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Enabling n-Channel Oligomer and Polymer Semiconductors Through Rational Design, Synthesis, Computational Modeling, and Temperature Dependent Field Effect Transistor Study

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ABSTRACT

Enabling n-Channel Oligomer and Polymer Semiconductors Through Rational Design, Synthesis, Computational Modeling, and Temperature Dependent Field Effect Transistor Study

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Conjugated organic molecules and polymers hold significant promise for use as active materials in electronic devices. Employing such "soft" materials can decrease cost of device fabrication, while enabling unique properties such as mechanical flexibility, large-area coverage, and highly tunable materials properties. A primary roadblock to the realization of this dream has been stability of mobile electrons in organic thin-films. In fact, very few semiconductors exhibit electron transport (n-channel) activity under ambient conditions in field effect transistors (FETs), a standard test-bed device for semiconductor thin-films. Even fewer organic semiconductors have desirable processing characteristics. This work addresses these challenges via computationally-aided rational design of novel electron transporting (n-channel) materials yielding new n-channel air-stable semiconductors, record-setting figures-of-merit for solution processed films, and two examples of rare n-channel FET polymeric semiconductors. Further characterization of charge trapping in organic semiconductors is studied by variable temperature transistor measurements and a direct correlation between charge trapping and mobility is observed.

A powerful and general approach to materials design is presented in the first two chapters of this work. DFT-level electronic structure calculations are employed to screen synthetically relevant candidate materials for desirable semiconductor properties. This rational molecular engineering method yields a family of phenacyl-thiophene and quinone-based semiconductors exhibiting mobilities up to ~ $0.3 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for solution processed films and temporally air-stable mobilities of $0.015 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ with high current modulation > 10^6 . Additionally, two of the first n-channel polymers are developed, exhibiting mobilities up to $0.012 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and remarkable polymer thin-film crystallinity.

The charge transport mechanism for a series of semiconductors is probed by variable temperature FET experiments, the first such study employing semiconductors with diverse molecular and device properties. Analysis of temperature activated FET behavior reveals an inverse correlation between increased charge trap filling and ambient-temperature mobility. Furthermore, there is no evidence for a relationship between conduction orbital energy and the mobility-limiting shallow trap states. This combination of rational design employing appropriate quantum chemical methods and synthetic practicality coupled with an enhanced understanding of trap-limited charge carrier mobility evidences the vibrant progress and continued promise of organic electronic materials.

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Dedication

To my Mother and Father.

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Chapter One

Introduction

Organic materials exhibit a broad array of mechanical, biological, colorimetric, chemical, and electrical properties and show promise for use in many applications where "hard" inorganic materials were once the only option. The inherent properties of organics bestow several key advantages for their use in certain applications, including low-temperature processing, solubility, and low-density as well as unique mechanical, electrical, and coating properties. Furthermore, these properties can be precisely tuned through synthetic modifications to the molecular structure of small molecules or polymers. One of the most exciting areas for the use of organics is in electronic materials in applications where "hard" inorganic materials are not well suited.¹⁻¹⁹ Specifically, organics have the most appeal for use in applications where large area coverage, low-cost, flexible devices, and conformal coverage are desired. The solubility and rheological properties of organic polymers and small molecules enable ambient condition printing, patterning, and spin coating of the active materials over large areas.²⁰⁻²² Additionally the use of conventional printing methods allows rapid device design changes and the potential for extremely-high device fabrication throughput greater than 1 m/s for certain types of reel-to-reel printing. 23-28

The three primary classes of materials required to fabricate electronics components are insulators, semiconductors, and conductors. While conductors and insulators have been developed with properties that generally satisfy desired requirements, semiconductors are currently the limiting component in organic-based electronic devices.^{29, 30} Charge transport in the great majority of these materials is postulated to proceed via hopping-type mechanism where electrons or holes migrate through the lowest unoccupied molecular orbital (LUMO) or highest occupied molecular orbital (HOMO), respectively, of conjugated organic materials.³¹⁻³⁶ While the intermolecular charge transfer rate governs the efficiency hopping events, studies have revealed

that the observed organic semiconductor (OSC) behavior is generally governed by trapping of charge carriers in localized shallow states, followed by thermally activated release.^{31, 32, 37.45} Furthermore, recent discoveries have revealed that mobile electrons, required for n-channel activity, can be completely quenched by energetically deep and highly-concentrated trap states, such as O₂, H₂O, and surface hydroxyl groups.^{46.49}

