed twice with saturated NaHCO<sub>3</sub> and once with brine. The organic layer was dried and the solvent evaporated. The resulting product was purified by flash chromatography through silica using 20% ethyl acetate in hexanes. The solvent was evaporated and the product was dried *in vacuo* to afford 0.64 g (86%) of a tan solid. <sup>1</sup>H NMR (300 MHz):  $\delta$  1.12 (s, 9H), 3.17-3.31 (m, 2H), 6.18 (dd, *J* = 6.0 and 8.1 Hz, 1H), 6.66 (d, *J* = 3.3 Hz, 1H), 6.83-6.85 (m, 2H), 6.98-7.22 (m, 7H). <sup>13</sup>C NMR (75 MHz):  $\delta$  27.27, 39.01, 43.21, 72.11, 123.33, 124.03, 124.77, 126.52, 127.05, 128.08, 128.73, 129.78, 136.91, 137.40, 137.57, 142.44, 177.64. HRMS (FAB) *m/z* calc for (C<sub>21</sub>H<sub>22</sub>O<sub>2</sub>S<sub>2</sub>) 370.1061; found 370.1067. Anal. Calcd for C<sub>21</sub>H<sub>22</sub>O<sub>2</sub>S<sub>2</sub>: C, 68.07; H, 5.98; S, 17.31. Found C, 68.20; H, 6.01; S, 17.59.

**2,2-Dimethylpropionic acid 1-(5'-bromo-[2,2']bithiophen-5-yl)-2-phenylethyl ester (4)** A flask containing 0.60 g (1.6 mmol) **3** and 10 mL DMF was protected from light and 0.28 g NBS was added. The mixture was allowed to stir at room temperature for 5 hours. The mixture was diluted with 100 mL ethyl acetate and washed twice with saturated NaHCO<sub>3</sub> and once with brine. The organic layer was dried and the solvent was evaporated. The resulting product was purified by flash chromatography through silica using 20% ethyl acetate in hexanes as the eluent. The solvent was evaporated and the product was dried *in vacuo* to afford 0.62 g (86%) of a light yellow solid. <sup>1</sup>H NMR (300 MHz):  $\delta$  1.12 (s, 9H), 3.15-3.30 (m, 2H), 6.16 (dd, *J* = 6.0 and 8.1 Hz), 6.82 (d, *J* = 3.6 Hz, 1H), 6.88 (d, *J* = 3.6 Hz, 1H), 6.92 (d, *J* = 3.6, 1H), 6.95 (d, *J* = 3.9 Hz, 1H), 7.32-7.17 (m, 5H). <sup>13</sup>C NMR (75 MHz):  $\delta$  27.26, 39.01, 43.19, 72.02, 111.33, 123.64, 124.09, 126.49, 127.10, 128.62, 129.77, 130.89, 136.31, 136.78, 139.04, 143.02, 177.62. HRMS (FAB) *m/z* calc for (C<sub>21</sub>H<sub>21</sub>O<sub>2</sub>S<sub>2</sub>Br) 448.0166; found 448.0175. Anal. Calcd for C<sub>21</sub>H<sub>21</sub>O<sub>2</sub>S<sub>2</sub>Br: C, 56.12; H, 4.71; S, 14.27. Found C, 55.16; H, 4.67; S, 14.14.

**2,2-Dimethylpropionic** acid 1-{5'''-[1-(2,2-dimethyl-propionyloxy)-2-phenylethyl]-[2,2';5',2'';5'',2''']quarterthiophen-5-yl}-2-phenylethyl ester (5). A mixture of 0.32 g (0.71 mmol) **4**, 0.181 g (0.71 mmol) bis(pinacolato)diboron, 25 mg (5 mol %) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and 0.206 g (2.1 mmol) potassium acetate were combined in 20 mL anhydrous DMF. The mixture was degassed with three freeze-pump-thaw cycles and backfilled with nitrogen. The flask was heated to 75 °C, stirred for three hours, and cooled to room temperature. The mixture was diluted with 150 mL ethyl acetate and washed twice with saturated NaHCO<sub>3</sub> and once with brine. The organic layer was dried and the solvent evaporated. The resulting product was purified by flash chromatography through silica using 2:1 chloroform:hexanes. The solvent was evaporated and the product was dried *in vacuo* to afford 0.10 g (38%) of a yellow solid. UV-vis  $\lambda_{max}$  (CHCl<sub>3</sub>) = 400 nm. <sup>1</sup>H NMR (400 MHz):  $\delta$  1.13 (s, 18H), 3.18-3.30 (m, 4H), 6.17 (dd, *J* = 6.0 and 8.1 Hz, 2H), 6.84 (d, *J* = 3.6 Hz, 2H), 6.99 (d, *J* = 3.6 Hz, 2H), 7.07 (m, 4H), 7.20-7.30 (m, 10H). <sup>13</sup>C NMR (125 MHz):  $\delta$  27.00, 38.69, 42.87, 71.76, 121.91, 123.03, 124.23, 124.33, 126.28, 126.74, 128.28, 129.45, 136.17, 136.50, 136.65, 142.40, 177.32. HRMS (FAB) *m*/*z* calc for (C<sub>42</sub>H<sub>42</sub>O<sub>4</sub>S<sub>4</sub>) 738.1966; found 738.1952. Anal. Calcd for C<sub>42</sub>H<sub>42</sub>O<sub>4</sub>S<sub>4</sub>: C, 68.26; H, 5.73; S, 17.35. Found C, 67.94; H, 5.82; S, 17.13.

1-{5'"-[1-(2,2-dimethyl-propionyloxy)-2-phenylethyl]-2,2-Dimethylpropionic acid [2,2';5',2'';5'',2''']quarterthiophen-5-yl}-2-phenylethyl ester (preDS4T). A mixture of 0.32 g (0.71 mmol) 4, 0.181 g (0.71 mmol) bis(pinacolato)diboron, 25 mg (5 mol %) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and 0.206 g (2.1 mmol) potassium acetate were combined in 20 mL anhydrous DMF. The mixture was degassed with three freeze-pump-thaw cycles and backfilled with nitrogen. The flask was heated to 75 °C, stirred for three hours, and cooled to room temperature. The mixture was diluted with 150 mL ethyl acetate and washed twice with saturated NaHCO<sub>3</sub> and once with brine. The organic layer was dried and the solvent evaporated. The resulting product was purified by flash chromatography through silica using 2:1 chloroform:hexanes. The solvent was evaporated and the product was dried in vacuo to afford 0.10 g (38%) of a yellow solid. UV-vis  $\lambda_{\text{max}}$  (CHCl<sub>3</sub>) = 400 nm. <sup>1</sup>H NMR (400 MHz):  $\delta$  1.13 (s, 18H), 3.18-3.30 (m, 4H), 6.17 (dd, J = 6.0 and 8.1 Hz, 2H), 6.84 (d, J = 3.6 Hz, 2H), 6.99 (d, J = 3.6 Hz, 2H), 7.07 (m, 4H), 7.20-7.30 (m, 10H). <sup>13</sup>C NMR (125 MHz): δ 27.00, 38.69, 42.87, 71.76, 121.91, 123.03, 124.23, 124.33, 126.28, 126.74, 128.28, 129.45, 136.17, 136.50, 136.65, 142.40, 177.32. HRMS (FAB) m/z calc for (C<sub>42</sub>H<sub>42</sub>O<sub>4</sub>S<sub>4</sub>) 738.1966; found 738.1952. Anal. Calcd for C<sub>42</sub>H<sub>42</sub>O<sub>4</sub>S<sub>4</sub>: C, 68.26; H, 5.73; S, 17.35. Found C, 67.94; H, 5.82; S, 17.13.

1-{5''''-[1-(2,2-dimethyl-propionyloxy)-2-phenyl-ethyl]-2,2-Dimethyl-propionic acid [2,2';5',2'';5'',2''']quinquethiophen-5-yl}-2-phenyl-ethyl ester (preDS5T). A mixture of 0.31 g (0.71 mmol) 4, 0.144 g (0.35 mmol) 2,5-bis-trimethylstannyl-thiophene, and 25 mg (5 mol %) Pd(Ph<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> were combined in 20 mL anhydrous DMF. The mixture was degassed with three freeze-pump-thaw cycles and backfilled with nitrogen. The flask was heated to 75 °C. stirred for two hours, and cooled to room temperature. The mixture was diluted with 150 mL ethyl acetate and washed twice with saturated NaHCO<sub>3</sub> and once with brine. The organic layer was dried and the solvent evaporated. The resulting product was purified by flash chromatography through silica using 2:1 chloroform:hexanes. The solvent was evaporated and the product was dried *in vacuo* to afford 0.10 g (35%) of an orange solid. UV-vis  $\lambda_{max}$  (CHCl<sub>3</sub>) = 424 nm. <sup>1</sup>H NMR (400 MHz):  $\delta$  1.13 (s, 18H), 3.18-3.30 (m, 4H), 6.17 (dd, J = 6.0 and 8.1 Hz, 2H), 6.85 (d, J = 3.6 Hz, 2H), 6.99 (d, J = 3.6 Hz, 2H), 7.07-7.09 (m, 6H), 7.20-7.30 (m, 10H). <sup>13</sup>C NMR (125 MHz): δ 26.95, 38.69, 42.87, 71.76, 123.06, 124.28, 124.33, 124.36, 126.30, 126.75, 128.29, 129.46, 135.84, 135.91, 136.23, 136.51, 136.65, 142.43, 177.32. HRMS (FAB) m/z calc for (C<sub>46</sub>H<sub>44</sub>O<sub>4</sub>S<sub>5</sub>) 820.1843; found 820.1830. Anal. Calcd for C<sub>46</sub>H<sub>44</sub>O<sub>4</sub>S<sub>5</sub>: C, 67.28; H, 5.40; S, 19.52. Found C, 67.18; H, 5.51; S, 19.27.

**2,2-Dimethyl-propionic** acid  $1-\{5''''-[1-(2,2-dimethyl-propionyloxy)-2-phenyl-ethyl] [2,2';5',2'';5'',2''';5''',2'''';5'''',2'''']sexithiophen-5-yl}-2-phenyl-ethyl ester (preDS6T). A mixture of 0.10 g (0.22 mmol)$ **4**, 0.08 g (0.11 mmol) 5,5'-bis-tributylstannyl-[2,2']bithiophene, and 8 mg (5 mol %) Pd(Ph<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> were combined in 10 mL anhydrous DMF. The mixture was degassed with three freeze-pump-thaw cycles and backfilled with nitrogen. The flask was heated to 75 °C, stirred for two hours, and cooled to room temperature. The mixture was diluted with 150 mL chloroform and washed twice with saturated NaHCO<sub>3</sub> and once with brine. The organic layer was dried and the solvent evaporated. The resulting product was purified by flash chromatography through silica using 20% hexanes in chloroform. The solvent was evaporated and the product was dried *in vacuo* to afford 0.04 g (40%) of a red-orange solid. UV-vis  $\lambda_{max}$  (CHCl<sub>3</sub>) = 436 nm. <sup>1</sup>H NMR (400 MHz):  $\delta$  1.13 (s, 18H), 3.18-3.30 (m, 4H), 6.17 (t, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 4.0 Hz, 2H), 7.00 (d, *J* = 3.6 Hz, 2H), 7.07-7.09 (m, 8H), 7.20-7.30 (m, 10H). <sup>13</sup>C NMR. (100 MHz):  $\delta$  27.02, 38.76, 42.95, 71.84, 123.14, 124.43, 126.35, 126.82, 128.36, 129.52, 135.96, 136.58, 136.72, 177.38 (only peaks resolvable due to low solubility). HRMS (FAB) *m*/*z* calc for (C<sub>50</sub>H<sub>46</sub>O<sub>4</sub>S<sub>6</sub>) 902.1720; found 902.1704. Anal. Calcd for C<sub>50</sub>H<sub>46</sub>O<sub>4</sub>S<sub>6</sub>: C, 66.49; H, 5.13. Found C, 65.67; H, 4.99.

2,2-Dimethyl-propionic acid 1-(5'''-decyl-[2,2';5',2'';5'',2''']quaterthiophen-5-yl)-2-phenylethyl ester (8). A mixture of 0.25 g (0.58 mmol) 4, 0.125 g (0.58 mmol) (5'-decyl-[2,2']bithiophen-5-yl)-trimethyl-stannane, and 20 mg (5 mol %) Pd(Ph<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> were combined in 20 mL anhydrous DMF. The mixture was degassed with three freeze-pump-thaw cycles and backfilled with nitrogen. The flask was heated to 75 °C, stirred for two hours, and cooled to room temperature. The mixture was diluted with 150 mL chloroform and washed twice with saturated NaHCO<sub>3</sub> and once with brine. The organic layer was dried and the solvent evaporated. The resulting product was purified by flash chromatography through silica using 75% chloroform in hexanes. The solvent was evaporated and the product was dried in vacuo to afford a yellow solid. UV-vis  $\lambda_{max}$  (CHCl<sub>3</sub>) = 400 nm. <sup>1</sup>H NMR (400 MHz):  $\delta$  0.88 (t, J = 6.6 Hz, 3H), 1.12 (s, 9H), 1.27-1.40 (m, 14H), 1.65-1.71 (m, 2H), 2.80 (t, J = 8 Hz, 2H), 3.18-3.30 (m, 2H), 6.17 (dd, J = 1.276.2 and 8.2 Hz, 2H), 6.69 (d, J = 3.2 Hz, 1H), 6.84 (d, J = 3.6 Hz, 1H), 6.98-7.05 (m, 6H), 7.20-7.30 (m, 5H). <sup>13</sup>C NMR (100 MHz): δ 14.11, 22.67, 26.95, 29.06, 29.31, 29.34, 29.53, 29.85, 30.17, 31.57, 31.88, 38.70, 42.89, 71.78, 122.95, 123.44, 123.55, 123.99, 124.23, 124.33, 124.84, 126.29, 126.75, 128.29, 129.47, 134.33, 135.04, 135.89, 136.17, 136.54, 136.77, 137.00, 142.30, 145.77, 177.33. HRMS (FAB) *m/z* calc for (C<sub>39</sub>H<sub>46</sub>O<sub>2</sub>S<sub>4</sub>) 674.2380; found 674.2395. Anal. Calcd for C<sub>39</sub>H<sub>46</sub>O<sub>2</sub>S<sub>4</sub>: C, 69.39; H 6.87; S, 19.0. Found: C, 69.26; H, 6.86; S, 18.97.

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# Chapter 3

# Morphological and Electrical Properties of Pentathiophene Monolayers Studied by Contact Mode Atomic Force Microscopy

# Abstract

Using contact mode atomic force microscopy (AFM) we have investigated the structural and electrical conduction properties of monolayer films of conjugated molecules on a SiO<sub>2</sub>/Si-p substrate. The Langmuir-Blodgett technique is used to deposit amphiphilic pentathiophene butyric acid derivatives. The topography and friction of the films is correlated with high resolution current measurements. The alkyl substitution pattern of the pentathiophene derivatives is shown to dramatically affect the morphology of monolayers and monolayer islands of the molecules. By a combination of current-voltage spectroscopy and current imaging we show that lateral charge transport takes place in the plane of crystalline monolayer islands via hole injection into the HOMO molecular orbitals of the pentathiophene unit. Furthermore, anisotropic conductivity relative to the crystalline directions of the molecular lattice was observed in monolayer islands of 4-(5<sup>IIII</sup>-decyl-pentathiophen-5-yl)-butyric acid, and is rationalized using calculations of electronic coupling of hole states. This work has implications for the application of oligothiophenes in molecular electronics.

### **1. Introduction**

The use of molecules as components of molecular scale electronic devices is a field of continuous and increasing interest, both in its fundamental scientific aspects and for potential applications. Conducting organic molecules are already finding applications in devices such as organic light emitting diodes and biosensors.<sup>1-3</sup> However, the electronic properties of the molecules and their correlation with their structure and assembly are still not well understood. Such understanding is necessary for the discovery of new properties and for the design of novel molecular scale electronic devices. Efforts in that direction are already underway in various laboratories. For example, intra- and inter molecular charge transport mechanisms have been studied in single molecules,<sup>4</sup> in molecular monolayers and in thin films,<sup>5,6</sup> in molecular crystals<sup>7</sup> and in biomolecular materials.<sup>8</sup> The structural and mechanical properties of self-assembled monolayers of 4-(5""-decyl-pentathiophen-5-yl)-butyric acid (D5TBA) and of a similar molecule, 4-(5""-tetradecyl-pentathiophen-5-yl)-butyric acid (TD5TBA) on mica, have been studied previously with atomic force microscopy (AFM).<sup>9-11</sup> In this chapter, we use currentsensing AFM to study the structure and conductivity of molecularly thin layers of pentathiophenes focusing on molecular scale structure and electrical properties. The junction geometry is that of a diode, where tip and substrate act as two electrodes. The substrate consists of an insulating thin layer on a conducting base (SiO<sub>2</sub> /  $p^+$ -Si), which, as shown below, allows us to separate conduction channels through and across the molecules.

We used pentathiophene derivatives for our experiments that all feature a butyric acid moiety that facilitates self-assembly at the air-water interface in a Langmuir-Blodgett (LB) trough. The structure of the pentathiophene derivatives is varied through alkyl substitution with the aim of affecting the monolayer morphology and electronic properties that are observed using AFM. Samples of 4-(pentathiophen-5-yl)butanoic acid (**5TBA**), **D5TBA** and 4-(3"",4'-dihexyl-pentathiophen-5-yl)butanoic acid (**DH5TBA**) are prepared and the syntheses of **5TBA** and **DH5TBA** are presented.

#### 2. Results

**2.1 D5TBA Sub-monolayers.** Sub-monolayers of **D5TBA** (Figure 1) were transferred onto doped silicon wafer substrates that featured a thin native oxide surface, and the films were imaged using contact mode AFM. Films were prepared in this manner because the substrates are conductive and have very low roughness. A conductive substrate allows two terminal current measurements, as depicted in Figure 2, and low roughness prevents disruption of two-dimensional molecular ordering in the monolayer. Spatial resolution of the topography, friction, and conductance of the monolayer is possible using this method and allows electrical properties to be correlated with structural properties over nanoscale areas.