Field effect transistors (FETs) provide a simple test bed for evaluating the performance of new OSCs and have been utilized as such in the field of organic electronics (Figure 1.1). The device acts as a current switch, modulating charge flow between source (S) and drain (D) electrodes. Charge is induced in the semiconductor channel by application of a voltage to the gate V_G that is capacitively coupled to the semiconductor by the dielectric layer. Mobile charge is then extracted by application of a drain voltage (V_D) to give an observed drain current (I_D). Important device fabrication parameters are the capacitance of the dielectric layer (C_{ox}), distance between the S and D electrodes (channel length, L), and width of the S and D electrodes (channel width, W). With these parameters known, the mobility (μ), or charge carrier drift velocity, can be calculated and is one of the primary figures of merit for an OSC. Other important performance figures are the current on:off ratio (I_{on-off}), which quantifies the magnitude of current modulation for the FET, and the threshold voltage (V_T), which is the V_G when the device turns on. The μ and V_T are calculated by fitting Eq1.1 to V_G vs. I_D data at a constant V_D .

$$I_{D,sat} = \frac{W}{2L} C_{ox} \mu \left(V_G - V_T \right)^2 \tag{1.1}$$

For organics to be competitive with low-cost hydrogenated amorphous silicon in lowperformance application, μ should be ~ 0.1 to ~1 cm²V⁻¹s⁻¹ and I_{on:off} >10⁵. Solution processability and ambient stability are also essential for the realization of organic electronics.



Figure 1.1. Top contact, bottom gate field effect transistor (FET).

Hole transporting (p-channel) and n-channel materials are required for many applications, such as organic light-emitting diodes,⁵⁰⁻⁵² sensors,⁵³⁻⁵⁷ organic photovoltaics,⁵⁸ and organic field-effect transistors (FETs).^{18, 19, 32, 33, 59} In addition to the processability requirements, important fundamental questions remain about long-range charge transport in organic solids, especially for OSCs used in organic field-effect transistors (FETs). Recent studies have demonstrated robust, air-stable performance in p-channel FETs using thiophene-based polymeric semiconductors (Figure 1).⁶⁰⁻⁶⁸ Unfortunately, there is a lack of polymeric semiconductors with comparable processing and performance characteristics for n-channel FETs. This is important since both types of materials are required to achieve low-power consumption complementary organic circuitry (CMOS).^{12, 24, 69} In addition to such logic and switching applications, polymers exhibiting efficient electron transport and high electron affinities should also be useful as novel acceptor materials in organic photovoltaics and electron transporting materials in polymer-based light-emitting diodes.^{13, 58, 70, 71}

Chapter 2 describes the discovery of a versatile class of organic semiconductors designed to enhance crystallinity, solution processability, and achieve air-stabile n-channel FET operation. Quaterthiophene is used as the π -core because of its affinity for favorable crystal packing, high μ , and the ability to modulate its LUMO energy via substitution. Previous work on fluorinated and non-fluorinated alkyl,³⁸⁻⁴³ aryl,⁴⁴ and alkyl-carbonyl³⁶ substituted thiophenes has revealed that high FET carrier mobility can be achieved concurrently with LUMO energy stabilization to enable n-channel FET operation. The new phenacyl family of semiconductors exhibits rich relationships between molecular-level electronic/structural properties, processability, thin-film morphology, and p-/n-channel FET device characteristics. The design strategy to concurrently enhance solubility and crystal packing yields high-performance solution processable n-channel

FET materials with u_{0} up to ~ 0.3 cm²V⁻¹s⁻¹ for solution cast films and one of the first n-channel polymers. Molecule-polymer blends enhance both solution rheology and FET device performance from $\mu_e \approx 10^{-6} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for neat polymer films to ~ 0.02 cm² V⁻¹ s⁻¹ for blend films. A computational study of additional LUMO stabilization reveals that introduction of quinone units into the π -conjugated core can enable air-stabile n-channel operation. Introduction of phenanthrenequinone, one of the three quinones identified, affords an air-stabile oligomer exhibiting n-channel FET operation with $\mu_e \approx 0.02 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and a high $I_{\text{on off}} = 10^6$ under ambient conditions. The non-fluorinated phenanthrenequinone analog exhibits diminished $\mu_e \approx 10^{-5} \text{ cm}^2 \text{V}^-$ ¹s⁻¹ and air-unstable FET operation, in agreement with the O₂-barrier model proposed in previous studies. Crystal structures of fluorinated and non-fluorinated quaterthiophene compounds reveal that both pack in a herringbone motif with short π -stacking distances and a layered structure. The first crystal structure of a quinone-containing thiophene-based molecule reveals anti-parallel dipole alignment and cofacial packing with a short 3.48 Å π - π stacking distance. This work demonstrates that rational design can yield extremely π -electron deficient monomer units for use in air-stable n-channel FET molecule and polymer semiconductors.

Chapter 3 builds on these discoveries through the synthesis and characterization of new electron-depleted *N*-alkyl-2,2'-bithiophene-3,3'-dicarboximide-based π -conjugated homopolymers and copolymers. A powerful, novel design approach is employed using computational modeling to identify favorable monomer properties such as core planarity, solubilizing substituent tailorability, and appropriate electron affinity with gratifying results. Monomeric compounds are synthesized to confirm these properties, and a crystal structure reveals a short 3.43 Å π - π stacking distance with favorable solubilizing substituent orientations. A family of ten

regioregular homopolymers and bithiophene copolymers is then synthesized via Yamamoto and Stille polymerizations, respectively. Two of these polymers are processable in common organic homopolymer poly(N-(2-octyldodecyl)-2,2'-bithiophene-3,3'-dicarboximide)solvents: the exhibits n-channel FET activity, and the copolymer poly(N-(2-octyldodecyl)-2,2':5',2'':5'',2'''quaterthiophene-3,3'-dicarboximide) exhibits air-stable p-channel FET operation. After annealing, homopolymer films exhibit a very high degree of crystallinity and an electron mobility $> 0.01 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ with a current on-off ratio of 10⁷, which is remarkably independent of film-deposition conditions. Extraordinarily, these polymer films also exhibit terracing in AFM images with a step height matching the X-ray diffraction d-spacing, a rare phenomena for polymeric organic semiconductors. Another fascinating property of these materials is the airstable p-channel FET performance of annealed copolymer films, which exhibit a hole mobility of ~ $0.01 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and a current on-off ratio of 10^7 . The leading-edge figures-of-merit of this new class of materials reveals the efficacy of the present novel and general computationally-aided materials design strategy, employed here for the first time in organic electronic materials.

Finally, Chapter 4 employs variable temperature measurement of FET activity to elucidate charge transport mechanism characteristics. Temperature activated FET behavior is observed for a series of organic semiconductor-based FETs that were chosen for their unique and varied materials and device characteristics. Variable temperature characterization of FETs based on this set of materials revealed that there is no correlation between the conduction state energy level and E_A while there is an inverse relationship between E_A and μ_{eff} . Fits of μ_{eff} data assuming a discrete trap energy MTR model reveal low E_A for high mobility semiconductors of ~ 20 meV, while higher E_A values of 40 meV - 70 meV are exhibited by lower mobility FETs. Analysis of the first variable temperature data for an ambipolar FET revealed that although n-channel

operation had an $E_A = 27$ meV, the p-channel regime exhibited evidence of significantly more trapping with an $E_A = 250$ meV. Interestingly, the calculated free carrier mobility (μ_0) is found to be 0.2 - 0.8 cm²V⁻¹s⁻¹ for all materials, largely independent of μ_{eff} , supporting a trap-limited mobility model such as multiple trapping and release. Finally, the effect of temperature on V_T revealed a two trapping regimes with N_T exhibiting a striking correlation with μ_{eff} . The lowtemperature regime reveals trapping by shallow states with an depth ~ 40 meV and density of ~ 10^{12} cm⁻², both consistent with previous orthogonal studies. This survey of the variable temperature behavior of several organic semiconductors reveals general trends in trapping for nchannel and p-channel operation and the ΔV_T data suggests that at least two trapping regimes can significantly influence room temperature FET performance. **Chapter Two**