Figure 1. The chemical structure of D5TBA features a hydrophilic carboxylic acid and a hydrophobic decyl group to facilitate self-assembly on water.



Figure 2. Diagram of a two-terminal measurement with conducting probe AFM and a conducting substrate.

Topographic images reveal two distinct phases in **D5TBA** sub-monolayers, as shown in Figure 3a. One phase is porous and the other consists of finger-like structures radiating outward from a central point -a flower phase. The two phases are easily distinguished in friction images, as shown in Figure 3b. The porous phase exhibits higher friction than the flower phase, and the boundaries between finger-like structures in the flower phase are visible. Interestingly, the currents measured over the flower phase are higher than those measured over the porous phase and the bare substrate, as is seen in Figure 3c. These island structures are attractive for structural and electronic characterization due to their easily observable structure and conductivity.



**Figure 3.** AFM (a) topographic, (b) friction and (c) current images of **D5TBA** monolayer islands. Greater height, friction and current is denoted by lighter coloring in the images.

**2.2 D5TBA Monolayer Islands.** The typical morphology of **D5TBA** monolayer islands is shown in Figure 4a. The film is always in the form of flower-like islands with a separation determined by the pressure during emersion of the sample in the trough. The height of the islands is 2.5 nm, which is smaller than the 3.65 nm expected for fully extended molecules, indicating that the molecules are tilted.<sup>9</sup> The islands, with sizes varying from hundreds to thousands of nanometers are composed of elongated domains extending roughly radially from the center. This is likely the result of nucleation from a point close to the center. The friction force is always lower on the islands than on the substrate (Figure 4b), due to the inert and lubricating properties of the exposed methyl groups of the alkane chain.

Figure 4c shows a lattice resolved friction image from one domain of the **D5TBA** islands. The lattice periodicity can also be observed in the topographic signal albeit with lower contrast. The Fourier transform of the image (inset in Figure 4c) shows a nearly hexagonal set of points. After correcting for distortions due to drift and piezo hysteresis using lattice resolved images of mica as reference, the spacing between rows of molecules was found to be  $5.5\pm0.4$  Å and the angle between lattice directions  $60\pm5^{\circ}$ .



**Figure 4.** (a) Topography of monolayer islands of **D5TBA** on SiO2/Si. The height of the islands is 2.5nm. (b) Friction image, with dark representing lower friction. Notice the higher friction at the boundary of crystalline domains. (c) High resolution friction image of the molecular lattice from one domain. The Fast Fourier transform is shown in inset (d) Schematic of the **D5TBA** molecule. (e) Side view and (f) top view of the calculated Herringbone structure. Alkyl chains and three bottom thiophene rings have been removed from the top view for clarity of the figure. Red lines represent directions where the molecules are the most closely packed (directions resolved in AFM).

We performed classical molecular dynamicss calculations to determine the most stable packing of the **D5TBA** molecules. The CFF91 force field,<sup>12</sup> as implemented in the LAMMPS code,<sup>13,14</sup> was used. Various initial structures and lattice constants were attempted. The lowest energy minimum resulting from relaxation is shown in Figure 4e (side view) and Figure 4f (top view). It is a herringbone structure with the **D5TBA** molecules inclined from the substrate. Its unit cell dimensions are equal to a=11Å and b=6.3Å, with a height of 2.4nm, which is very close to the 2.5nm measured by AFM. Red lines in Figure 4e are drawn along the directions of closer molecular packing: 2 equivalent diagonal directions and a third direction parallel to the lattice vector b. The alkyl chains exposed to the tip mask the difference in orientation of the underlying thiophene rings. From the calculated unit cell dimensions the spacing between parallel lines is 5.5Å, in excellent agreement with the periodicity measured in the AFM images.

High resolution images of the narrow (5-7 nm) regions of high friction separating domains do not show order, as expected from a finite tip-surface contact area transitioning across the boundary between crystalline domains. The higher friction is consistent with the general observation that disorder gives rise to higher friction.<sup>15</sup> Images acquired in adjacent domains reveal that one of the lattice directions is always orthogonal to the long axis of the domains, which corresponds to the growth direction. Symmetry arguments suggest that the direction parallel to **b** is the one which is orthogonal to grain growth since the diagonal directions are equivalent. This has important consequences in the lateral conductivity of the film.

The electrical conduction properties of the **D5TBA** islands and of the exposed SiO<sub>2</sub> substrate were studied by current-voltage (I-V) spectroscopy. On the bare substrate, the I-V curves of the Pt-SiO<sub>2</sub>-Si junction are consistent with tunneling through the oxide with no rectifying effect from a Schottky barrier. The doping level of the Si is such that it can be considered as a metal, with the oxide acting as a tunneling barrier. In contrast to the bare substrate, the I-V curves acquired on top of the islands show a rectifying behavior. For negative sample voltages the current on the islands is two orders of magnitude higher than at positive sample bias (e.g. 133 pA at -2.0V versus 1 pA at +2.0V). Oligothiophenes are typically p-type semiconductors, so negative sample bias must allow facile injection of mobile holes from the high work function Pt electrode while positive sample bias does not.

Even more striking is the observation that at negative voltage the current is higher on the islands than on the bare SiO<sub>2</sub>. This is counterintuitive: by adding material with an electrical resistance (the molecular layer), which separate the metallic tip by 2.5 nm from the substrate, the resistance of the junction decreases. This can only be explained by an efficient lateral conduction channel across molecules that increases the effective electrical contact area.<sup>16-20</sup> The range of the lateral charge spreading, which is well beyond of the estimated ~7nm tip-**D5TBA** contact diameter,<sup>21</sup> can be determined from measurements of the island-size dependence of the current. As a control experiment, we prepared samples with stearic acid and **D5TBA** islands coexisting on the SiO2/Si substrate. The current on the 2nm high stearic acid layer was negligibly small even at large voltages. It is worth noticing that it is thanks to the thin insulating SiO<sub>2</sub> layer that the lateral intermolecular charge transport can be clearly observed. On a conductive substrate (e.g., Au) the vertical transport is dominant and obscures the lateral component.

Figure 5 shows average current values measured on different islands as a function of size. The scatter in the data is due to structural inhomogeneities in the islands, both in shape and in internal structure. A linear curve fitting resulted in a correlation coefficient equal to 0.84 for the current plotted as a function of diameter and 0.19 when plotted as a function of area. It is apparent that the current as a function of area would be better fitted by a square root curve. We found that at the location where two domains join into a wider domain the current level makes a stepwise increase. A plot of the current as a function of local domain width (in the direction of the short axis as illustrated in Figure 5c) is shown in Figure 5d. The current shows a clear linear dependence and exhibits much less scatter. This clearly indicates that the preferred or easy direction for lateral transport is orthogonal to the long axis of the fingerlike domains.



Figure 5. Plot of current versus (a) diameter (the diameter of an island was obtained by averaging its size in two orthogonal directions), and (b) area of the D5TBA islands at -2V sample voltage. (c) Schematic illustration of the structure of a D5TBA island with arrows in the direction of the short axis of the crystalline domains. (d)
Dependence of the current on the local width of the domains (w), as illustrated in (c), at -2V sample voltage. (e) Top five hole wavefunctions for a room temperature molecular dynamics snapshot of the 7x7 Herringbone structure. Isosurfaces correspond to the 98% probability of finding the hole inside the surface. Lines are given as a guide to the eye to indicate the directions of the strongest hole coupling. The energies of the levels are 2.787eV (blue), 2.758eV (red), 2.746eV (pink), 2.738 (black), 2.735(gray).

Electronic structure calculations were carried out for a room temperature molecular dynamics snapshot of the Herringbone structure shown in Figure 5e. The calculation was performed using the charge patching method<sup>22</sup> which yields accuracy similar to density functional theory in local density approximation. For hole states, we found that, depending on the specific hole wavefunction, the strongest coupling could be in the b direction as well as in the 2 diagonal directions of the unit cell, as shown in Figure 5e. This gives a preferable hole conductance along the b-direction compared to its orthogonal counterpart –the a-direction. As described above, lattice resolution AFM suggested that the **b** direction is orthogonal to the long axis of fingerlike domains. Experimental results and calculations therefore both point at a larger lateral conduction along the **b** direction of the unit cell.

**2.3 Sub-monolayers of 5TBA.** The molecule **5TBA** lacks the decyl chain featured in the structure of **D5TBA**, as shown in Figure 6. Sub-monolayers were prepared in order elucidate the morphological and electronic effects of this structural change. In particular, removal of the insulating decyl chain was expected to decrease the vertical resistance of the monolayers, and

allow direct observation of the molecular packing of pentathiophenes instead of the surface alkyl chains of **D5TBA**.



Figure 6. The chemical structure of 5TBA lacks the decyl group present on D5TBA.

Samples were prepared in an analogous fashion to **D5TBA**, and topographic images reveal roughly circular structures scattered among a porous phase. **5TBA** was not observed to form a flower phase, and there is little contrast between the two phases in the friction image shown in Figure 7b. The circular structures are roughly 3 nm in height while the porous phase is 2 nm in height. This same trend was observed in **D5TBA** films and suggests that the molecular packing is tighter in the circular structures. Also consistent with **D5TBA** data is the higher currents measured in the circular structures relative to the porous phase. However, the circular structures lack the anisotropic character of the flower phase of **D5TBA**, so the decyl chain is clearly important for its formation. This lack of structural anisotropy prevents a study of anisotropic charage conduction that would supplement the data from **D5TBA** monolayer islands.



Figure 7. (a) topographic, (b) friction and (c) current AFM images of **5TBA** sub-monolayers. The darker portions of the images correspond to lower height and friction, and higher current.

**2.4 Mixed Sub-monolayers of D5TBA and 5TBA.** While monolayer islands of **5TBA** lacked the distinctive structural features of **D5TBA**, current images suggested that monolayer islands of **5TBA** formed a more conductive bridge between the AFM tip and the substrate. The vertical current on islands was measured to be about 500 pA at -1 V (substrate) compared to 100 pA for **D5TBA**. However, this measurement was observed to vary significantly with different substrates and AFM tips. Therefore, a mixed sample of **D5TBA** and **5TBA** was deposited onto a single substrate and imaged with a single AFM tip to remove those sources of variability. A representative set of topographic, friction, and current images is shown in Figure 8a, 8b, and 8c, respectively.



**Figure 8.** (a) topographic, (b) friction and (c) current images of a mixed sub-monolayer of **D5TBA** and **5TBA**. Lighter color represents greater height, friction, and current.

Domains of **D5TBA** can be easily distinguished from **5TBA** in the friction and current images shown in Figure 8b and 8c. **D5TBA** monolayer islands present a low friction aliphatic surface and correspond to the dark areas in Figure 8b. Current imaging reveals that **5TBA** domains produce higher current levels relative to **D5TBA** monolayer islands. This contrast is the result of the insulating barrier presented by the surface decyl chains of **D5TBA**. Removal of this functional group to give **5TBA** decreases the vertical resistance of the tip-pentathiophene-silicon junction and yields higher current levels.

**2.5 Monolayers of DH5TBA.** The anisotropic structure and charge transporting properties of **D5TBA** motivated us to design a new molecule that might exhibit these same properties to a greater degree. In the slip-stacked packing mode of  $\beta$ -alkyl oligothiophenes and polythiophenes, the direction of pi-stacking provides the highest charge mobility. This effect is best exemplified by the enhanced charge mobility of highly oriented poly(3-hexylthiophene) films in OFETs.<sup>23</sup> Two  $\beta$ -hexyl substituents were introduced onto the **5TBA** structure to yield **DH5TBA**, and the structure is shown in Figure 9. The structure of **DH5TBA** was hoped to yield crystalline monolayer islands with distinctive structures that exhibit highly anisotropic lateral charge transport. However, the topographic image in Figure 10 reveals a completely featureless film. Scratching the surface removes the organic film, which is measured to be about 1 nm thick. Crystalline monolayer islands of **5TBA** and **D5TBA** were measured to be 2-3 nm in height, so **DH5TBA** likely forms amorphous films under the same conditions used previously. The molecules are loosely held together and not oriented normal to the substrate.



Figure 9. The chemical structure of DH5TBA features a pair of  $\beta$ -hexyl chains that block edge-to-face or herringbone packing.



Figure 10. Topographic AFM image of DH5TBA on mica.

**DH5TBA** cannot adopt the natural herringbone packing of oligothiophenes because of its alkyl substitution pattern, and this dramatically increases its solubility relative to **D5TBA** and **5TBA**. Slip-stacking is much less favorable than herringbone packing and is clearly not a strong enough driving force for self-assembly of crystalline monolayer islands of **DH5TBA**. Experimentation with thermal annealing conditions is underway to evaluate its effect on film morphology.

## **3.** Conclusions

We have demonstrated that the structure and electronic properties of pentathiophene monolayer islands is sensitive to the alkyl substitution of the amphiphilic molecules. **D5TBA** forms a flower phase that features anisotropic lateral charge transporting properties, as shown by conducting probe AFM imaging. The experimentally observed direction of highest conductivity corresponds to the calculated theoretical direction of greatest electronic coupling for hole transport. This anisotropy has implications for the application of oligothiophenes in molecular electronic devices that depend on charge transport across monolayer single crystal grains. Specifically, alignment of crystal grains with electrodes should be critical for consistent IV relationships.

Anisotropy of hole transport was not observed in **5TBA** monolayer islands because of the symmetry of the islands, but **5TBA** was observed to produce a more conductive tip-monolayersubstrate junction in mixed monolayer samples with **D5TBA** because of the absence of the insulating decyl group. Introduction of  $\beta$ -hexyl substituents in the case of **DH5TBA** resulted in the formation of amorphous films. The self-assembly of pentathiophene is highly dependent upon its ability to adopt a herringbone packing mode.

Future work on pentathiophene monolayers will focus on their application in FET test structures. These test structures will be fabricated with source and drain electrodes in the plane of the substrate, and will allow three-terminal IV measurements using **D5TBA** and **5TBA** monolayer islands as the active layer. Such devices will enable further insight into lateral charge transporting properties of the monolayer islands and will allow experiments focusing on the effect of mechanical manipulation on charge transport.

## 4. Methods

**4.1 Materials.** 4-(5""-Decyl-[2,2':5',2":5",2"":5"",2""]-pentathiophen-5-yl)-butyric acid (**D5TBA**), benzyl 4-(2-bromo-thiophen-5-yl)butanoate and benzyl 4-(5"-bromo-[2,2':5',2"]-terthiophen-5-yl)butanoate were prepared according to a previously published procedure.<sup>9</sup> The preparation of (3,3"-dihexyl-[2,2':5',2":5",2"]-quaterthiophen-5-yl)trimethylstannane has been described elsewhere.<sup>24</sup> All other chemicals were purchased from Aldrich and used without further purification unless otherwise noted. All reactions were performed under dry N<sub>2</sub> unless otherwise noted. All extracts were dried over MgSO<sub>4</sub> and solvents were removed by rotary evaporation with aspirator pressure. Flash chromatography was performed using Merck Kieselgel 60 (230-400 mesh) silica. DMF was purchased from Fisher and vigorously purged with nitrogen for 1h. The solvent was further purified by passing it under nitrogen pressure through two packed columns (Glass Contour) of activated molecular sieves.

**4.2 Monolayer Formation and Characterization** Monolayers of pentathiophene (5T) derivatives were prepared by the Langmuir-Blodgett method. A volume of 1 ml of 0.1mM 5T dissolved in chloroform was deposited on the surface of ultrapure water contained in a teflon Langmuir-Blodgett trough. After evaporation of the chloroform the amphiphilic molecular layer floating on the water was compressed to surface pressures in the range of 0-10mN/m. The submerged substrate was then moved out vertically so that the molecular monolayer was transferred to its surface. The substrates were degenerately doped p-type Si(001) wafers with a resistivity <0.00099 Ohm.cm. They were covered by a native oxide layer 2.2 nm thick, as determined by ellipsometry. Before measurements the 5T covered sample was heated to 90-100°C for several hours in a N<sub>2</sub> atmosphere to remove traces of water.

Topography, friction, and current images were obtained using a Pico Plus AFM (Agilent) in contact mode in a dry nitrogen atmosphere. For high resolution contact-mode imaging, 0.27 N/m non-conductive SiN tips were used.<sup>25</sup> Current imaging and I-V spectroscopy were performed using 0.2 N/m Pt-coated Si tips.<sup>26</sup> Typically a net load of 15nN was applied that gave a reliable electrical contact without noticeable perturbation of the molecules.

**4.3 Synthesis of 5TBA.** The oligothiophene derivative 4-([2,2';5',2";5",2"';5"',2"']pentathiophen-5-yl)-butyric acid (**5TBA**) was prepared via a Suzuki cross-coupling of benzyl 4-(5"-bromo-[2,2':5',2"-terthiophen]-5-yl)butanoate and 2-([2,2'-bithiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2dioxaborolane to yield **1**, follow by deprotection with aqueous base to yield **5TBA**.



**benzyl 4-([2,2':5',2'':5'',2''':5''',2'''']pentathiophen-5-yl)butanoate** (1). A flask was charged with 0.252 g (0.5 mmol) 4-(5"-bromo-[2,2':5',2"]terthiophen-5-yl)butanoate and 0.146 g (0.5 mmol) 2-([2,2'-bithiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 17 mg Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, 127 mg K<sub>2</sub>CO<sub>3</sub>, and 10 mL DMF. The mixture was degassed with one freeze-pump-thaw cycle and then stirred under nitrogen at 80 °C overnight. The mixture was then cooled to 0 °C, and the resulting solids were filtered and washed with a little DMF and then copious amounts of 1 M aqueous HCl. The crude product was air dried and then suspended in boiling hexanes. The mixture was then filtered hot and the solids were washed with hexanes. The solids were air-dried and further dried *in vacuo* to yield 0.214 g (73 %) of an organge solid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  2.01-2.06 (m, 2H), 2.45 (t, *J* = 7.2 Hz, 2H), ), 2.85 (t, *J* = 7.5 Hz, 2H), 5.13 (s, 2H), 6.68 (d, *J* = 3.6 Hz, 1H), 6.98 (d, *J* = 3.0 Hz, 1H), 7.00 (d, *J* = 3.6 Hz, 1H), 7.02-7.04 (m, 1H), 7.05-7.09 (m, 5H), 7.17-7.18 (m, 1H), 7.22-7.24 (m, 1H), 7.32-7.39 (m, 5H). HRMS (FAB) *m/z* calc for (C<sub>31</sub>H<sub>24</sub>O<sub>2</sub>S<sub>5</sub>) 588.0374; found 588.0351. Anal. Calcd for C<sub>31</sub>H<sub>24</sub>O<sub>2</sub>S<sub>5</sub>: C, 63.23; H, 4.11; S, 27.23. Found C, 63.32; H, 4.03; S, 26.95.