Phenacyl-thiophene and Quinone Semiconductors Designed for Solution Processability and Air-Stability in High Mobility n-channel FETs

2.1 Introduction

The promise of lower-cost electronics and unique application has fueled research in organic electronic materials. Organics hold several key attractions, including low-temperature solution processing, tunable molecular/polymeric structures, and unique mechanical/device properties. These characteristics are valuable in applications where low-cost, mechanical flexibility, large area coverage, and low-temperature processing are desired, such as, organic light-emitting diodes,¹⁻³ sensors,⁴⁻⁸ organic photovoltaics,⁹ and organic field-effect transistors (FETs).¹⁰ Organic semiconductors (OSCs) are an essential component for many of these applications, yet fundamental scientific questions and materials challenges remain concerning long-range charge transport, processability, and ambient stability, especially for electron transporting (n-channel) FET materials.¹¹⁻¹⁴

Simultaneously enabling semiconductor film solution processability and n-channel FET ambient stability remains one of the most significant challenges for organic electronics. There are two primary reasons for this difficulty: 1) to enable efficient n-channel transport, planar π -conjugated cores must be functionalized with strong electron-withdrawing groups, which typically yield flat polar molecules with extremely high crystal packing energies and very low solubility, and 2) mobile electron stabilization in ambient is challenging because of charge trapping by device-born and ambient species.¹⁵⁻¹⁸ The solubility limitation has typically been addressed by adding bulky solubilizing substituents to disrupt solid state π - π stacking, which frequently leads to diminished mobility.¹⁹⁻²³ In one study, the polymer BBL²⁴ (Figure 2.1) is solubilized by coordination with strong Lewis acids, which must then be leached from the film with water.

Initial studies addressing ambient sensitivity of n-channel organic FETs, by de Leeuw, et. al revealed that H₂O and O₂ in ambient atmosphere can trap electron charge carriers, and it was postulated that OSCs with a reduction potential more negative than \sim -0.66 V vs. SCE are susceptible to H₂O-oxidation.¹⁷ Furthermore, recent studies have revealed that, for several OSCs, a reduction potential more positive than ~ -0.2 ± 0.1 V vs. SCE is required to stabilize electron charge carriers in the presence of O₂.^{18, 25, 26} Typically, electron trapping by these gaseous species does not result in chemical degradation of the semiconductor and is reversed when the devices are tested under *in vacuuo*. Air-stable n-channel FET operation has been demonstrated by inhibiting O2 from reaching the semiconductor film charge-transporting region^{16, 27} or by designing a semiconductor that sufficiently stabilizes mobile electrons to make them resistant to O₂ trapping (Figure 2.1).^{18, 25, 26} The O₂ barrier model was originally proposed by Katz, et. al, for the air-stability of N,N'-fluorocarbon substituted naphthalene diimide (NDI-F),^{16, 28, 29} and has also been observed in perfluorinated copper phthalocyanine $(CuF_{16}Pc)^{27, 30-35}$ and fluorocarbonsubstituted oligothiophenes (DFCO-4TCO).³⁶ Unfortunately, each of these materials exhibits device performance degradation over periods of hours to days in air. Other OSCs achieve temporally stable n-channel operation in air by having a reduction potential near \sim -0.2 V vs. SCE or greater, although in some cases $I_{on:off}$ is also dpressed.^{26, 37} These extremely π -deficient, air-stable n-channel molecules are core-cyanated naphthalene diimides, NDI-CN₂, core-cyanated perylene diimides, PDI-CN₂,^{18, 37} cyanated anthracene diimide, ADI-8CN₂,²⁵, BBL,²⁴ and several dicyanomethylene-substituted terthienoquinoids (DCMTs).²⁶ The recently reported investigation of a solution-processed DCMT derivative has yielded the highest $\mu_e = 0.16 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for an airstable material reported to date, although the $I_{on:off} = 10^3$ is diminished due to substantial doping at $V_G = 0$ V.



Figure 2.1. Examples of air-stable organic n-type semiconductors.



Chart 2.1. Phenacyl-thiophene and quinone semiconductors and model compounds.

This contribution describes a versatile new class of organic semiconductors designed to enhance crystallinity, solution processability, and to achieve air-stabile n-channel FET operation. Quaterthiophene is used as the building block for materials **1** - **4** because of its proclivity for favorable crystal packing, substantial μ , and amenability to LUMO energy modulation via core substitution. Previous work on fluorinated and non-fluorinated alkyl,³⁸⁻⁴³ aryl,⁴⁴ and alkylcarbonyl³⁶ substituted thiophenes has revealed that very large FET carrier mobilities can be achieved while sufficiently stabilizing LUMO energies stabilization to enable n-channel FET operation. A phenacyl substitutent is appended to the quaterthiophene π -core to introduce four important characteristics: 1) enhanced solubility via the planarity-breaking induced by the appreciable phenyl group-planar π -core dihedral angle, 2) enhanced crystallinity from phenylphenyl π -stacking, 3) more positive reduction potential resulting from LUMO stabilization by the carbonyl and fluoroaryl substituents, 4) ready adaptability to polymeric structures via substitution at the phenyl ring *para* position to enhance solution rheology and processability.

Previously, it was briefly communicated that materials **1** - **3** enable record-setting figures of merit for solution-cast oligomeric (~ $0.3 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) and n-channel polymeric (~ $10^{-6} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) semiconductors.⁴⁵ In the present contribution, the effect of alkyl solubilizing group position on solid state packing in **3** is investigated in detail by installing the substitutents from the inner pair of thiophenes in **3** to the outer thiophenes in model compound **4**. The possibility of additional LUMO stabilization is first investigated by DFT-level electronic structure computation, revealing that introducing quinone-based subunits, 2,2'-bithiophene-3,3'-oxalaldehyde (**19**), 9,10-phenanthrenequinone, or pyrene-4,5,9,10-tetraone (**21**), into the core of **1**, lowers the reduction potential to -0.5 V, -0.4 V, and -0.2 V vs. SCE, respectively. These reduction potentials span the aforementioned ~ -0.6 V to ~ -0.2 V vs. SCE window required for air-stable n-channel operation

in fluorinated OSCs without incurring ambient carrier doping when the reduction potential is > ~ -0.1 V. The diffraction-derived crystal structure of model compound 7 confirms a cofacial, antiparallel quinone π -stacking motif with a short 3.48 Å π - π distance. Oligomers 5 and 6 both exhibit n-channel FET activity, with 5 having $\mu_e = 0.015 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ while maintaining a large I_{on:off} = 10⁶ for a period greater than one year in air. This family of materials demonstrates that a balance of high-crystallinity and processability can be achieved with appropriate molecular engineering and lays the groundwork for future incorporation of novel, extremely π -electron deficient monomers into polymer semiconductor electronic circuitry.

2.2 Experimental

2.2.1 Materials.

All reagents were purchased from commercial sources and used without further purification unless otherwise noted. Anhydrous diethyl ether and THF were distilled from Na/benzophenone and toluene was distilled from Na. The Stille reagent 5,5'-bis(tributylstannyl)-2,2'-bithiophene was synthesized according to published procedure.⁴⁶ Conventional Schlenk techniques were used and reactions were carried out under N₂ unless otherwise noted. Microwave-assisted reactions were run in sealed vessels using a CEM Discover microwave reactor in the temperature-controlled mode. UV-visible spectra were recorded on a Cary Model 1 UV-visible spectrophotometer. NMR spectra were recorded on a Varian Unity Plus 500 spectrometer (¹H, 500 MHz). Electrochemistry was performed on a C3 Cell Stand electrochemical station equipped with BAS Epsilon software (Bioanalytical Systems, Inc., Lafayette, IN). Elemental analysis was performed by Midwest Microlab (Indianapolis, IN).