**4**-([2,2':5',2'':5'',2''':5''',2'''']**pentathiophen-5-yl)butanoic acid** (**5TBA**). A flask was charged with 0.200 g (0.34 mmol) **1**, 10 mL 5% aqueous KOH, and 100 mL THF. The flask was purged with nitrogen, equipped with a reflux condenser, and stirred at 70 °C overnight. The mixture was then cooled to room temperature and acidified to pH = 2 with 1 M aqueous HCl. The THF was evaporated under reduced pressure and the resulting orange solids were filtered. The solids were then washed with 1 M aqueous HCl, water, methanol, and hexanes. The product was air-dried and further dried *in vacuo* to yield 0.143 g (84 %) of an orange solid. <sup>1</sup>H NMR (600 MHz, *d*<sub>8</sub>-THF):  $\delta$  1.81-1.88 (m, 2H), 2.27-2.31 (m, 2H), ), 2.79-2.83 (m, 2H), 6.84 (s, 1H), 7.11-7.36 (m, 9H), 7.53-7.55 (m, 1H). HRMS (FAB) *m/z* calc for (C<sub>24</sub>H<sub>18</sub>O<sub>2</sub>S<sub>5</sub>) 497.9905; found 497.9883. Anal. Calcd for C<sub>24</sub>H<sub>18</sub>O<sub>2</sub>S<sub>5</sub>: C, 57.80; H, 3.64; S, 32.15. Found C, 57.50; H, 3.53; S, 31.78.

**4.4 Synthesis of DH5TBA.** The target pentathiophene, **DH5TBA**, was assembled via crosscoupling of benzyl 4-(5"-bromo-[2,2':5',2"-terthiophen]-5-yl)butanoate and  $\beta$ -dihexylquaterthiophenyl trimethylstannane. The benzyl ester was treated with aqueous base to yield the free butyric acid.



4-(3''',4'-dihexyl-[2,2':5',2'':5'',2''']pentathiophen-5-yl)butanoic acid (DH5TBA). A flask was charged with 0.089 g (0.26 mmol) benzyl 4-(2-bromo-thiophen-5-yl)butanoate and 0.174 g (0.26 mmol) (3,3"'-dihexyl-[2,2':5',2":5",2"']-quaterthiophen-5-yl)trimethylstannane, 15 mg Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and 5 mL DMF. The mixture was degassed with one freeze-pump-thaw cycle and then stirred at 80 °C overnight. The mixture was then poured into 50 mL of dilute aqueous HCl and the product was extracted twice with 50 mL DCM. The organic layers were combined, washed with a little water, dried with MgSO<sub>4</sub> and filtered through basic alumina. The product was purified via flash chromatography with 40% DCM in hexanes to yield 116 mg (59%) of the benzyl protected product. Saponification of the benzyl ester was achieved by heating the product in THF with 5% aqueous KOH overnight. The resulting mixture was acidified to pH = 2, and the THF was evaporated. The product was then extracted twice with 25 mL DCM. The organic layers were combined and dried with MgSO<sub>4</sub>. Hexanes was added to the DCM and the product precipitated after slow evaporation of the DCM to yield 50 mg (50%) of a red solid. <sup>1</sup>H NMR (600 MHz): δ 0.86-0.91 (m, 6H), 1.30-1.42 (m, 12H), 1.62-1.69 (m, 4H), 1.98-2.06 (m, 2H), 2.45 (t, J = 7.2 Hz, 2H), 2.74-2.79 (m, 4H), 2.88 (t, 7.5 Hz, 2H), 6.71 (d, J = 3.6 Hz, 1H), 6.94-6.95 (m, 2H), 6.98 (d, J = 3.6 Hz, 1H), 7.01-7.03 (m, 2H), 7.12-7.13 (m, 2H), 7.18 (d, J = 4.8 Hz, 1H). <sup>13</sup>C NMR (150 MHz): δ 14.05, 14.06, 22.58, 26.28, 29.17, 29.19, 29.22, 29.25, 29.47, 30.42, 30.60, 31.63, 32.57, 123.38, 123.81, 123.83, 123.84, 125.55, 126.11, 126.23, 126.51, 128.87, 130.05, 130.27, 135.03, 135.12, 135.34, 135.47, 136.66, 136.70, 139.86, 140.41, 143.33. HRMS (FAB) m/z calc for (C<sub>36</sub>H<sub>42</sub>O<sub>2</sub>S<sub>5</sub>) 666.1783; found 666.1771. Anal. Calcd for C<sub>36</sub>H<sub>42</sub>O<sub>2</sub>S<sub>5</sub>: C, 64.82; H, 6.35. Found C, 63.40; H, 6.52.

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- (24)see Chapter 4, section 5.8 for synthetic details
- (25)Budget sensors SiNi AFM probes.
- (26)Budget sensors ElectriCont-E AFM probes.

# Chapter 4

# Hierarchical Assembly of Block Copolymer-based Supramolecules with Hydrogen-bonded Oligothiophene Semiconductor Side Chains

## Abstract

A modular approach to assemble oligothiophene semiconductors and control their macroscopic alignment in thin films is presented. Quaterthiophene and sexithiophene organic semiconductors are attached to either poly(4-vinylpyridine) or poly(styrene)-*b*-poly(4-vinylpyridine) via non-covalent hydrogen-bonds to form supramolecular assemblies. The structure of the assemblies is studied in bulk samples by transmission electron microscopy and small angle X-ray scattering, confirming successful formation of supramolecular assemblies. Thin films are studied further by grazing incidence X-ray scattering, and their charge transporting properties are evaluated in organic field-effect transistors. The materials act as p-type semiconductors in field-effect transistors with field-effect mobilities of  $10^{-7} - 10^{-4}$  cm<sup>2</sup>/Vs. Since the organic semiconductors and polymers can be readily exchanged, this modular supramolecular approach is a viable method for the fabrication of functional, nanostructured organic semiconductor films.

## 1. Introduction

Organic electronic materials with well-controlled nanostructures are ideal for low cost, high efficiency device fabrication. While the synthesis of organic semiconductors is well-developed, the control of their macroscopic alignment in thin films is more difficult to achieve. Often the dewetting of the organic semiconductor makes it difficult to fabricate devices using solution processing. Block copolymers (BCPs) phase separate and form well-defined arrays of microdomains, tens of nanometers in size.<sup>1,2</sup> Thin films of conjugated BCP with microdomains oriented normal to the surface over macroscopic areas are of particular interest since they provide ideal morphologies for high efficiency organic photovoltaics (OPVs) or light emitting diodes (OLEDs).<sup>3-7</sup> However, in the case of rod-coil type conjugated copolymers where one block is a conducting polymer, it is difficult to manipulate the BCP morphology due to the strong interactions between the rod blocks.<sup>8-11</sup> Electronic properties can also be built-in through the covalent attachment of conjugated molecules to the side chains of one block of the BCP.<sup>6,12-15</sup> However, the generality of this approach is limited, since the synthesis of such block copolymers is challenging, as monomers containing conjugated molecules have limited solubility and the covalently linked side-groups significantly reduce the mobility of the polymer chain. Control of the orientation of the BCP microdomains in thin films is required to optimize device performance, but this is often difficult to achieve with conjugated BCPs due to their poor solubility, low mobility and high tendency to aggregate.

Supramolecular assemblies can be readily constructed by attaching small molecules to pendant functionalities of one of the blocks via hydrogen bonding, electrostatic interactions or metal ligation.<sup>16-18</sup> In the case of BCP-based supramolecules, the assemblies phase separate into arrays of well-defined microdomains similar to what is seen in BCPs alone. The small molecules order within the microdomains that generate a rich library of supramolecular assemblies such as lamellae-within-lamellae and cylinders-within-lamellae.<sup>17,19-22</sup> In thin films, the macroscopic orientation of hierarchical nanostructures can be simultaneously tailored over multiple length scales, i.e. the small molecule assembly at a few nanometers and the BCP assembly on the tens of nanometers length scale.<sup>18,23-27</sup>

Constructing supramolecules using conjugated oligomers imparts functionality to the block copolymer domains through non-covalent interactions between the polymer block and the organic semiconductor. Tailored hierarchical structures allow spatial and orientational control over the BCP microdomains and functional small molecules.<sup>19-23,25,28</sup> The non-covalent linking of an organic semiconductor onto a BCP block may preserve the chain mobility of the polymer necessary for ordered self-assembly during annealing and eliminate the constraints that would result from covalent bonding to the polymer chain hindering crystallization of the small molecule within the microdomains. The supramolecular approach circumvents some of the synthetic challenges inherent to the preparation of conjugated BCPs and also enables the tailoring of electronic properties without the need to synthesize new polymers.

In this chapter, the rational design and preparation of quaterthiophene (4T) and sexithiophene (6T) semiconductors that bear phenol substituents for hydrogen bonding to pyridine is presented. Self-assembly is studied on multiple length scales: tens of nanometers for BCP microphase separation, nanometers for non-covalent comb block lamellae, and sub-nanometer for intermolecular packing. A detailed analysis of the hierarchical structure of poly(styrene)-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) assemblies with **4T** in the bulk and thin films is presented first to demonstrate our spatial and orientational control of the semiconductor, which is shown to

function in organic field-effect transistors (OFETs). Then, a comparison of the behavior and properties of 4T and 6T in supramolecular assemblies is presented that has implications for the further development of this method for applications in functional electronic devices.



Figure 1. Phenol-pyridine hydrogen bonds facilitate formation of a non-covalent comb block copolymer architecture. The three-component design of the non-covalent side group allows tailoring of its properties for the desired application.

## 2. Results and Discussion of 4T

2.1 Synthetic Design and Thermal Properties of 4T. 5"'-(3,7-Dimethyloctyl)-5-(3-(3hydroxyphenyl)propyl)-[2,2';5',2'';5'',2''']quarterthiophene, a semiconductor with a pendant phenol moiety identified as "4T," was designed to hydrogen bond to the 4-vinylpyridine units of either a homopolymer, P4VP(46.7K), or a BCP, PS(40K)-b- P4VP(5.6K) as shown in Figure 1. The resultant supramolecules are identified as  $PS-b-P4VP(4T)_r$  and  $P4VP(4T)_r$  (in which r denotes the ratio of 4T to 4VP unit). As mentioned, the end group of 4T is a phenolic moiety that hydrogen-bonds to the pyridyl side chains of the polymer; this is attached through a short spacer to the semiconducting quaterthiophene and a terminal alkyl group is used to tailor the crystallinity and improve the solubility of 4T. A delicate balance between several competing processes including BCP phase separation, macrophase separation of the BCP and semiconductor, and crystallization of the semiconductor is required in order to obtain the desired hierarchical assemblies. The favorable interaction between the phenolic end group of the semiconductor and the pyridyl side group of the BCP must balance the tendency of the quaterthiophene semiconductor to crystallize and phase separate from the BCP as a result of strong  $\pi$ - $\pi$  interactions. The crystallization and melting temperatures of the semiconductor must also be tailored such that the amorphous state of the semiconductor is accessible without completely breaking its non-covalent link to the BCP side groups. This will provide some mobility to the comb block while preserving the integrity of the hierarchical assemblies. A solution to this problem is to inhibit crystallization of the quaterthiophene through the use of a branched alkyl chain, while preserving its ability to transport charge.

The target disubstituted quaterthiophene was assembled via cross-coupling of functionalized 2,2'-bithiophene partners. First, 2,2'-bithiophene was metallated with *n*-BuLi and quenched with **1** to yield the alkylated product **2**. The benzyl ether **2** was converted to the free phenol **3** with TMS iodide generated *in situ*. A Boc protecting group was then installed to yield **4**, which could be cleanly brominated with NBS at the unsubstituted bithiophene  $\alpha$ -carbon to yield coupling partner **5**, as shown in scheme 1. Coupling partner **7** was prepared by treating 2,2'-bithiophene with *n*-BuLi and quenching with 3,7-dimethyloctyl bromide to yield **6**, which was treated again with *n*-BuLi and quenched with trimethylstannyl chloride, as shown in scheme 2. A Stille cross-coupling of **5** and **7** followed by removal of the Boc group with silica yielded **4T**, as shown in scheme 3.

Scheme 1





Figure 2. DSC thermogram of 4T from the second scan.

The **4T** molecule is highly soluble in various organic solvents, such as chloroform, and differential scanning calorimetry reveals a pair of endotherms at 126 and 138 °C upon heating and exotherms at 142 and 106 °C upon cooling, as shown in Figure 2. The first transition is significantly lower than the melting point of unsubstituted quaterthiophene, which is in excess of 200 °C. The H-bond between the phenol group and the 4VP is stable at ~110°C and is not significantly reduced until ~130 - 150 °C.<sup>29</sup> The melting temperature of **4T** is therefore on the edge of the temperature range necessary to enable annealing manipulations of the BCP assemblies in thin films.



**Figure 3.** SAXS profiles of **4T** and P4VP(**4T**)<sub>1</sub> confirming the formation of hydrogen bonds between **4T** and the 4VP unit to form a P4VP(**4T**)<sub>1</sub> comb supramolecule. Lamellae of **4T** alone have a spacing of 5.6 nm while P4VP(**4T**)<sub>1</sub> forms lamellae, 6.3 nm in periodicity.

**3.2 SAXS and TEM Characterization of 4T Supramolecules.** Characterization of bulk film samples was performed with SAXS and TEM to demonstrate that the self-assembly of **4T** with

P4VP was successful and to gain insight into the hierarchical structure produced. SAXS was used to investigate the phase behavior of **4T**, P4VP(**4T**)<sub>1</sub>, PS-*b*-P4VP(**4T**)<sub>1</sub>, and PS-*b*-P4VP(**4T**)<sub>1.5</sub> in the bulk. The SAXS profiles of **4T** and P4VP(**4T**)<sub>1</sub> are shown in Figure 3. For **4T** alone, two diffraction peaks, q = 0.11 and  $0.22 \text{ Å}^{-1}$  are seen indicating that **4T** alone forms lamellar structures with a periodicity of ~5.7 nm, which corresponds to roughly twice the molecular length of **4T**. Upon hydrogen bonding of **4T** to P4VP to form P4VP(**4T**)<sub>1</sub>, similar diffraction peaks are also seen at q = 0.096 and  $0.194 \text{ Å}^{-1}$ , corresponding to a lamellar spacing of ~6.5 nm. This increased spacing is also observed in PS-*b*-P4VP(**4T**)<sub>1</sub>. Molecular modeling suggests that it may be due to the space occupied by P4VP. The full-width at half maximum (FWHM) also decreases upon attaching **4T** to P4VP, indicating the P4VP(**4T**)<sub>1</sub> lamellae are more uniform than those of **4T**. The crystalline structure of pristine **4T** persists, as indicated by the small peak at  $q = 0.114 \text{ Å}^{-1}$ , which suggests that a small fraction of free **4T** exists in the films while most of the **4T** is incorporated into the P4VP(**4T**)<sub>1</sub> comb.

In the SAXS profile of PS-*b*-P4VP(**4T**)<sub>1</sub>, shown in Figure 4a, the first order diffraction that originated from BCP assembly is seen at  $q^* = 0.0186 \text{ Å}^{-1}$ , with diffraction peaks at 2q\*, 3q\* and 4q\*, a characteristic of lamellar morphology with a periodicity of ~33.7 nm. In addition, diffraction peaks at q = 0.096 and  $0.194 \text{ Å}^{-1}$  were observed, indicating a periodicity of ~6.3 nm, originating from P4VP(**4T**)<sub>1</sub> lamellae assembly. Thus, the SAXS results indicate that PS-*b*-P4VP(**4T**)<sub>1</sub> self-assembles into lamellae-within-lamellae hierarchical structure. The SAXS profiles for **4T** and P4VP(**4T**)<sub>1</sub> showed similar results (see Figure 3).



**Figure 4.** (a) SAXS profile and (b) TEM image of PS-*b*-P4VP(**4T**)<sub>1</sub>, showing a lamellae-within-lamellae morphology. Rectangular microdomains are also seen. In the SAXS profile, diffraction peaks indicating BCP lamellar morphology are labeled as *q*\*, 2*q*\*, 3*q*\*, 4*q*\*. (c, d) TEM images of PS-*b*-P4VP(**4T**)<sub>1.5</sub>. (c) The TEM image shows a mixture of two BCP morphologies. One is well ordered perforated-lamellar morphology (right hand side) and the other is lamellar with many defects. Panel 2d clearly shows that two lamellae are jointed via a stack of lamellae with a smaller periodicity of ~6 nm (circled region).