2.2.2 Synthesis

Synthesis of (5-bromothien-2-yl)(perfluorophenyl)methanone (13). To a mixture of

perfluorobenzoyl chloride (2.51 g, 10.9 mmol) and 2-bromothiophene (1.86 g, 11.4 mmol) in carbon disulfide (80 mL), aluminum chloride (2.90 g, 21.8 mmol) was added in portions over 10 min with vigorous mechanical stirring. The reaction mixture turned red and was stirred for 2.5 h before being quenched with water (80 mL). The organics were then separated, the aqueous layer extracted with carbon disulfide (3 x 50 mL), and the combined organics washed with water (3 x 100 mL) and dried over MgSO₄. After filtration, the organics were concentrated in vacuo and the chromatographed on a silica gel column (hexane : ether = 9 : 1) to yield 1.23 g (32 %) green crystals. mp 51-54 °C; ¹H NMR (DMSO): δ 7.78 (d, 2H, ³J = 3.6 Hz), 7.54 (d, 2H, ³J = 4.4 Hz); ¹⁹F NMR (DMSO): δ -142.1 (m, 2H), -151.6 (m, 1H), -160.6 (m, 2H) Anal. Calcd for C₁₁H₂BrF₅OS: C 37.00, H 0.56. Found: C 37.37, H 0.83; MS (EI): m/z (%) 355.8 (92) [M⁺].

Synthesis of 5,5"-bis(perfluorophenacyl)-2,2":5",2":5",2"-quaterthiophene (1). А mixture of (2,3,5,6-tetrafluorophenyl)(5-bromothien-2-yl)methanone (6) (0.511 g, 1.43 mmol), 5,5'-bis(tributylstannyl)-2,2'-dithiophene (0.532)7.15 mmol), and g, tetrakis(triphenylphosphine)palladium(0) (0.0250 g, 0.0215 mmol) was degassed with nitrogen three times before 8 mL anhydrous DMF was added. The reaction mixture was heated to 80 °C for 10 h with stirring. A red-brown precipitate formed and upon cooling was collected by filtration, washed with hexanes (3 x 10 mL) and methanol (3 x 10 mL). Gradient sublimation (2x) afforded a bright orange crystalline material (0.305 g, 60 %) with some crystals suitable for x-ray diffraction. mp 291-294 °C; ¹H NMR (DMSO): δ 7.87 (d, 2H, ³J = 3.2 Hz), 7.70 (d, 2H, ³J = 3.2 Hz), 7.60 (d, 2H, ${}^{3}J = 4.4$ Hz), 7.54 (d, 2H, ${}^{3}J = 4.0$ Hz); ${}^{19}F$ NMR (DMSO): δ -142.3 (m), -152.0 (m), -160.7 (m); Anal. Calcd for $C_{30}H_8F_{10}O_2S_4$: C 50.14, H 1.12, F 26.11. Found: C 50.00, H 1.30, F 26.11; MS (EI): m/z (%) 717.8 (100) [M⁺].

Synthesis of (5-bromothien-2-yl)(phenyl)methanone (14). To a mixture of benzoyl chloride (2.81 g, 20.0 mmol) and 2-bromothiophene (3.42 g, 21.0 mmol) in carbon disulfide (120 mL) aluminum chloride (5.34 g, 40.0 mmol), was added in portions over 10 min with vigorous magnetic stirring. The reaction was next allowed to stir for 2.5 h before being quenched with 100 mL 1 M HCl(aq). The organics were separated, the aqueous layer extracted with carbon disulfide (3 x 50 mL), and the combined organics washed with water (3 x 100 mL) and dried over MgSO₄. After fisltration, the organics were concentrated in vacuo and the residue chromatographed on a silica gel column (hexane : ether = 9 : 1) to yield 5.14 g (96 %) of yellow crystals. mp 41-43 °C ; ¹H NMR (CDCl₃): δ 7.84 (d, 2H, ³J = 8.0 Hz), 7.62 (t, 1H, ³J = 7.2 Hz), 7.52 (t, 2H, ³J = 7.5 Hz), 7.40 (d, 2H, ³J = 3.5 Hz), 7.15 (d, 2H, ³J = 4.0 Hz).

Synthesis of 5,5"'-bis(phenacyl)-2,2':5',2":5",2"'-quaterthiophene (2). A mixture of 2bromo-5-benzoylthiohene (1.07 g, 4.00 mmol), 5,5'-bis(tributylstannyl)-2,2'-dithiophene (1.49 g, 2.00 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.0693 g, 0.0600 mmol) was degassed with nitrogen three times before 20 mL anhydrous DMF was added. The reaction mixture was heated to 80 °C for 15 h with stirring. A deep red precipitate formed and upon cooling and was collected by filtration, then washed with hexanes (3 x 10 mL) and methanol (3 x 10 mL). Gradient sublimation (2x) afforded an orange-red crystalline material (0.689 g, 64 %) with some crystals suitable for x-ray diffraction. mp 307-310 °C; ¹H NMR (DMSO): δ 7.85 (2H), 7.84 (2H), 7.67 (4H), 7.59 (2H), 7.53 (2H), 7.48 (1H), 7.44 (1H); Anal. Calcd for C₃₀H₁₈O₂S₄: C 66.88, H 3.37. Found: C 66.93, H 3.42; MS (EI): m/z (%) 538.0 (100) [M⁺].

Synthesisofpoly[5,5'''-(perfluorophenac-4-yl)-4',4''-dioctyl-2,2':5',2''quaterthiophene)(3).A mixture of 4,4'-dioctyl-5,5'-bis(tributylstannyl)-2,2'-dithiophene

(0.969 g, 1.00 mmol), 1,4-bis((5-bromothien-2-yl)carbonyl)-2,3,5,6-tetrafluorobenzene (0.530 g, 1.00 mmol), and tetrakis(triphenylphosphine)palladium(0) (34.7 mg, 0.0300 mmol, 0.03 equiv.) was degassed with nitrogen three times before 10 mL anhydrous DMF was added. The reaction mixture was then heated to 110 °C for an additional 72 h during which time four equal amounts of tetrakis(triphenylphosphine)palladium(0) (34.7 mg, 0.0300 mmol, 0.03 equiv.) were added at intervals of 12 h. After cooling, a red precipitate was isolated by filtration through a 0.45 um filter and washed with methanol (200 mL). The powder was next dissolved in CHCl₃, precipitated with methanol, and centrifuged to give black pellets which became translucent red upon drying in a vacuum oven. This process was repeated three times to give **3** (342 mg) as translucent red flakes soluble in toluene, xylenes, trichlorobenzene, thiophene, and THF. This material has a M_w of 15,300 and M_n of 6100 by HT-GPC (140 °C, trichlorobenzene, calibrated vs. polystyrene). ¹H NMR (CDCl₃): δ 7.51 (m, 2H), 7.13 (s, 1H); ¹⁹F NMR (CDCl₃): δ -138.97 (s), -139.03 (s); ¹¹⁹Sn NMR δ -4.2 (s); Anal. Calcd for C₄₀H₄₀F₄O₂S₄: C 63.46, H 5.33. Found: C 63.20, H 5.44.

Synthesis of 2-bromo-3-octylthiophene (8). NBS (9.00 g, 50.6 mmol) was added to a solution of 3-octylthiophene (9.93 g, 50.6 mmol) in 22 mL glacial acetic acid maintained at 15 °C. After allowing the reaction mixture to stir for 2 h, it was poured into 200 mL hexane and extracted four times with 50 mL of water, once with 50 mL NaHSO₄ (aq, 5% w/v), once with 50 mL brine, and dried over MgSO₄. After filtration and concentration, 13.7 g of a colorless oil **8** was obtained (98% yield) and was used without further purification in the substituent step. Anal. Calcd. for $C_{12}H_{19}BrS$: C, 52.36; H, 6.96; Found: C, 52.28; H, 7.05; ¹H NMR (CDCl₃): δ 7.19 (d, J = 4.0 Hz,
1H), 6.87 (d, J = 4.5 Hz, 1H), 2.63 (t, J = 5.0 Hz, 2H), 1.60 (t, J = 5.0 Hz, 2H), 1.2-1.3 (b, 10H), 0.89 (t, J = 7.5 Hz, 3H); MS (EI): m/z (%) 274.0 (100) [M⁺].