Figure 4b shows the TEM image of PS-*b*-P4VP(4T)<sub>1</sub> in the bulk where the lamellar microdomains can be clearly seen, consistent with the SAXS profile. In addition to the lamellae, there are also rectangular-shaped microdomains. The sizes of the rectangular microdomains are not uniform, indicating an inhomogeneous distribution of 4T within the supramolecular assembly in these regions. The formation of rectangular microdomains may also be attributed to the presence of "T"-junction defects.<sup>30</sup> It is very likely that the PS-*b*-P4VP(4T)<sub>1</sub> supramolecule

mainly forms lamellar microdomains. Once **4T** crystallizes the comb block, P4VP(**4T**)<sub>1</sub>, stiffens. Packing rigid P4VP(4T)<sub>r</sub> lamellae into a curved morphology requires the lamellae to spread apart, which is not energetically favorable. Despite the energetic cost to stabilize sharp curvatures in the rectangular microdomains or the "T"-junction defects, the  $\pi$ - $\pi$  interactions between the  $P4VP(4T)_1$  comb blocks are strong enough to overcome the energetic barrier and stabilize the morphologies shown in Figure 4b. Figure 4c and 4d show the TEM images of PS-b- $P4VP(4T)_{15}$  in the bulk. Further increasing the 4T to 4VP stoichiometry to 1.5 did not result in macrophase separation and no large aggregates of 4T were observed in TEM studies. As shown in Figure 4c, the PS-b-P4VP(4T)<sub>1.5</sub> supramolecule microphase separated and formed a mixed morphology. Lamellar microdomains can be clearly seen on the left side of the image. On the right side, P4VP(4T)<sub>1.5</sub> microdomains appear to pack into hexagonal arrays embedded in the PS matrix, suggesting a cylindrical morphology. Upon addition of 4T, the volume fraction of the  $P4VP(4T)_r$  block increases. Thus, we speculate the PS-*b*-P4VP(4T)<sub>1.5</sub> supramolecule forms a mixed morphology of lamellae and perforated lamellae. In the lamellar morphology region, the ordering is poor and there are many defects. Interestingly, there are many regions where two BCP lamellae are 'fused' together by lamellae with much smaller periodicity of ~6 nm (Figure 4d). It is highly likely that these lamellae are assemblies of 4T alone, which provide a unique path to transport charges between two BCP lamellae.

Overall, the SAXS and TEM results indicate that a BCP-based supramolecular assembly with **4T** was successfully constructed without interfering with the self-assemblies of BCPs. The resultant supramolecule,  $PS-b-P4VP(4T)_r$ , formed hierarchical structures in the bulk containing BCP microdomains, tens of nanometers in periodicity and  $P4VP(4T)_1$  lamellae, ~6 nm in size.

**2.3 GISAXS Characterization of 4T Supramolecules.** Control of the orientation of BCP domains containing a supramolecular semiconductor comb block is critical to the application of these thin films in organic electronic devices. In thin films, BCP microdomains tend to orient parallel to the surface due to the preferential interaction between one block with the underlying substrate and the lower surface tension of one component. Various approaches have been used to orient BCP microdomains perpendicular to the surface, such as surface, electric and solvent fields. Recently, using model supramolecules containing alkyl-like small molecules, perpendicular orientation of BCP microdomains was achieved by tuning the small molecule loading and annealing under a solvent field.<sup>27</sup> This approach was applied here to control the macroscopic orientation of P4VP(**4T**)<sub>1</sub> and PS-*b*-P4VP(**4T**)<sub>r</sub> (r = 1, 1.5) in thin films.

Thin films of PS-*b*-P4VP(**4T**)<sub>r</sub>, ~40 - 100 nm in thickness, were spun cast onto silicon wafers without surface treatment and subsequently subjected to solvent and thermal annealing. Figure 5 shows the 2D GISAXS pattern of ~50 nm PS-*b*-P4VP(**4T**)<sub>1.5</sub> films after (a) solvent and (b) thermal annealing at ~100 – 110 °C under N<sub>2</sub> for an hour. The incidence angles ( $\alpha_{in}$ ) are in the range of 0.19 - 0.20°, and the incident x-rays penetrate the whole film and probe structural information throughout the film. For both samples, features in both  $q_z$  and  $q_y$  directions are seen. The  $q_z$  and  $q_y$  scans are plotted in Figure 5 (c) and (d), respectively. After solvent annealing, the  $q_z$  scan at  $q_y = 0.018$  Å<sup>-1</sup> shows a series of broad peaks, indicating P4VP(**4T**)<sub>r</sub> lamellae with a periodicity of ~6.2 - 6.6 nm are oriented parallel to the substrate, as illustrated in Figure 1. However, the distribution of the lamellar spacing is wide and the ordering of P4VP(**4T**)<sub>r</sub> lamellae is rather poor. The  $q_y$  scan only shows a first order diffraction peak at  $q_y = 0.017$  Å<sup>-1</sup>, corresponding to the BCP phase separation of PS-*b*-P4VP(**4T**)<sub>1.5</sub> with a periodicity of ~37 nm. Only diffraction spots, instead of rings, were seen in the GISAXS pattern, indicating the BCP microdomains are mainly oriented normal to the substrate. Similar results are also found for PS-b-P4VP(**4T**)<sub>1</sub> (see Figure 6).



**Figure 5.** GISAXS patterns of a ~50 nm PS-*b*-P4VP(**4T**)<sub>1.5</sub> thin films after (a) solvent annealing for 24 h and after (b) thermal annealing for an hour at 100 – 110 °C under N<sub>2</sub> at incident angles of 0.19 - 0.2°. The  $q_z$  scans at  $q_y = 0.018 \text{ Å}^{-1}$ (c), show the solvent and thermally annealed P4VP(**4T**)<sub>1.5</sub> lamellae, ~6.5 nm and ~5.7 nm in periodicity, respectively, are oriented parallel to the surface. The  $q_y$  scans at  $q_z = 0.025 \text{ Å}^{-1}$ (d), show the solvent and thermally annealed BCP lamellae, ~37 nm and ~52 - 55 nm in periodicity, respectively, are oriented perpendicular to the surface. All scans are extracted from the right side of the GISAXS pattern.

Thermal annealing resulted in a sharpening of peaks in the  $q_y$  and  $q_z$  scans. In the  $q_y$  scan at  $q_z = 0.025 \text{ Å}^{-1}$ , the first order diffraction at  $q_y = 0.0121 \text{ Å}^{-1}$  is significantly sharpened and second and third order diffractions at  $q_y = 0.0361$  and  $0.0592 \text{ Å}^{-1}$ , respectively, can also be seen, corresponding to lamellae with a periodicity of ~52 nm. The  $q_z$  scan at  $q_y = 0.018 \text{ Å}^{-1}$  shows a first order peak at  $q_z = 0.110 - 0.111 \text{ Å}^{-1}$ , corresponding to lamellae with a smaller periodicity of ~5.7 nm. Strong second and third peaks are also seen. Diffraction peaks along the  $q_z$  direction originate from the lamellar ordering parallel to the surface. For PS-*b*-P4VP(**4T**)<sub>1.5</sub>, this can either

be lamellar assemblies from the P4VP(4T)<sub>r</sub> comb block or 4T alone. As shown in the SAXS profiles in Figure 3, the spacing of P4VP(4T)<sub>1</sub> lamellae is 6.3 nm and that of 4T is 5.6 nm. For PS-*b*-P4VP(4T)<sub>1.5</sub>, only one peak near q = 0.11 was observed, corresponding to a periodicity of ~5.7 nm. Since the phenol-4VP H-bond has been found to be stable at 110°C, and there were no observed decreases in film thicknesses, we speculate the periodicity of P4VP(4T)<sub>r</sub> reduced upon heating due to changes in packing of the supramolecules.<sup>29</sup>



PS-*b*-P4VP(**4T**)<sub>1</sub>

**Figure 6.** GISAXS patterns of a ~60 nm PS-*b*-P4VP(**4T**)<sub>1</sub> thin films (a) after solvent annealing for 24 h and (b) after thermal annealing for an hour at 100 – 110 °C under N<sub>2</sub> at incident angles of 0.19 – 0.2°. The  $q_z$  scans at  $q_y = 0.018 \text{ Å}^{-1}$ (c), show the solvent and thermally annealed P4VP(**4T**)<sub>1</sub> lamellae, ~6.3 nm and ~5.7 nm in periodicity, respectively, are oriented parallel to the surface. The  $q_y$  scans at  $q_z = 0.025 \text{ Å}^{-1}$ (d), show the solvent and thermally annealed BCP lamellae, ~30 nm and ~52 - 55 nm in periodicity, respectively, are oriented perpendicular to the surface. All scans are extracted from the right side of the GISAXS pattern.

Films of P4VP(4T)<sub>1</sub> were prepared in an analogous fashion to the BCP samples, and the GISAXS data is shown in Figure 7. Diffraction spots are seen in the  $q_z$  direction, indicating that

the P4VP(4T)<sub>1</sub> forms lamellar domains and are mainly oriented parallel to the substrate. The spreading of the diffraction spots suggests that a small fraction of P4VP(4T)<sub>1</sub> lamellae are tilted from the parallel orientation. Figure 7b shows a schematic representation of the assembly of P4VP(4T)<sub>1</sub> in thin films. A reduction in periodicity is seen after thermal annealing, similar to the BCP based supramolecular films. Nevertheless, the increase in intensity and sharpness of the diffraction peaks indicates a large improvement in ordering and macroscopic parallel alignment of the P4VP(4T)<sub>1</sub> lamellae upon thermal annealing.



**Figure 7**. GISAXS pattern of a ~60 nm P4VP(**4T**)<sub>1</sub> thin film at an incident angle of  $0.15^{\circ}$  (a) after solvent annealing for 36 h and (c) after thermal annealing for an hour at 100 – 110 °C under N<sub>2</sub>. (d) The  $q_z$  scans at  $q_y = 0.017$  Å<sup>-1</sup>, showing the solvent and thermally annealed P4VP(**4T**)<sub>1</sub> lamellae, ~6.5 nm and ~5.6 nm in periodicity, respectively,
are oriented parallel to the surface as schematically shown in (b). Each pattern shows smaller periodicities of  $\sim 3.0$  nm,  $\sim 2.0$  nm, and  $\sim 1.5$  nm as well, likely due to various **4T** spacings. The "shoulder" observed at q < 0.1 Å<sup>-1</sup> is due to the scattering from the beamstop. Both scans are extracted from the left side of the GISAXS pattern.

Overall, the GISAXS studies confirm that  $P4VP(4T)_1$  and  $PS-b-P4VP(4T)_{1.5}$  form macroscopically oriented nano structures in thin films. The  $PS-b-P4VP(4T)_{1.5}$  microdomains resulting from the BCP phase separation are mainly oriented normal to the surface and the comb block  $P4VP(4T)_r$  forms lamellae oriented parallel to the surface. Thermal annealing improves both ordering and macroscopic alignment of the hierarchical assemblies of the supramolecules in thin films, as evidenced by the improved clarity of the diffraction spots along the  $q_z$  and  $q_y$ directions.

**2.4 4T OFET Results.** Analysis of OFET data enables the calculation of charge mobility for the organic semiconductor and also provides for a qualitative evaluation of the level of dopants and charge traps introduced into the films during the process of supramolecule formation. In order to demonstrate that our supramolecular structures are electronically functional, OFET test structures were constructed incorporating either **4T**, P4VP(**4T**)<sub>1</sub>, PS-*b*-P4VP(**4T**)<sub>1</sub> or PS-*b*-P4VP(**4T**)<sub>1.5</sub> as the active layer. While the **4T** films were observed to dewet the device substrates, decreasing the OFET device yield, uniform films of controlled thicknesses were readily cast from the P4VP(**4T**)<sub>1</sub> and PS-*b*-P4VP(**4T**)<sub>1</sub> (r = 1, 1.5) supramolecules.



**Figure 8.** A plot of |ID| (solid symbols) and  $|ID|^{1/2}$  (outlined symbols) for an unannealed **4T** device with W = 400  $\mu$ m and L = 10  $\mu$ m.

Control films of **4T** failed to provide ideal transfer curves as evidenced by the non-linear plot of  $|I_D|^{1/2}$ , as shown in Figure 8. While the film did exhibit gate-modulated conductivity, this non-ideal behavior precludes a calculation of charge mobility in these films. Thermal annealing of the **4T** films at 135 °C for 10 minutes results in a significant increase in saturation currents measured in OFETs that produce a linear plot of  $|I_D|^{1/2}$  in transfer IV curves and charge mobilities of  $10^{-4}$  cm<sup>2</sup>/Vs. Low off-currents, the minimum  $I_D$  measured in the devices, suggest a low level of doping in the pristine small molecule films.<sup>31</sup> A representative transfer plot of an annealed **4T** device is shown in Figure 9a.



**Figure 9**. (a) A plot of |ID| (solid diamonds) and  $|ID|^{1/2}$  (outlined diamonds) for a thermally annealed **4T** device with W = 400 µm and L = 10 µm. The charge mobility was calculated to be  $10^{-4}$  cm<sup>2</sup>/Vs. (b) A transfer IV plot for a P4VP(**4T**)<sub>1</sub> device with W = 400 µm and L = 20 µm. The on/off ratio of the devices is  $10^{3}$ .



Figure 10. A set of three consecutive (squares, circles, then triangles) scans of a thermally annealed (a) 4T and a (b) P4VP(4T)<sub>1</sub> OFET. Consecutive scanning of the 4T device gives nearly identical IV curves while bias stress is observed in the P4VP(4T)<sub>1</sub> device.

Having validated **4T** as an organic semiconductor in p-channel OFETs, we probed the charge transporting capabilities of the P4VP(**4T**)<sub>1</sub> comb structure. The P4VP(**4T**)<sub>1</sub> composite films functioned as the active layer in OFETs with charge mobilities of  $10^{-4}$  cm<sup>2</sup>/Vs. A representative transfer IV plot is shown in Figure 9b. The saturation current levels were similar to those obtained in annealed pristine **4T** OFETs, and off-currents remained low. Consecutive scans of V<sub>G</sub> showed bias stress effects (BSEs) in the devices (see Figure 10). Charge traps or defect formation in OFET device channels are thought to produce BSEs.<sup>32-35</sup> Since these effects were absent in **4T** OFETs, defect formation or charge trapping that leads to bias stress effects cannot be attributed to the structure of **4T**. It is unclear if the chemistry of P4VP leads to defect

formation in active device channels or if the  $P4VP(4T)_1$  films simply contain more trap sites due to the greater thickness of the films obtained from the supramolecule.<sup>35</sup>

Brief thermal annealing of P4VP(4T)<sub>1</sub> films at temperatures of 135-145 °C or more extended 1 h annealing at 100 °C did not increase saturation currents, or eliminate BSEs, despite the fact the GISAXS data clearly showed that the ordering and macroscopic alignment of 4T in supramolecule films were enhanced significantly after thermal annealing. In fact, the saturation currents measured in OFETs decreased. The quality of the semiconductor-dielectric interface is critical to OFET performance because the majority of charge transport occurs in the first few molecular layers of the oligothiophene semiconductor.<sup>36,37</sup> P4VP has a very favorable interfacial interaction with the oxidized silicon substrate.<sup>24,25</sup> During solvent annealing, chloroform mediates the interactions between the P4VP and **4T** with the underlying substrate, possibly preventing significant enrichment of P4VP at the interfaces. With thermal annealing it is highly likely that P4VP enriches at the semiconductor-dielectric interface, possibly deteriorating OFET performance. However, making the OFET substrates more hydrophobic by reaction with trichloropropylsilane prior to film casting did not improve the device results obtained with annealed films, which makes this explanation unlikely. Instead, thermal annealing may result in the formation of crystalline domains with insufficient connectivity to allow enhancement of field-effect mobility.<sup>38</sup>

Top-contact devices were prepared with PS-*b*-P4VP(4T)<sub>1</sub> films to determine if the domains of P4VP(4T)<sub>1</sub> within the BCP film could provide conductive pathways in OFET channels. Device testing yielded saturation currents an order of magnitude lower than 4T and P4VP(4T)<sub>1</sub> films. The threshold voltages of the devices are generally shifted to slightly more negative values, which suggest that restriction of 4T into block copolymer lamellae hampers the injection of mobile charge carriers. The weight percent of 4T in these films was 42 % compared to 85 % in P4VP homopolymer films.



**Figure 11.** A comparison of IV plots for PS-*b*-P4VP(**4T**)<sub>r</sub> OFETs where r = 1 (black) and r = 1.5 (red). The devices are the same geometry with  $W = 200 \ \mu\text{m}$  and  $L = 10 \ \mu\text{m}$ . The charge mobility was calculated to be  $10^{-6}$  and  $10^{-4} \ \text{cm}^2/\text{Vs}$  for r = 1 and 1.5, respectively. The on/off ratio for PS-*b*-P4VP(**4T**)<sub>1.5</sub> OFETs was  $10^3$ .

Increasing the ratio of **4T** to 4VP enhances the **4T** fraction in the film. It also increases the backbone stiffness of the P4VP block and possibly the comb block packing. The TEM images shown in Figure 5 (c) and (d) show that the **4T** lamellae bridge the BCP lamellae in different grains and improve the electronic connectivity between BCP lamellae in PS-*b*-P4VP(**4T**)<sub>1.5</sub> films. To determine if this effect would increase charge mobility in the BCP films, PS-*b*-

P4VP(4T)<sub>1.5</sub> OFETs were fabricated as described above. A comparative plot of saturation currents in PS-*b*-P4VP(4T)<sub>r</sub> OFETs, where r = 1 and 1.5, is shown in Figure 11. The saturation currents in these devices increased an order of magnitude relative to analogous PS-*b*-P4VP(4T)<sub>1</sub> OFETs, and the charge mobility of PS-*b*-P4VP(4T)<sub>1.5</sub> was calculated to be 10<sup>-4</sup> cm<sup>2</sup>/Vs, which is comparable to 4T and P4VP(4T)<sub>1</sub>.

Although effectively measuring the mobility of charge in a thin layer (~5-10 nm) of the organic semiconductor next to the SiO<sub>2</sub> dielectric instead of the bulk property,<sup>36,37</sup> the OFET experiments demonstrate the functionality of the supramolecular film assemblies. A bottom-gate and top-contact test structure requires a film with semiconducting properties through its entire thickness for measurement of gate-modulated current.<sup>39</sup> Furthermore, the affinity of P4VP for SiO<sub>2</sub> and the tendency of **4T** to dewet that surface decreases the likelihood that a segregated layer of **4T** transports charge at the dielectric surface. Thin films of PS-*b*-P4VP(**4T**)<sub>1.5</sub> were also prepared on either silicon nitride or silicon oxide grids to carry out TEM studies on the in-plane structure of the supramolecules. No large aggregates of **4T** were observed, confirming that **4T** incorporates into the P4VP(**4T**)<sub>r</sub> block in thin films. Therefore, the OFET data suggests that the P4VP(**4T**)<sub>1</sub> and PS-*b*-P4VP(**4T**)<sub>r</sub> (r = 1, 1.5) supramolecules indeed function as a p-type semiconductors.

## 3. Results and Discussion of 6T

**3.1 Synthetic Design and Thermal Properties of 6T.** As noted earlier, the synthetic design of **4T** was motivated by the need to access a fluid state of composite films during annealing. To this end, a remotely branched alkyl chain was appended to a quaterthiophene semiconductor, which increased the solubility of the molecule and depressed phase transitions to well below 200 °C. An alternative method is to block the normal edge-to-face packing of oligothiophenes with  $\beta$ -alkyl substitution –a substitution pattern ubiquitous in polythiophene chemistry that grants exceptional solubility accompanied with high charge mobility.<sup>41</sup> This approach was realized with a 3,4"'-dihexyl quaterthiophene building block that was coupled to a phenol-functionalized bithiophene coupling partner to yield **6T**. The structure of **6T** is shown in Figure 12.



Figure 12. The  $\beta$ -alkyl substituted sexithiophene 6T is highly soluble in chlorinated solvents.

The target sexithiophene was assembled via cross-coupling of a functionalized 2,2'bithiophene (Scheme 4) and a  $\beta$ -dihexylquaterthiophenyl stannane. First, 2,2'-bithiophene was metallated with *n*-BuLi and quenched with dibromopropane to yield the alkylated product 1, which could be cleanly brominated with NBS at the unsubstituted bithiophene  $\alpha$ -carbon to yield 2. A Boc protected phenol group was introduced via nucleophilic substitution of the bromide with tert-butyl (3-hydroxyphenyl) carbonate under basic conditions, to yield coupling partner 3, as shown in scheme 4. Coupling partner 4 was prepared by treating 3,3"'-dihexyl-[2,2':5',2":5",2"]-quaterthiophene with *n*-BuLi and quenching with trimethylstannyl chloride. A Stille cross-coupling of 3 and 4 followed by removal of the Boc group with silica yielded 6T, as shown in scheme 5.

Scheme 4



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DSC analysis of **6T** reveals that the molecule melts below 100 °C, as shown in Figure 13. The DSC thermogram exhibits only a single endotherm upon heating, which indicates that **6T** lacks a mesophase like that observed for the rod-shaped **4T**. Despite possessing a longer conjugated system of six thiophene units, **6T** melts at a significantly lower temperature than **4T**. This fact demonstrates the powerful effect of the alkyl substituents at inhibiting the crystallization of the oligothiophene.



Figure 13. DSC thermogram of 6T

**3.2 TEM and GISAXS Characterization of 6T Supramolecules.** TEM and GISAXS data are presented here for PS-*b*-P4VP(**6T**)<sub>1.5</sub> bulk and thin film samples, respectively, to demonstrate that supramolecular assembly is successful. The TEM image, shown in Figure 14a., reveals that PS-*b*-P4VP(**6T**)<sub>1.5</sub> forms a cylindrical morphology, which is in contrast to the lamellar morphology formed by PS-*b*-P4VP(**4T**)<sub>1.5</sub>. Because **6T** is a larger molecule than **4T**, the weight fraction of the P4VP(**6T**) comb block is greater than that of P4VP(**4T**) in BCP films. This increase in molecular weight explains the contrast in phase behavior.

In thin films, the BCP microdomains orient relative to the substrate, which results in scattering in the  $q_z$  direction for the comb-block lamellae and scattering in the  $q_y$  direction for the BCP microdomains. The absence of semicircular signals shows that peak spreading from a lack of preferential orientation is minimal. These results are directly analogous to those obtained for **4T** on the nanometer length scale. However, the charge transporting properties of the supramolecular assembly will depend on intermolecular  $\pi$ - $\pi$  interactions between the **6T** molecules.



**Figure 14.** (a) TEM image of a PS-*b*-P4VP(**6T**)<sub>1.5</sub> sample. The image shows PS cylinders in a P4VP(**6T**) matrix. (b) GISAXS analysis shows that BCP domains (37-40 nm in periodicity) are oriented normal to the substrate in thin films. Comb-block lamellae produce a periodicity of 5.5 nm.

**3.3 OFET Results for 6T.** Films were cast of **6T** and also  $P4VP(6T)_1$  to act as the active layer in OFETs. Thin films of **6T** proved to be more uniform than those obtained with **4T** in terms of surface coverage, and annealing films at 85 °C was required to yield functional OFETs. The hole mobility of **6T** was calculated to be  $10^{-5}$  cm<sup>2</sup>/Vs, which is an order of magnitude lower than that obtained for **4T**. This result is consistent with the well-known tendency of  $\beta$ -alkyl oligothiophenes to provide lower charge mobilities than their  $\alpha$ -alkyl counterparts.<sup>48</sup> Factors such as backbone twisting and decreased overall crystallinity in thin films are believed to contribute to this effect. More interesting is the decreased OFET performance of P4VP(**6T**) supramolecular films relative to **6T** films, as seen in Figure 15. Coordination of **6T** to P4VP results in a drop of two orders of magnitude in charge mobility and saturation current in transistors, which is in contrast to the identical performances of **4T** and P4VP(**4T**) in OFETs.



**Figure 15.** Transfer curves shown for (a) **6T** thin film cast from chloroform and annealed at 85 °C for 10 minutes and (b)  $P4VP(6T)_1$  thin film cast from chloroform and solvent annealed. The device dimensions for (a) and (b) are W = 400 and  $L = 20 \ \mu\text{m}$ . The charge mobility is (a)  $10^{-5} \text{ cm}^2/\text{Vs}$  and (b)  $10^{-7} \text{ cm}^2/\text{Vs}$ .

**3.4 GIWAXS Characterization for 4T and 6T.** Intermolecular ordering results in periodicities that are less than 1 nm, and therefore lead to wide angle X-ray scattering. Small molecule crystallinity is known to be critical for high charge mobility, so the ability of our non-covalent side chains to pack in a crystalline fashion when coordinated to P4VP will be critical for the device performance of our supramolecular assemblies. Therefore, grazing incidence wide angle X-ray scattering (GIWAXS) was used to evaluate the crystallinity of the supramolecular comb structure in thin films.

Thin films were chosen so that the weight fraction of **4T** and **6T** was about 60 % in each case, and the stoichiometry of small molecule to P4VP repeat unit was 1.5:1. Figure 16 shows the scattering patterns obtained. While PS-*b*-P4VP(**4T**)<sub>1.5</sub> films produce scattering patterns with many signals at high q, or wide angles, the PS-*b*-P4VP(**6T**)<sub>1.5</sub> film produces only low q signals. This lack of high q signals means that PS-*b*-P4VP(**6T**)<sub>1.5</sub> films do not possess structure that is periodic on sub-nanometer length scales. Clearly, **4T** forms a crystalline comb block in supramolecular assemblies, but **6T** does not.



Figure 16. GIWAXS scattering patterns for (a) PS(24k)-b-P4VP(9.5k)(4T)<sub>1.5</sub> and (b) PS(40k)-b-P4VP(5.6k)(6T)<sub>1.5</sub>.

Films of **6T** were analyzed to determine if the molecule would produce crystalline films in the absence of P4VP. An identical experiment with **4T** was not possible because of the poor film quality obtained without polymer. But interestingly, annealed films of **6T** actually produce many

high q signals, as shown in Figure 17. This result explains why 6T films transport charge better than P4VP(6T) films. And since small molecule crystallinity persists in P4VP(4T) comb assemblies, those films transport charge just as well as films of pure 4T.



Figure 17. GIWAXS scattering pattern for an annealed 6T film.

# 4. Conclusions

We have shown that a molecular design strategy involving the non-covalently linking of organic semiconductors to a polymer chain successfully allows ordering of semiconductor molecules into hierarchical assemblies with vertically aligned microdomains. The supramolecular comb block, P4VP(4T or 6T)<sub>r</sub>, transports charge in OFET channels, which proves that these films can act as nanostructured semiconductor composites. The charge mobilities of the supramolecular assemblies depend on the ability of non-covalent side chains to achieve crystalline packing. While both 4T and 6T feature almost identical H-bonding groups separated from the oligothiophene moieties by an alkyl spacer, 4T side chains crystallize while edge-to-face packing of 4T, in contrast to the relatively unfavorable slip-stacking of 6T.

While the charge mobilities of **4T** and P4VP(**4T**)<sub>r</sub> measured in OFETs are several orders of magnitude lower than commonly used organic semiconductors like  $\alpha, \omega$ -dihexylquaterthiophene<sup>40</sup> and poly(3-hexylthiophene),<sup>41</sup> the charge transporting capabilities of these films are comparable to organic semiconductors that have seen use in OLEDs<sup>42</sup> and OPVs.<sup>43,44</sup> Furthermore, this mobility value is greater than that measured in poly(*p*-phenylene vinylene) films where supramolecular assembly is not possible.<sup>45,46</sup> This system provides a versatile method to access films with spatial and orientational control of the semiconductor, which is otherwise difficult. This approach based on non-covalent assembly of components may be readily applied to other small molecules with improved electronic properties for high performance device fabrication. However, future molecules must be designed to favor the formation of crystalline supramolecular comb polymer structures.

# 5. Methods

**5.1 Materials.** PS(40,000)-*b*-P4VP(5,600) (PDI=1.09), and P4VP(46,700) (PDI=1.14) were purchased from Polymer Source, Inc. Chloroform purchased from Fisher was filtered through basic alumina. N-bromosuccinimide was recrystallized from water prior to use. All other chemicals were purchased from Aldrich and used as received. All reactions were performed under dry  $N_2$  unless otherwise noted. All extracts were dried over MgSO<sub>4</sub> and solvents were

removed by rotary evaporation with aspirator pressure. Flash chromatography was performed using Merck Kieselgel 60 (230-400 mesh) silica. Methylene chloride, THF, toluene, pyridine, DMF, and triethylamine were purchased from Fisher and vigorously purged with nitrogen for 1h. The solvents were further purified by passing them under nitrogen pressure through two packed columns (Glass Contour) of neutral alumina (for THF and methylene chloride), neutral alumina and copper(II) oxide (for toluene), or activated molecular sieves (for DMF).

**5.2 Sample Preparation**. The PS-*b*-P4VP or the P4VP was first dissolved in chloroform to form 1% - 2% (wt/v) stock solutions. The desired amount of **4T** was dissolved in chloroform. The polymer solution was then added to the **4T** solution, followed by stirring overnight. Thin films were prepared by spin-coating the mixed solutions onto silicon wafers at spinning speeds between 1000 and 4000 rpm. **4T** is light and oxygen sensitive and so cautions were paid to avoid light exposure during the sample preparation process. Sample thicknesses were measured using a Filmetrics<sup>TM</sup> F20 interferometer. For solvent annealing, thin films were placed together with a beaker of 40 ml chloroform at 22 °C inside an inverted dish (170 Dia. x 90 H mm) on which a ~ 2 kilogram weight was loaded for 24-48 hours. For thermal annealing, samples were wrapped in aluminum foil inside an inverted dish and placed in an oven under a nitrogen atmosphere at 100°C for 1 hour.

**5.3 Small Angle X-ray Scattering (SAXS) and Grazing Incidence Small Angle X-ray Scattering (GISAXS)**. Bulk samples were prepared by casting and drying the PS-*b*-P4VP(4T)<sub>1</sub> and P4VP(4T)<sub>1,1.5</sub> solutions in a Teflon® beaker, inside an inverted dish, and allowing the solvent to evaporate over 48 hours. Samples were then thermally annealed at ~100°C under vacuum overnight and then slowly cooled to room temperature. The SAXS data were collected on beamline 7.3.3 in the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory. X-rays, with a wavelength of 1.240 Å (10KeV) were used, and the scattering spectra were collected on an ADSC Quantum 4u CCD detector with an active area of 188 mm by 188 mm (2304 by 2304 pixels) and a dynamic range of 16 bit. The scattering profiles, after a 20 s collection time, were obtained by integrating the 2-D scattering pattern. GISAXS measurements were made on beamline 7.3.3 in ALS and beamline 8-ID-E in the Advanced Photon Source (APS) at the Argonne National Laboratory. X-ray wavelengths of 1.240 Å (ALS) and 1.687 Å (APS) were used. The scattering profiles were collected on a Mar-CCD at APS and an ADSC Quantum 4u CCD detector at ALS. Line-averaged intensities are reported as *I* vs. q, where  $q = (4\pi/\lambda)*\sin(\theta/2)$ ,  $\lambda$  is the wavelength of incident x-rays and  $\theta$  is the scattering angle.

**5.4 Transmission Electron Microscopy (TEM)**. The same samples used for SAXS was embedded in resin and cured at 60 °C overnight before being microtomed for TEM imaging. The thin sections of PS(40,000)-*b*-P4VP(5,600)(4T)<sub>1</sub> were exposed to iodine vapor for 10 minutes that selectively stains the P4VP(4T) block to enhance the contrast. TEM images were collected on a FEI Tecnai 12 transmission electron microscope at an accelerating voltage of 100kV.

**5.5 OFET Fabrication.** The devices were fabricated on low resistivity n-type silicon wafers, using 1000 Å of thermally grown  $SiO_2$  as the dielectric, in top contact geometry. Sample thin films were prepared as previously described. Gold contacts were patterned on top of the films, using various shadow masks, giving channel lengths from (5 to 40)  $\mu$ m and widths from (200 to 400)  $\mu$ m. All devices were tested as p-type OFETs in the accumulation regime and saturation

mobilities were calculated using the equation,  $\mu = g_m^2 / 2I_D C_{ox}(W/L)$ , where  $g_m = transconductance$ ,  $I_D = current$  measured at the drain electrode,  $C_{ox} = capacitance$  of the insulator, W = width of the electrodes, and L = channel length. The electrical measurements were performed in a nitrogen atmosphere using an Agilent 4156C Precision Semiconductor Parameter Analyzer.

**5.6 Characterization.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded with Bruker AV-300, AVQ 400, or DRX-500 instruments using CDCl<sub>3</sub> as the solvent. High Resolution Mass Spectometry (HRMS) using Fast Atom Bombardment (FAB) was done with a Micromass ZAB2-EZ double focusing mass spectrometer (BE geometry). Elemental analyses were performed at the UC Berkeley Microanalysis Laboratory. Differential scanning calorimetry (DSC) measurements were performed on a TA instrument DSC Q200. The samples (~2 mg) were heated from 30 °C to 200 °C at a heating rate of 10 °C/min under nitrogen.

### 5.7 Synthetic Details for 4T.

**1-(benzyloxy)-3-(3-bromopropyl)benzene (1)** was prepared according to a previously published procedure.<sup>47 1</sup>H NMR (400 MHz):  $\delta$  2.13-2.20 (m, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 3.39 (t, *J* = 6.4 Hz, 2H), 5.06 (s, 2H), 6.81-6.84 (m, 3H), 7.20-7.24 (m, 1H), 7.32-7.46 (m, 5H). <sup>13</sup>C NMR (100 MHz):  $\delta$  33.16, 34.02, 34.04, 69.96, 112.37, 115.36, 121.28, 127.58, 128.01, 128.63, 129.55, 137.05, 142.23, 158.98.

**5-(3-(benzyloxy)phenyl)propyl)-[2,2']bithiophene (2).** A solution of 2.18 g (13.1 mmol) 2,2'-bithiophene in 80 mL THF was cooled to -78 °C and 4.22 mL (10.6 mmol) 2.5 M *n*-BuLi in hexanes was added slowly via syringe. The mixture was stirred at -78 °C for 1 hour and then 2.68 g (8.8 mmol) **1** was added via syringe. The mixture was then stirred at room temperature overnight followed by evaporation of the solvent under reduced pressure. The resulting oil was purified by flash chromatography through silica using 5% ethyl ether in hexanes as the eluent. The solvent was evaporated and the product dried *in vacuo* to afford 1.76 g (51 %) of a white solid. <sup>1</sup>H NMR (400 MHz):  $\delta$  1.98-2.06 (m, 2H), 2.68 (t, J = 7.6 Hz, 2H), 2.82 (t, J = 7.4 Hz, 2H), 5.07 (s, 2H), 6.69 (d, J = 3.2 Hz, 1H), 6.81-6.84 (m, 3H), 6.99-7.01 (m, 2H), 7.11 (d, J = 3.6 Hz, 1H), 7.17 (d, J = 5.2 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.31-7.46 (m, 5H). <sup>13</sup>C NMR (100 MHz):  $\delta$  29.47, 32.85, 35.05, 69.87, 112.03, 115.19, 121.17, 123.02, 123.37, 123.76, 124.97, 127.49, 127.66, 127.90, 128.54, 129.33, 134.94, 137.06, 137.82, 143.42, 144.53, 158.85. HRMS (FAB) *m/z* calc for (C<sub>24</sub>H<sub>22</sub>OS<sub>2</sub>) 390.1112; found 390.1117. Anal. Calcd for C<sub>24</sub>H<sub>22</sub>OS<sub>2</sub>: C, 73.81; H, 5.68; S, 16.42. Found C, 74.11; H, 5.45; S, 16.29.

**3-(3-([2,2']bithiophen-5-yl)propyl)phenol (3).** A mixture of 1.40 g (3.6 mmol) **2** and 1.6 g (10.7 mmol) NaI was dissolved in 20 mL anhydrous acetonitrile and 1.17 g (10.7 mmol) chlorotrimethylsilane was added via syringe. The resulting mixture was stirred at 50 °C overnight and then quenched with methanol. The solvent was evaporated and the resulting mixture was dissolved in 100 mL ethyl acetate and washed twice with 1 M HCl and water and once with brine. The organic layer was dried and the solvent evaporated. The resulting product was purified by flash chromatography through silica using 20% ethyl acetate in hexanes. The solvent was then evaporated and the product was dried *in vacuo* to afford 1.02 g (94%) of a white solid. <sup>1</sup>H NMR (400 MHz):  $\delta$  1.97-2.06 (m, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.82 (t, *J* = 7.4 Hz, 2H), 4.66 (s, 1H), 6.66 (m, 3H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.99-7.01 (m, 2H), 7.11 (dd, *J* =

1.0 Hz and 3.4 Hz, 1H), 7.15-7.18 (m, 2H). <sup>13</sup>C (100 MHz):  $\delta$  29.54, 32.86, 34.94, 112.85, 115.41, 121.01, 123.21, 123.46, 123.85, 125.05, 127.73, 129.80, 135.04, 137.89, 143.83, 144.55, 155.54. HRMS (FAB) *m*/*z* calc for (C<sub>17</sub>H<sub>16</sub>OS<sub>2</sub>) 300.0643; found 300.0635. Anal. Calcd for C<sub>17</sub>H<sub>16</sub>OS<sub>2</sub>: C, 67.96; H, 5.37; S, 21.35. Found C, 68.11; H, 5.28; S, 21.21.

**3-(3-([2,2']bithiophen-5-yl)propyl)phenyl** *tert*-butyl carbonate (4). A mixture of 1.02 g (3.4 mmol) **3**, 0.56 mL (4.0 mmol) triethylamine, and 21 mg (0.2 mmol) DMAP was dissolved in 10 mL DCM, and 0.89 g (4.1 mmol) di-*tert*-butyl dicarbonate was added under air. The mixture was stirred for 2 hours during which time vigorous gas evolution occurred. The resulting mixture was diluted with 100 mL ethyl acetate and was washed twice with water and once with brine. The organic layer was dried and the solvent evaporated. The product was dried *in vacuo* to yield 1.30 g (96%) of a white solid. <sup>1</sup>H NMR (400 MHz):  $\delta$  1.57 (s, 9H), 1.99-2.06 (m, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.83 (t, *J* = 7.4 Hz, 2H), 6.69 (d, *J* = 3.6 Hz, 1H), 6.99-7.02 (m, 4H), 7.06 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 3.6 Hz, 1H), 7.17 (d, *J* = 5.2 Hz, 1H), 7.27-7.31 (m, 1H). <sup>13</sup>C (100 MHz):  $\delta$  27.76, 29.50, 32.77, 34.81, 83.44, 118.79, 121.30, 123.12, 123.46, 123.84, 125.13, 125.92, 127.71, 129.27, 135.09, 137.87, 143.48, 144.37, 151.16, 151.98. HRMS (FAB) *m/z* calc for (C<sub>22</sub>H<sub>24</sub>O<sub>3</sub>S<sub>2</sub>) 400.1166; found 400.1159. Anal. Calcd for C<sub>22</sub>H<sub>24</sub>O<sub>3</sub>S<sub>2</sub>: C, 65.97; H, 6.04; S, 16.01. Found C, 66.14; H, 6.32; S, 15.72.

**3-(3-(5'-bromo-[2,2']bithiophen-5-yl)propyl)phenyl** *tert-butyl* carbonate (5). A flask containing 1.29 g (3.2 mmol) 4 in 10 mL DMF was protected from light and 0.57 g (3.2 mmol) NBS was added. The mixture was stirred overnight and was then diluted with 100 mL ethyl acetate. The resulting solution was washed twice with water and once with brine. The organic layer was dried and the solvent evaporated to yield a product that was dried *in vacuo* to yield 1.48 g (97%) of a white solid. <sup>1</sup>H NMR (500 MHz):  $\delta$  1.56 (s, 9H), 1.98-2.05 (m, 2H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.81 (t, *J* = 7.3 Hz, 2H), 6.68 (d, *J* = 4.0 Hz, 1H), 6.84 (d, *J* = 4.0 Hz, 1H), 6.92 (d, *J* = 3.5 Hz, 1H), 6.94 (d, *J* = 3.5 Hz, 1H), 7.00-7.06 (m, 3H), 7.27-7.30 (m, 1H). <sup>13</sup>C (125 MHz):  $\delta$  27.68, 29.41, 32.65, 34.71, 83.40, 110.20, 118.75, 121.22, 123.10, 123.70, 125.15, 125.84, 129.22, 130.46, 133.99, 139.28, 143.31, 144.87, 151.07, 151.91. HRMS (FAB) *m/z* calc for (C<sub>22</sub>H<sub>23</sub>BrO<sub>3</sub>S<sub>2</sub>) 478.0272; found 478.0266. Anal. Calcd for C<sub>22</sub>H<sub>23</sub>BrO<sub>3</sub>S<sub>2</sub>: C, 55.11; H, 4.84; S, 13.38. Found C, 54.95; H, 4.89; S, 13.05.

**5-(3,7-dimethyloctyl)-[2,2']bithiophene (6).** A solution of 1.20 g (7.2 mmol) 2,2'-bithiophene in 40 mL THF was cooled to -78 °C and 3.4 mL (7.2 mmol) 2.1 M *n*-BuLi in hexanes was added slowly via syringe. The mixture was stirred for 1 hour at -78 °C and then 1.5 mL (7.2 mmol) 3,7-dimethyloctyl bromide was added slowly via syringe. The mixture was then stirred overnight at room temperature followed by quenching with 1 M HCl. The solvent was evaporated and the product was purified via flash chromatography with 5% DCM in hexanes. The product was dried *in vacuo* to yield 1.12 g (51%) of a colorless oil. <sup>1</sup>H NMR (400 MHz):  $\delta$  0.88 (d, *J* = 6.8, 6H), 0.93 (d, *J* = 6.4, 3H), 1.09-1.37 (m, 7H), 1.46-1.59 (m, 2H), 1.68-1.74 (m, 1H), 2.73-2.88 (m, 2H), 6.68 (d, *J* = 3.6 Hz, 1H), 6.98-7.00 (m, 2H), 7.10 (dd, *J* = 1.0 Hz and 3.4 Hz, 1H), 7.16 (dd, *J* = 5.2 Hz and 1.2 Hz, 1H). <sup>13</sup>C (100 MHz):  $\delta$  19.55, 22.70, 22.79, 24.75, 27.85, 28.04, 32.33, 37.11, 38.95, 39.36, 123.01, 123.42, 123.74, 124.62, 127.71, 134.76, 138.03, 145.65. HRMS (FAB) *m/z* calc for (C<sub>18</sub>H<sub>26</sub>S<sub>2</sub>) 306.1476; found 306.1476. Anal. Calcd for C<sub>18</sub>H<sub>26</sub>S<sub>2</sub>: C, 70.53; H, 8.55; S, 20.92. Found C, 70.82; H, 8.91; S, 20.69.

(5'-(3,7-dimethyloctyl)-[2,2']bithiophen-5-yl)trimethylstannane (7). A solution of 0.71 g (2.3 mmol) 6 in 30 mL THF was cooled to -78 °C and 1.2 mL (2.5 mmol) 2.1 M *n*-BuLi in hexanes was added slowly via syringe. The mixture was stirred for 1 hour at -78 °C and then the reaction was quenched by adding 2.3 mL (2.3 mmol) 1.0 M chlorotrimethylstannane in THF via syringe. The mixture was allowed to warm to room temperature and was stirred overnight. The solvent was evaporated and the resulting product was taken up in 100 mL ethyl acetate and washed twice with dilute aqueous HCl and once with brine. The organic layer was dried and the solvent was evaporated to yield 0.99 g (91%) of a green oil that was used without further purification. <sup>1</sup>H NMR (300 MHz):  $\delta$  0.28-0.47 (m, 9H), 0.87 (d, *J* = 6.6 Hz, 6H), 0.92 (d, *J* = 6.3 Hz, 3H), 1.07-1.33 (m, 7H), 1.44-1.60 (m, 2H), 1.67-1.75 (m, 1H), 2.70-2.89 (m, 2H), 6.67-6.68 (m, 1H), 6.97 (d, *J* = 3.6 Hz, 1H), 7.07 (d, *J* = 3.3 Hz, 1H), 7.20 (d, *J* = 3.3 Hz, 1H).

### 5"'-(3,7-dimethyloctyl)-5-(3-(3-hydroxyphenyl)propyl)-[2,2';5',2";5",2""]

quaterthiophene (4T). A flask was charged with 0.54 g (1.1 mmol) 5 and 0.81 g (1.7 mmol) 7, 38 mg Pd(PPh<sub>3</sub>)Cl<sub>2</sub> and 20 mL DMF. The mixture was degassed with one freeze-pump-thaw cycle and then stirred at 80 °C overnight. The mixture was then diluted to 200 mL with methanol and a little water to ensure complete precipitation of the crude yellow product. The solids were filtered and washed with copious amounts of water. The crude product was air dried and then dissolved in 150 mL DCM. The mixture was then heated at reflux with silica until conversion of the tert-butylcarbonate to the phenol was complete, as indicated by thin-layer chromatography. The DCM was then evaporated from the silica, which was then loaded onto a silica column. The product was eluted with 3:1 DCM:hexanes to yield 0.57 g (86%) of a yellow solid. <sup>1</sup>H NMR (500 MHz):  $\delta 0.87 \text{ (d, } J = 6.5 \text{ Hz, } 6\text{H}), 0.93 \text{ (d, } J = 6.0 \text{ Hz, } 3\text{H}), 1.14-1.33 \text{ (m, } 6\text{H}), 1.51-1.54$ (m, 3H), 1.68-1.73 (m, 1H), 1.98-2.04 (m, 2H), 2.66 (t, 7.5 Hz, 2H), 2.74-2.87 (m, 4H), 6.67-6.70 (m, 4H), 6.80 (d, J = 7.5 Hz, 1H), 6.97-7.00 (m, 4H), 7.03-7.04 (m, 2H), 7.15-7.18 (m, 1H). <sup>13</sup>C (125 MHz): δ 19.44, 22.58, 22.68, 24.63, 27.79, 27.92, 29.50, 32.22, 32.78, 34.85, 36.99, 38.82, 39.24, 112.77, 115.32, 121.03, 123.34, 123.36, 123.52, 123.62, 123.97, 124.01, 124.69, 125.13, 129.54, 134.35, 134.67, 135.25, 135.42, 136.53, 136.73, 143.69, 144.74, 145.90, 155.46. HRMS (FAB) m/z calc for (C<sub>35</sub>H<sub>40</sub>OS<sub>4</sub>) 604.1962; found 604.1965. Anal. Calcd for C<sub>35</sub>H<sub>40</sub>OS<sub>4</sub>: C, 69.49; H, 6.66; S, 21.20. Found C, 69.20; H, 6.87; S, 21.02.

### 5.8 Synthetic Details for 6T.

**5-(3-bromopropyl)-[2,2']bithiophene (1).** A solution of 3.2 g (19.3 mmol) 2,2'-bithiophene in 100 mL THF was cooled to -78 °C and 8.8 mL (19.3 mmol) 2.2 M *n*-BuLi in hexanes was added slowly via syringe. The mixture was stirred at -78 °C for 1 hour and then 19.49 g (96.5 mmol) 1,3-dibromopropane was added via syringe. The mixture was then stirred at room temperature overnight followed by evaporation of the solvent under reduced pressure. The resulting oil was purified by flash chromatography through silica using 5% dichloromethane in hexanes as the eluent. The solvent was evaporated and the product dried *in vacuo* to afford 2.41 g (44 %) of a white solid. <sup>1</sup>H NMR (500 MHz):  $\delta$  2.19-2.24 (m, 2H), 2.99 (t, *J* = 7.0 Hz, 2H), 3.46 (t, *J* = 6.5 Hz, 2H), 6.75 (d, *J* = 3.5 Hz, 1H), 7.00-7.02 (m, 2H), 7.12 (dd, *J* = 3.8 Hz and 1.0 Hz, 1H), 7.19 (dd, *J* = 5.0 Hz and 1.0 Hz, 1H). <sup>13</sup>C NMR (125 MHz):  $\delta$  28.22, 32.60, 34.03, 123.23, 123.48, 123.99, 125.72, 127.72, 135.51, 137.57, 142.28. HRMS (FAB) *m/z* calc for (C<sub>11</sub>H<sub>11</sub>BrS<sub>2</sub>) 287.9465; found 287.9467. Anal. Calcd for C<sub>11</sub>H<sub>11</sub>BrS<sub>2</sub>: C, 46.00; H, 3.86; S, 22.32. Found C, 46.29; H, 3.70; S, 22.14.

**5-bromo-5'-(3-bromopropyl)-[2,2']-bithiophene (2).** A flask containing 2.41 g (8.4 mmol) **1** in 10 mL DMF was protected from light and 1.5 g (8.4 mmol) NBS was added. The mixture was stirred overnight and was then diluted with 100 mL ethyl acetate. The resulting solution was washed twice with water and once with brine. The organic layer was dried and the solvent evaporated to yield a product that was dried *in vacuo* to yield 2.99 g (97%) of a white solid. <sup>1</sup>H NMR (400 MHz):  $\delta$  2.19-2.24 (m, 2H), 2.98 (t, *J* = 7.2 Hz, 2H), 3.45 (t, *J* = 6.4 Hz, 2H), 6.73 (d, *J* = 3.6 Hz, 1H), 6.84 (d, *J* = 4.0 Hz, 1H), 6.92-6.96 (m, 2H). <sup>13</sup>C (100 MHz):  $\delta$  28.28, 32.54, 34.03, 110.52, 123.35, 123.86, 125.85, 130.57, 134.55, 139.13, 142.92. HRMS (FAB) *m/z* calc for (C<sub>11</sub>H<sub>10</sub>Br<sub>2</sub>S<sub>2</sub>) 363.8591; found 363.8592. Anal. Calcd for C<sub>11</sub>H<sub>10</sub>Br<sub>2</sub>S<sub>2</sub>: C, 36.08; H, 2.75; S, 17.52. Found C, 36.11; H, 2.85; S, 17.49.

**3-(3-(5'-bromo-[2,2']-bithiophen-5-yl)propoxy)phenyl tert-butyl carbonate (3).** A mixture of 2.93 g (8.0 mmol) **2,** 2.52 g (12.0 mmol) tert-butyl (3-hydroxyphenyl) carbonate, 1.66 g (12.0 mmol) K<sub>2</sub>CO<sub>3</sub> and 32 mg (0.12 mmol) 18-crown-6 was dissolved in 20 mL anhydrous DMF. The resulting mixture was stirred at 60 °C overnight and then diluted to 100 mL with ethyl acetate. The resulting solution was washed twice with water and once with brine. The organic layer was dried and the solvent evaporated. The resulting product was purified by flash chromatography through silica using 10% ethyl ether in hexanes. The solvent was then evaporated and the product was dried *in vacuo* to afford 3.61 g (91%) of a white solid. <sup>1</sup>H NMR (600 MHz):  $\delta$  1.56 (s, 9H), 2.12-2.16 (m, 2H), 2.99 (t, *J* = 7.2 Hz, 2H), 3.99 (t, *J* = 6.0 Hz, 2H), 6.70 (d, *J* = 3.6 Hz, 1H), 6.73-6.74 (m, 1H), 6.76-6.77 (m, 2H), 6.84 (d, *J* = 3.6 Hz, 1H), 6.92 (d, *J* = 3.6 Hz, 1H), 6.94 (d, *J* = 3.6 Hz, 1H) 7.26 (m, 1H). <sup>13</sup>C (150 MHz):  $\delta$  26.48, 27.68, 30.88, 66.56, 83.49, 107.91, 110.31, 111.99, 113.54, 123.21, 123.80, 125.47, 129.73, 130.48, 134.21, 139.20, 144.06, 151.74, 151.95, 159.70. HRMS (FAB) *m/z* calc for (C<sub>22</sub>H<sub>23</sub>BrO<sub>4</sub>S<sub>2</sub>) 494.0221; found 494.0223. Anal. Calcd for C<sub>17</sub>H<sub>16</sub>OS<sub>2</sub>: C, 53.33; H, 4.68; S, 12.94. Found C, 53.39; H, 4.58; S, 13.11.

(3,3"'-dihexyl-[2,2':5',2":5",2"']-quaterthiophen-5-yl)trimethylstannane (4). A solution of 0.78 g (1.56 mmol) 3,3"'-dihexyl-[2,2':5',2":5",2"']-quaterthiophene in 20 mL THF was cooled to -78 °C and 0.62 mL (1.56 mmol) 2.5 M *n*-BuLi in hexanes was added slowly via syringe. The mixture was stirred for 1 hour at -78 °C and then the reaction was quenched by adding 1.56 mL (1.56 mmol) 1.0 M chlorotrimethylstannane in THF via syringe. The mixture was allowed to warm to room temperature and was stirred overnight. The mixture was diluted with 20 mL of hexanes and filtered through basic alumina. Additional DCM was filtered through the alumina until no more product eluted. The solvent was evaporated to yield 1.04 g (99%) of a yellow oil that was used without further purification. <sup>1</sup>H NMR (600 MHz):  $\delta$  0.34-0.43 (m, 9H), 0.88-0.90 (m, 6H), 1.31-1.42 (m, 12H), 1.63-1.69 (m, 4H), 2.77-2.81 (m, 4H), 6.94-6.95 (m, 1H), 7.01-7.03 (m, 3H), 7.12-7.13 (m, 2H), 7.17-7.19 (m, 1H).

## 3-(3-(3'''',4''-dihexyl-[2,2':5',2'':5'',2''':5''',2'''']-sexithiophen-5-

**yl)propoxy)phenol (6T).** A flask was charged with 0.37 g (0.56 mmol) **4** and 0.28 g (0.56 mmol) **3**, 32 mg Pd(PPh<sub>3</sub>)<sub>4</sub> and 5 mL DMF. The mixture was degassed with one freeze-pump-thaw cycle and then stirred at 80 °C overnight. The mixture was then poured into 50 mL water and the product was extracted twice with 50 mL DCM. Aqueous HCl was added to the water and the product was further extracted twice with 50 mL DCM. The organic layers were combined, washed with a little water and dried with Na<sub>2</sub>SO<sub>4</sub>. The product was purified via flash chromatography with 1:1 DCM:hexanes to yield the Boc-protected product, which was

recrystallized in hexanes and DCM. Removal of the Boc group was achieved by heating with silica in DCM at reflux to yield 0.188 g (41%) of an orange solid. <sup>1</sup>H NMR (600 MHz):  $\delta$  0.90-0.91 (m, 6H), 1.25-1.43 (m, 12H), 1.63-1.71 (m, 4H), 2.13-2.18 (m, 2H), 2.77-2.78 (m, 4H), 3.00-3.02 (m, 2H), 4.00 (t, 6.0 Hz, 2H), 6.41-6.43 (m, 2H), 6.49-6.51 (m, 1H), 6.73 (d, *J* = 3.6 Hz, 1H), 6.94-7.08 (m, 7H), 7.12-7.18 (m, 4H). HRMS (FAB) *m*/*z* calc for (C<sub>45</sub>H<sub>48</sub>O<sub>2</sub>S<sub>6</sub>) 812.1973; found 812.1978. Anal. Calcd for C<sub>45</sub>H<sub>48</sub>O<sub>2</sub>S<sub>6</sub>: C, 66.46; H, 5.95. Found C, 64.24; H, 5.78.

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# Chapter 5 Boron(subphthalocyanine)s with Conjugated Thiophene Axial Ligands for Organic Solar Cells

# Abstract

The preparation of boron(subphthalocyanine) derivatives with bithiophene and quaterthiophene axial ligands and their application in thin film organic photovoltaic cells (OPVs) is presented. Thin films of the SubPc derivatives cast from solution form the electron donor layer in bilayer OPVs with evaporated  $C_{60}$  as the electron acceptor layer. The photophyscial and morphological properties of the SubPc derivatives are studied to rationalize OPV device characteristics. The single crystal X-ray structure is solved for two derivatives, and UV-vis spectroscopy and fluorescence spectroscopy is used to show that the conjugated ligands introduce absorption bands and dramatically affect photoluminescence quantum yield ( $\Phi_{\rm F}$ ). Cyclic voltammetry (CV), density functional theory (DFT), and low temperature photoluminescence spectra show that  $\Phi_{\rm F}$ depends on the overall flexibility of the SubPc derivatives and not the oxidation potential or electronic relationship of the ligand and macrocycle molecular orbitals. We show with grazingincidence X-ray scattering (GIXS) and atomic force microscopy (AFM) that careful choice of ligand structure can facilitate solution deposition of polycrystalline thin films that lead to a relative increase in short-circuit current (J<sub>SC</sub>) in OPV test structures. This work demonstrates that SubPcs can be used as light harvesting chromophores in a matrix of a crystalline organic semiconductor that forms the active layer in OPVs.

## **1. Introduction**

Organic small molecule or polymer semiconductors are widely studied in large part due to their potential application in low-cost thin film organic photovoltaics (OPVs).<sup>1,2</sup> The development of new materials and device structures has led to an improvement in power conversion efficiency (PCE) over the past decade from about 1% to over 5%.<sup>3-8</sup> One attractive class of small molecule materials is boron subphthalocyanine (SubPc) and its derivatives. SubPc has a nonplanar pyramid-shaped structure, in which the boron atom is surrounded by three coupled benzoisoindole units to give a 14- $\pi$ -electron aromatic macrocycle.<sup>9</sup> This unique cone-shaped geometry of SubPc contrasts with the flat or nearly flat structure of most phthalocyanines and provides them with relatively high solubility and low tendency of aggregation, which makes them attractive for solution-based OPV fabrication techniques. Furthermore, the strong absorption in the visible light region with extinction coefficients of ca.  $5 \times 10^4$  M<sup>-1</sup>cm<sup>-1</sup> enables them to be used as effective light harvesting materials. Indeed, efficient organic photovoltaic cells with power conversion efficiency (PCE) in excess of 2% have been demonstrated by using vacuum deposited SubPc films as the electron donor and  $C_{60}$  as the electron acceptor.<sup>10,11</sup> Furthermore, axial and peripheral functionalization has been used to facilitate solution deposition of the active layer in SubPc and sub(naphthalocyanine) solar cells with PCE over 1.5%.<sup>12,13</sup>

SubPcs are superior to phthalocyanines in terms of the open circuit voltage ( $V_{OC}$ ) obtained in OPVs. In this case, a relative increase in the energy difference ( $I_G$ ) between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor enhances the  $V_{OC}$ .<sup>11,14</sup> However, the short-circuit current ( $J_{SC}$ ) of SubPc OPVs is limited because of a narrow absorption spectrum and the amorphous morphology of thin films that increases the series resistance of the cell.<sup>11</sup> Both of these factors limit the PCE of SubPc cells, so addressing these issues offers a route to improve SubPc OPVs.

In this chapter, we seek to tune the properties of SubPc films through introduction of axial conjugated ligands that will offer additional light absorption bands and a driving force for self-assembly.<sup>15</sup> Conjugated ligands featuring bithiophene (2T) and quaterthiophene (4T) moieties were chosen because of the strong  $\pi$ - $\pi$  interactions of oligothiophenes that make them crystalline high mobility semiconductors. The preparation of 2T-SubPcs and 4T-SubPcs is presented, and we show that varying the structure of the SubPc derivatives affects the photophysical, electronic and thin film morphological properties of the materials. Finally, these factors are linked to the observed solar cell device characteristics of nT-SubPcs.

### 2. Results and Discussion

**2.1 Rational Design and Synthesis of nT-SubPcs.** The target axially substituted boron(subphthalocyanine)s (SubPcs) were assembled via Suzuki cross-coupling of thiophene boronic esters and SubPcs bearing an axial phenyl bromide. Phenoxy derivatives were prepared by first treating boron(subphthalocyanine) chloride (Cl-SubPc) with 4-bromophenol in toluene heated at reflux, which yielded **1**. A Suzuki cross-coupling of **1** and either 2-([2,2'-bithiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane or 2-[2,2':5',2'':5'',2'''-quarterthiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane yielded, respectively, **2Tp-SubPc** and **4Tp-SubPc**. Alkynyl derivatives, **2Ta-SubPc** and **4Ta-SubPc**, were prepared in an analogous fashion from **2**, which was prepared by treating Cl-SubPc with ((4-bromophenyl)ethynyl)magnesium bromide.





The two different linking strategies were chosen because of their effect on the 3-dimensional shape of the resulting molecules. The bent ether bond in the phenoxy SubPcs reduces the symmetry and increases the flexibility of the molecular structure, but the alkynyl SubPcs feature a linear carbon-carbon triple bond that results in much more symmetrical and rigid molecules.



Figure 1. View showing the crystal packing of (a) 2Tp-SubPc and (b) 4Tp-SubPc. In crystals, layers of SubPc macrocycle are separated by layers of the conjugated axial ligand.

**2.2 Single Crystal Structures.** Conjugated thiophene ligands were introduced to take advantage of the strong  $\pi$ - $\pi$  interactions that make oligothiophenes very crystalline and high mobility semiconductors. Crystals of nT-SubPcs were grown and large single crystals of **2Tp-SubPc** and **4Tp-SubPc** were obtained that allowed solution of their crystal structures. The crystal structures reveal the packing mode of these SubPc derivatives, which features layers of the conjugated ligands separated by layers of the SubPc macrocycle, as shown in Figure 1a and 1b. Formation of polycrystalline thin films that feature the same molecular packing mode would be interesting for OPV experiments, because the conjugated ligand lamellae may provide high mobility current pathways through the film. Single crystals suitable for structure determination were not obtained for nTa-SubPcs.

**2.3 Electronic and Photophysical Properties.** Conjugated ligands give rise to new absorption bands in the UV-visible thin film absorption spectra of nT-SubPcs, as shown in Figure 2, that are independent of the SubPc low energy Q-band and high energy Soret band. The absorption of bithiophene ligands overlaps considerably with the Soret band, but the absorption of quaterthiophene is clearly visible in the gap between the two SubPc absorption bands. There is little difference in the absorption spectra of the SubPcs that can be attributed to the structure of the boron-ligand bond, and there is very little relative shift of the absorption bands among the molecules. This similarity means that differences in OPV performance are not tied to absorption spectra, except when comparing 2T-SubPcs with the more broadly absorbing 4T-SubPcs.



Figure 2. UV-visible absorption spectra for (a) 2T-SubPc and (b) 4T-SubPc thin films spun cast from chlorobenzene.

In addition to absorption spectra, the photoluminescence of the nTa-SubPcs and nTp-SubPcs was studied to gain insight into the effects of the conjugated ligands on the excited state of the molecules. Photoluminescence was qualitatively observed only from the SubPc chromophore for all of the nT-SubPcs, which suggests efficient energy transfer from the axial ligands to the SubPc macrocycle. In addition, the nTa-SubPcs are highly fluorescent, but nTp-SubPcs exhibit significant photoluminescence quenching in solution. This phenomenon has previously been observed for SubPcs bearing electron-rich axial ligands that transfer an electron to the excited SubPc.<sup>15</sup> Yet, there is no clear correlation between the photoluminescence quantum yield ( $\Phi_F$ ) and the HOMO level of the nT-SubPcs, as shown in Table 1. In addition,  $\Phi_F$  does not depend on the calculated energy difference between the HOMO and HOMO-1 of nT-SubPcs. This difference is relevant because excitation of the SubPc chromophore leads to a partially filled HOMO-1 in the case of molecules that feature a HOMO localized on the ligand.

	HOMO <sup>a</sup>	$HOMO^{b}$	HOMO-1 <sup>b</sup> (eV)	$\Phi_{ m F}$
2Ta-SubPc	-5.6	-5.15 <sup>m</sup>	-5.18 <sup>1</sup>	0.37
4Ta-SubPc	-5.5	-4.89 <sup>1</sup>	-5.16 <sup>m</sup>	0.35
2Tp-SubPc	-5.5	-5.06 <sup>1</sup>	-5.22 <sup>m</sup>	0.02
4Tp-SubPc	-5.3	$-4.81^{1}$	-5.24 <sup>m</sup>	0.02

**Table 1.** <sup>a</sup>The HOMO levels were estimated from the onset of oxidation relative to ferrocene in dichloromethane. <sup>b</sup>The HOMO and HOMO-1 energies were calculated using DFT (see section 4.3). Photoluminescence was measured at room temperature in chloroform solutions, and quantum yields were calculated relative to a cresyl violet perchlorate standard in ethanol, exciting at 546 nm. Orbitals are localized on the <sup>m</sup>macrocycle or <sup>1</sup>ligand. The HOMO of each molecule was visualized to determine if it was located spatially on the ligand or the SubPc macrocycle. The electron donating nature of the boryloxy group in nTp-SubPcs clearly destabilizes the ligand  $\pi$  electrons relative to nTa-SubPcs. This effect results in the highest energy electrons residing on the ligand of **2Tp-SubPc** and **4Tp-SubPc**, as shown in Figure 3. In contrast, the HOMO of **2Ta-SubPc** is on the macrocycle, which could explain the molecule's high  $\Phi_F$ . Yet, the electron rich quaterthiophene ligand of **4Ta-SubPc** contains the HOMO for that emissive molecule, which suggests that the photoluminescence quenching of nTp-SubPcs is a geometric effect.



Figure 3. Graphical illustrations of the structures of nT-SubPcs overlayed with their respective HOMOs. See section 4.3 for details.

Non-radiative relaxation of the excited state of nTa-SubPcs is unfavorable because their overall rigid structure prevents conversion of electronic energy to rotational or vibrational energy. We believe that the bent ether bond in nTp-SubPcs facilitates internal conversion through motion of the axial ligand, a "free rotor" effect. Indeed, freezing the motion of the molecules at 77 K leads to comparable relative fluorescence intensities for each molecule, regardless of the structure, as shown in Figure 4.



Figure 4. Relative fluorescence of nT-SubPcs in 2-methyltetrahydrofuran at 77 K, excite at 530 nm.

The photophysical data presented demonstrates that our conjugated axial ligands contribute to excitation of the SubPc chromophore through energy transfer, but excitation of the SubPc does not necessarily result in electron transfer from the electron rich ligands. However, hole transport in the nT-SubPc films is likely mediated by the relatively easily oxidized conjugated ligands. Therefore, coupling of nT-SubPcs with  $C_{60}$  in bilayer solar cells will create a donor-acceptor interface where both ligand and SubPc can contribute to exciton generation, charge separation, and hole transport.

**2.4 Film Morphology Characterization.** Films of nT-SubPcs prepared for analysis by AFM and GIXS. AFM was used to visualize the roughness of the films and to look for signs of a crystalline morphology. AFM images are shown in Figure 5. Films of 2T-SubPcs were mostly featureless and very smooth with a RMS roughness of about 0.5 nm. For films of **4Tp-SubPc**, roughness increased to 1.4 nm. Films of **4Ta-SubPc** exhibited the highest roughness of 5.1 nm, and a textured film is clearly visible in Figure Xd. Amorphous films are typically smooth while molecules that tend to aggregate into crystals form relatively rough films, so this data suggests that **4Ta-SubPc** films are polycrystalline.



**Figure 5.** 2.0 x 2.0 μm AFM images of (a) **2Tp-SubPc** (b) **2Ta-SubPc** (c) **4Tp-SubPc** (d) **4Ta-SubPc**. All films were cast from chlorobenzene.

In addition, GIXS patterns for **4Ta-SubPc** exhibit many signals that prove explicitly that the film is polycrystalline, as shown in Figure 6. The signals are stretched into arcs, which show that crystalline domains are not oriented relative to the substrate. Amorphous 2T-SubPcs and **4Tp-SubPc** films do not scatter X-rays significantly. The  $\pi$ - $\pi$  interactions of the bithiophene ligands do not provide a strong enough driving force for crystallization to occur in solution-cast thin films. We believe the films of **4Tp-SubPc** are amorphous because the lack of symmetry introduced by the bent boron-oxygen-carbon bond linking the ligand to the macrocycle inhibits rapid crystallization. Replacement of this ether linkage with an alkyne results in a much more symmetrical molecule, **4Ta-SubPc**, and dramatically affects the morphology of thin films.



Figure 6. GIXS patterns for films of (a) 2Tp-SubPc (b) 2Ta-SubPc (c) 4Tp-SubPc (d) 4Ta-SubPc.

**2.5 OPV Results.** Bilayer solar cells were fabricated using solution deposited nT-SubPcs as the donor and evaporated  $C_{60}$  as the acceptor. The solar cell results are summarized in Table 2 and representative JV curves are shown in Figure 7. **2Ta-SubPc** and **2Tp-SubPc** OPVs were optimized to give the same average PCE of 1.39% with very similar J<sub>SC</sub>, V<sub>OC</sub>, and FF. **4Tp-SubPc** solar cells performed relatively poorly with a significantly decreased FF. This decrease in FF is likely due to an increase in the series resistance of the cells. The origin of this effect in this system is not clear, because the space-charge limited mobility of **4Tp-SubPc** was measured and was found to be the same order of magnitude as that found for 2T-SubPcs ( $10^{-6}$ cm<sup>2</sup>/Vs). However, doping the donor layer in CuPc/C<sub>60</sub> cells with rubrene has been shown to decrease FF because of charge trapping by rubrene.<sup>16</sup> Indeed, **4Tp-SubPc** features the highest energy ligand HOMO (see Table 1), so ligand charge trapping may play a role in the decreased FF observed.

Charge trapping can affect photocurrent measurements more than mobility measurements because mobility measurements are conducted at greater current density than that present in OPVs.<sup>17</sup>



Figure 7. Representative JV curves for nT-SubPc/C<sub>60</sub> solar cells. PCE(%) for devices shown: **2Tp-SubPc** (1.43%), **2Ta-SubPc** (1.44%), **4Tp-SubPc** (0.85%), **4Ta-SubPc** (1.17%).

The small decrease in  $V_{OC}$  exhibited by **4Tp-SubPc** cells may be explained by its higher lying HOMO level (see Table 1) that decreases  $I_G$ , which is proportional to  $V_{OC}$  in otherwise equivalent systems.<sup>14</sup> However, **4Ta-SubPc** cells possess the lowest  $V_{OC}$  of the set, which cannot be explained using this argument because its HOMO level is close to that of **2Tp-SubPc** and lower lying than that of **4Tp-SubPc**. Furthermore, **4Ta-SubPc** cells supplied the highest  $J_{SC}$  of the set (-4.48 mA/cm<sup>2</sup> for device shown), which suggests the morphology of the **4Ta-SubPc** film is affecting these trends instead of the HOMO-LUMO offset. Specifically, crystalline small molecule donors are known to exhibit higher  $J_{SC}$  and lower  $V_{OC}$  than their amorphous counterparts in bilayer OPVs.<sup>18</sup> Therefore, the differences in device characteristics of **4Ta-SubPc** due to inadequate film thickness, so higher charge mobility could not be proven to accompany greater thin film crystallinity.

	$V_{OC}(V)$	$J_{SC}$ (mA/cm <sup>2</sup> )	FF	<b>PCE(%)</b>
2Tp-SubPc	0.73	-3.72	0.51	1.39
2Ta-SubPc	0.70	-3.90	0.50	1.39
4Tp-SubPc	0.63	-3.30	0.34	0.70
4Ta-SubPc	0.57	-4.05	0.45	1.04

Table 2. Average OPV device characteristics for nT-SubPc/C<sub>60</sub> bilayer cells.

The intensity of light absorption in thin films may play a role in the PCE of nT-SubPc solar cells, and Figure 8 shows that the intensity of spectral bands in thin films depends on the structure of the chromophores. The intensity of the SubPc Q-band is likely the most important variable because it overlaps well with the solar spectrum and not with the absorption of  $C_{60}$ , which becomes significant around 400 nm. However, 2Ta and **2Tp-SubPc** produce the same PCE despite showing different Q-band absorbance, so this effect may not be very significant. The biggest difference in the Q-band is between 2Tp and **4Tp-SubPc**. In fact, **4Tp-SubPc** seems to have the weakest Q-band absorbance of all the nT-SubPcs. The bulky 4T ligand may displace SubPc spatially in thin films and decrease the thin film absorption coefficient of the SubPc chromophore. In contrast to nTp-SubPcs, 2Ta and **4Ta-SubPc** exhibit identical Q-band absorbance. The polycrystalline morphology of **4Ta-SubPc** likely leads to more optically dense films relative to amorphous **4Tp-SubPc** films.



Figure 8. Thin film absorbance relative to film thickness of nT-SubPcs.

#### **3.** Conclusions

Subphthalocyanine derivatives have been prepared via axial functionalization using phenoxy and alkynyl substitution schemes, and further elaborated with bithiophene and quaterthiophene moieties. The resulting contrast in structure leads to differences in geometry, photophysical properties, electronics, and thin film morphology. nTp-SubPcs are more easily oxidized than analogous nTa-SubPcs, and exhibit efficient photoluminescence quenching through internal conversion. Films cast from solution are only crystalline for the case of **4Ta-SubPc**, as shown by AFM and GIXS. This result shows that the tendency of nT-SubPcs to crystallize depends on both the length of the conjugated ligand and the overall symmetry of the molecule.

We have shown that nT-SubPcs perform well in bilayer solar cells with efficiencies over 1%. The films of 2T-SubPcs are amorphous and therefore provide relatively high values of Voc in solar cells. Formation of crystalline films by **4Ta-SubPc** leads to an increase in  $J_{SC}$ , but this increase is not enough to improve the PCE of the cell because of a concomitant decrease in  $V_{OC}$ . However, this method shows that SubPc macrocycles can be utilized as light harvesting chromophores in a matrix of a crystalline semiconductor that functions as the active layer in

OPVs. Further development of this approach will focus on lower band-gap semiconductors that will interact synergistically with SubPc to achieve higher power conversion efficiencies.

# 4. Methods

**4.1 Materials.** For OPV device fabrication, patterned indium-tin oxide (ITO) coated glass substrates were purchased from Thin Film Devices Inc. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) (Clevios-PH) was purchased from H. C. Starck. 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) (96%),  $C_{60}(99.9\%)$ , sublimed), silver shot (1-3 mm, 99.99+%), and chlorobenzene (anhydrous, 99.8%) were purchased from Aldrich. 2-[2,2':5',2'':5'',2'''-quarterthiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared according to a previously published procedure.<sup>19</sup> All other chemicals were purchased from Aldrich and used without further purification unless otherwise noted. All reactions were performed under dry N<sub>2</sub> unless otherwise noted. All extracts were dried over MgSO<sub>4</sub> and solvents were removed by rotary evaporation with aspirator pressure. Flash chromatography was performed using Merck Kieselgel 60 (230-400 mesh) silica. DMF was purchased from Fisher and vigorously purged with nitrogen for 1h. The solvent was further purified by passing it under nitrogen pressure through two packed columns (Glass Contour) of activated molecular sieves.

**4.2 Characterization.** <sup>1</sup>H NMR spectra were recorded with a Bruker AV-600 instrument using CDCl<sub>3</sub> as the solvent. High Resolution Mass Spectometry (HRMS) using Fast Atom Bombardment (FAB) was done with a Micromass ZAB2-EZ double focusing mass spectrometer (BE geometry). Elemental analyses were performed at the UC Berkeley Microanalysis Laboratory. Cyclic voltammetry (CV) was performed using a Solartron 1285 potentiostat. The cyclic voltammograms were measured in dichloromethane solution with a Pt wire working electrode. All measurements were performed using a silver wire pseudoreference electrode, a platinum auxiliary electrode, and were referenced to the ferrocene/ferrocenium couple, which was taken to be -5.1 eV relative to vacuum.<sup>20</sup> Tetrabutylammonium tetrafluoroborate (NBu<sub>4</sub>BF<sub>4</sub>) was the supporting electrolyte for all measurements. Photoluminescence was measured at room temperature in chloroform solutions, and quantum yields were calculated relative to cresyl violet perchlorate ( $\Phi_F = 0.50$  in ethanol), exciting at 546 nm.

(eq. 1) 
$$\Phi_{\rm s} = \Phi_{\rm r} \left( \frac{\eta_{\rm s}^2 A_{\rm r} I_{\rm s}}{\eta_{\rm r}^2 A_{\rm s} I_{\rm r}} \right)$$

Equation 1 was used to calculate quantum yields where  $\Phi_s$  is the quantum yield of the sample,  $\Phi_r$  is the quantum yield of the reference,  $\eta$  is the refractive index of the solvent,  $A_s$  and  $A_r$  are the absorbance of the sample and the reference at the wavelength of excitation, and  $I_s$  and  $I_r$  are the integrated areas of emission bands.

**4.3 DFT calculations.** Molecular geometries for **2Tp-SubPc**, **4Tp-SubPc**, **2Ta-SubPc** and **4Ta-SubPc** were optimized to an energy minimum using Gaussian 09 at the DFT B3LYP level with 6-31+g(d,p) basis set.<sup>21</sup> Their nature as energy minima was confirmed through a vibration calculation at the same level which yielded no negative frequencies. Energies for the HOMO and HOMO-1 molecular orbitals (MOs) were obtained from the energy minimized checkpoint file.

The HOMO MO surface was visualized at isovalue 0.02 and imported into the molecular visualization program VMD to obtain high quality images.<sup>22</sup>

**4.4 Single Crystal X-ray Crystallography.** Single crystals of **2Tp-SubPc** and **4Tp-SubPc** were grown by slowly evaporating 1,2-dichloroethane from a cyclohexane solution. Single crystal structures were obtained from the UC Berkeley College of Chemistry X-ray Crystallography Facility

**2Tp-SubPc.** A red plate 0.25 x 0.14 x 0.01 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 60 mm and exposure time was 3 seconds per frame using a scan width of 0.3°. Data collection was 99.7% complete to 30.00° in  $\theta$ . A total of 8925 reflections were collected covering the indices, -27 <=h<=25, 0<=k<=11, 0<=l<=29. 8925 reflections were found to be symmetry independent, with an R<sub>int</sub> of 0.0382. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P2(1)/n (No. 14). The data were integrated using the Bruker SAINT software program and scaled using the TWINABS software program. Solution by direct methods (SIR-97) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97.

**4Tp-SubPc.** A red block 0.12 x 0.10 x 0.10 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 5 seconds per frame using a scan width of 1.0°. Data collection was 98.2% complete to 67.00° in  $\theta$ . A total of 26878 reflections were collected covering the indices, -12 <=h<=8, -13 <=k<=13, -19 <=l<=19. 6422 reflections were found to be symmetry independent, with an R<sub>int</sub> of 0.0165. Indexing and unit cell refinement indicated a primitive, triclinic lattice. The space group was found to be P-1 (No. 2). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SIR-2004) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97

crystal data and structure refinement						
2Tp-SubPc	4Tp-SubPc					
C38 H21 B N6 O S2	C46 H25 B N6 O S4					
652.54	816.77					
100(2) K	100(2) K					
0.77490 Å	1.54178 Å					
Monoclinic	Triclinic					
P2(1)/n	P-1					
a = 19.6146(18) Å	a = 10.9792(3) Å					
	ment 2Tp-SubPc C38 H21 B N6 O S2 652.54 100(2) K 0.77490 Å Monoclinic P2(1)/n a = 19.6146(18) Å					

	b = 8.2310(7) Å	b = 11.0799(3) Å	
	c = 20.4254(18)  Å	c = 16.4213(4) Å	
	$\alpha = 90^{\circ}$	$\alpha = 70.5320(10)^{\circ}.$	
	$\beta = 116.5660(10)^{\circ}.$	$\beta = 81.6310(10)^{\circ}.$	
	$\gamma = 90^{\circ}$ .	$\gamma = 74.2410(10)^{\circ}$ .	
Volume	2949.5(5) Å <sup>3</sup>	1809.29(8) Å <sup>3</sup>	
Z	4	2	
Density (calculated)	1.470 Mg/m <sup>3</sup>	1.499 Mg/m <sup>3</sup>	
Absorption coefficient	0.281 mm <sup>-1</sup>	2.809 mm <sup>-1</sup>	
F(000)	1344	840	
Crystal size	0.25 x 0.14 x 0.01 mm <sup>3</sup>	0.12 x 0.10 x 0.10 mm <sup>3</sup>	
Crystal color/habit	red plate	red block	
Theta range for data collection	2.96 to 33.61°.	2.86 to 68.27°.	
Index ranges	-27<=h<=25, 0<=k<=11,	-12<=h<=8, -13<=k<=13,	
	0<=1<=29	-19<=l<=19	
Reflections collected	8925	26878	
Independent reflections	8925 [R(int) = 0.0382]	6422 [R(int) = 0.0165]	
Completeness to theta = $67.00^{\circ}$	99.7 %	98.2 %	
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.9972 and 0.9331	0.7664 and 0.7292	
Refinement method	Full-matrix least-squares on F <sup>2</sup>		
Data / restraints / parameters	8925 / 0 / 435	6422 / 0 / 524	
Goodness-of-fit on F <sup>2</sup>	1.015	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0426, wR2 = 0.1066	R1 = 0.0335, wR2 = 0.0874	
R indices (all data)	R1 = 0.0543, wR2 = 0.1139	R1 = 0.0373, wR2 = 0.0910	
Largest diff. peak and hole	0.464 and -0.445 e.Å <sup>-3</sup>	0.463 and -0.368 e.Å <sup>-3</sup>	

**4.5 Device Fabrication and Characterization.** ITO-coated glass substrates ( $R = 20 \ \Omega^{-1}$ , prepatterned) were cleaned using the following procedure: sonication in soap solution, rinsing in deionised water and sonication in acetone and isopropanol for 10 min. each step. Finally the substrates were treated with UV ozone for 30 minutes. A thin-layer (30-40 nm) of PEDOT:PSS was spin-coated onto the ITO glass at 4000 RPM for 40 s and then baked at 140 °C for 15 min in air. Solutions of SubPc (2.5-3 mg/mL in chlorobenzene) were prepared inside the glove box and stirred at 110 °C overnight to ensure a complete dissolution. Prior the spin-coating the solutions were passed through a 0.45  $\mu$ m polytetrafluoroethylene syringe filter. Thin films (about 20nm) of SubPc were prepared by spin-coating the solutions at 2000 rpm for 10sec., then the substrates were covered by a petri-dish in order to obtain slow evaporation of the solvent. The devices were completed by the thermal evaporation of the acceptor layer, C<sub>60</sub> (32nm) and the exciton blocking

layer BCP (10nm). An Ag cathode (100 nm) was then thermally evaporated through a shadow mask defining an active device area of ~ 0.03 cm<sup>2</sup>. The current-voltage (J-V) curves were measured using a Keithley 236 source-measure unit under AM 1.5 G solar illumination at 100 mW cm<sup>-2</sup> (1 sun) using a Thermal-Oriel 300W solar simulator. The hole mobility was measured using a SCLC model and the device structure was ITO/PEDOT:PSS/SubPc /Au.

**4.6 AFM** and **Grazing-Incidence X-ray Scattering (GIXS).** GIXS experiments were conducted at the Stanford Synchrotron Radiation Laboratory on beamline 11-3. The sample is irradiated at a fixed incident angle on the order of a tenth of a degree and the GIXS patterns are recorded with a 2-D image detector (MAR345 image plate detector). GIXS patterns were recorded with an X-ray energy of 12.72 keV ( $\lambda$ =0.975Å). To maximize the intensity from the sample, the incident angle (~0.1°-0.12°) was carefully chosen so that the X-ray beam penetrates the SubPc layer completely but not the silicon substrate. Typical exposure times were 90-180 sec. To produce identical surface condition as samples for device fabrication, a thin layer (20-30 nm) of PEDOT:PSS (Clevios PH) was spun onto silicon substrates with a native oxide. And then GIXS samples were prepared by spin-coating the same solutions used for fabricating solar cells onto silicon substrates at 2000 rpm for 10sec. Then the substrates were covered by a petri-dish in order to obtain slow evaporation of the solvent. All atomic force microscopy was performed using a Digital Instruments (Veeco) Multimode AFM with a Nanoscope V controller and TESP tips, and films were prepared as described above.

## **4.7 Synthetic Details**

**4-bromophenoxy SubPc (1)** was prepared according to a previously published procedure.<sup>23</sup> <sup>1</sup>H NMR (600 MHz):  $\delta$  5.27 (d, J = 9.0 Hz, 2H), 6.84 (d, J = 9.0 Hz, 2H), 7.91-7.93 (m, 6H), 8.85-8.86 (m, 6H).

(4-bromophenyl)ethynyl SubPc (2) was prepared according to a previously published procedure.<sup>15 1</sup>H NMR (600 MHz):  $\delta$  6.58 (d, *J* = 9.0 Hz, 2H), 7.07 (d, *J* = 9.0 Hz, 2H), 7.90-7.92 (m, 6H), 8.86-8.89 (m, 6H).

**2Tp-SubPc.** A flask was charged with 0.100 g (0.18 mmol) **1** and 0.080 g (0.27 mmol) 2-([2,2'bithiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 6 mg Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, 44 mg K<sub>2</sub>CO<sub>3</sub>, and 5 mL DMF. The mixture was degassed with one freeze-pump-thaw cycle and then stirred at 80 °C for 5 h. The mixture was then poured into 200 mL of water to precipitate the product. The solids were filtered and washed with copious amounts of water and then 2:1 methanol:water. The crude product was air dried and then purified via flash chromatography. The quaterthiophene byproduct was eluted with DCM and the product was eluted with 1% ethyl acetate in DCM to yield 0.070 g (61%) of a dark red solid. <sup>1</sup>H NMR (600 MHz):  $\delta$  5.40 (d, *J* = 9.0 Hz, 2H), 6.89 (d, *J* = 3.6 Hz, 1H), 6.97-7.01 (m, 4H), 7.09-7.10 (m, 1H), 7.16-7.17 (m, 1H), 7.92-7.94 (m, 6H), 8.87-8.90 (m, 6H). HRMS (FAB) *m*/*z* calc for (C<sub>38</sub>H<sub>21</sub>BN<sub>6</sub>OS<sub>2</sub>) 652.1311; found 652.1316. Anal. Calcd for C<sub>38</sub>H<sub>21</sub>BN<sub>6</sub>OS<sub>2</sub>: C, 69.94; H, 3.24; N, 12.88. Found C, 69.57; H, 3.33; N, 12.55.

**4Tp-SubPc.** A flask was charged with 0.083 g (0.15 mmol) **1** and 0.100 g (0.22 mmol) 2-[2,2':5',2'':5'',2'''-quarterthiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 8 mg Pd(PPh<sub>3</sub>)<sub>4</sub>, 53 mg K<sub>2</sub>CO<sub>3</sub>, and 5 mL DMF. The mixture was degassed with one freeze-pumpthaw cycle and then stirred at 80 °C for 5 h. The mixture was then poured into 200 mL of water to precipitate the product. The solids were filtered and washed with copious amounts of water and then 2:1 methanol:water. The crude product was air dried and then purified via flash chromatography. Unreacted quaterthiophene was eluted with DCM and the product was eluted with 1% ethyl acetate in DCM to yield 0.055 g (45%) of a dark red solid. <sup>1</sup>H NMR (600 MHz):  $\delta$ 5.40 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 3.6 Hz, 1H), 6.99-7.08 (m, 8H), 7.17 (s, 1H), 7.21 (s, 1H), 7.92-7.94 (m, 6H), 8.86-8.90 (m, 6H). HRMS (FAB) *m*/*z* calc for (C<sub>46</sub>H<sub>25</sub>BN<sub>6</sub>OS<sub>4</sub>) 816.1065; found 816.1042. Anal. Calcd for C<sub>46</sub>H<sub>25</sub>BN<sub>6</sub>OS<sub>4</sub>: C, 67.64; H, 3.09; N, 10.29. Found C, 67.25; H, 2.96; N, 9.89.

**2Ta-SubPc.** A flask was charged with 0.106 g (0.18 mmol) **1** and 0.080 g (0.27 mmol) 2-([2,2'-bithiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 6 mg Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, 44 mg K<sub>2</sub>CO<sub>3</sub>, and 5 mL DMF. The mixture was degassed with one freeze-pump-thaw cycle and then stirred at 80 °C for 3 h. The mixture was then poured into 200 mL of water to precipitate the product. The solids were filtered and washed with copious amounts of water and then 2:1 methanol:water. The crude product was air dried and then purified via flash chromatography. The product was eluted with DCM to yield 0.073 g (61%) of a dark red solid. <sup>1</sup>H NMR (600 MHz):  $\delta$  6.75 (d, *J* = 9.0 Hz, 2H), 6.94-6.95 (m, 1H), 7.01-7.09 (d, *J* = 3 Hz, 1H), 7.14 (d, *J* = 5.4 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.86-7.87 (m, 6H), 8.85-8.86 (m, 6H). HRMS (FAB) *m*/*z* calc for (C<sub>40</sub>H<sub>21</sub>BN<sub>6</sub>S<sub>2</sub>) 660.1362; found 660.1358. Anal. Calcd for C<sub>40</sub>H<sub>21</sub>BN<sub>6</sub>S<sub>2</sub>: C, 72.73; H, 3.20; N, 12.72. Found C, 71.57; H, 3.19; N, 12.05.

**4Ta-SubPc.** A flask was charged with 0.050 g (0.09 mmol) **2** and 0.059 g (0.13 mmol) 2-[2,2':5',2'':5'',2'''-quarterthiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 5 mg Pd(PPh<sub>3</sub>)<sub>4</sub>, 32 mg K<sub>2</sub>CO<sub>3</sub>, and 5 mL DMF. The mixture was degassed with one freeze-pumpthaw cycle and then stirred at 80 °C for 5 h. The mixture was then poured into 200 mL of water to precipitate the product. The solids were filtered and washed with copious amounts of water and then 2:1 methanol:water. The crude product was air dried and then purified via flash chromatography. The product was eluted with DCM to yield 0.040 g (54%) of a dark red solid. <sup>1</sup>H NMR (600 MHz):  $\delta$  6.74 (d, *J* = 8.4 Hz, 2H), 7.01-7.05 (m, 7H), 7.15-7.18 (m, 3H), 7.21 (d, *J* = 4.8 Hz, 1H), 7.91-7.92 (m, 6H), 8.88-8.89 (m, 6H). HRMS (FAB) *m/z* calc for (C<sub>48</sub>H<sub>25</sub>BN<sub>6</sub>S<sub>4</sub>) 824.1117; found 824.1136. Anal. Calcd for C<sub>48</sub>H<sub>25</sub>BN<sub>6</sub>S<sub>4</sub>: C, 69.90; H, 3.06; N, 10.19. Found C, 69.11; H, 3.07; N, 9.44.

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