Synthesis of 3-octylthiophene-2-carbaldehyde (9). Compound 8 (30 g, 0.109 mol) was slowly added to Mg turnings (5.3 g, 0.22 mol) vigorously stirring in 120 mL dry THF in a round bottom flask equipped with a reflux condenser. The reaction mixture was next heated at reflux for 4 h before it was allowed to cool, and transferred through a 0.45 μ m syringe filter into a second dry flask, where DMF (0.28 mol, 20 g) was added and the reaction mixture refluxed overnight. Once cool, the reaction mixture was poured into 600 mL hexane, extracted six times with 150 mL of water, and dried over MgSO₄. The oil obtained after filtration and concentration was purified by column chromatography on silica gel, eluting with a 9:1 mixture of hexanes:diethyl ether, to give 11.7 g colorless oil (48% yield). Anal. Calcd. for C₁₃H₂₀OS: C, 69.59; H, 8.98; Found: C, 69.52; H, 8.79; ¹H NMR (CDCl₃): δ 10.04 (s, 1H), 7.65 (d, J = 4.0 Hz, 1H), 7.02 (d, J = 4.5 Hz, 1H), 2.97 (t, J = 5.0 Hz, 2H), 1.67 (t, J = 5.0 Hz, 2H), 1.2-1.4 (b, 10H), 0.90 (t, J = 7.5 Hz, 3H); MS (EI): m/z (%) 224.2 (100) [M⁺].

Synthesis of (3-octylthien-2-yl)(perfluorophenyl)methanol (10). A solution of pentafluorobenzene (4.38 g, 26.0 mmol) in 250 mL dry THF was cooled to -78 °C with stirring before n-BuLi (1.6 M in hexanes, 17.9 mL, 28.6 mmol) was added over the course of 15 min. The reaction mixture was then maintained at -78 °C for 2 h before compound **9** (5.83 g, 26.0 mmol) was added and the reaction mixture allowed to stir for another 6 h at -78 °C before being quenched with 20 mL 5% HCl (aq) (CAUTION: Allowing the lithium salt of pentafluorobenzene to warm to room temperature may result in the potentially-explosive formation of benzyne). The reaction mixture was next poured into 300 mL hexane and extracted three times with 50 mL of

water, once with 50 mL brine, and dried over MgSO₄. The oil obtained after filtration and concentration was purified by column chromatography on silica gel, eluting with a 9:1 mixture of hexanes:diethyl ether, to afford 7.91 g of a colorless oil (77% yield). Anal. Calcd. for $C_{19}H_{21}F_5OS$: C, 58.15; H, 5.39; Found: C, 58.03; H, 5.36; ¹H NMR (CDCl₃): δ 7.23 (d, J = 4.5 Hz, 1H), 6.89 (d, J = 4.5 Hz, 1H), 6.46 (s, 1H), 2.62 (t, J = 5.5 Hz, 2H), 1.2-1.4 (b, 12H), 0.90 (t, J = 7.5 Hz, 3H); MS (EI): m/z (%) 392.1 (100) [M⁺].

Synthesis of (5-bromo-3-octylthien-2-yl)(perfluorophenyl)methanol (11). NBS (3.41 g, 19.1 mmol) was added in one portion to a solution of alcohol 10 (7.51 g, 19.1 mmol) in 150 mL glacial acetic acid and allowed to stir overnight. The reaction mixture was then poured into 300 mL hexane and extracted four times with 50 mL of water, once with 50 mL NaHSO₄ (aq, 5% w/v), once with 50 mL brine, and dried over MgSO₄. Upon filtration and concentration, 9.031 g of a colorless oil was obtained (98% yield) and used without further purification for the next step. Anal. Calcd. for C₁₉H₁₉BrF₃OS: C, 48.42; H, 4.28; Found: C, 48.35; H, 4.31; ¹H NMR (CDCl₃): δ 6.81 (s, 1H), 6.38 (s, 1H), 2.62 (t, J = 5.5 Hz, 2H), 1.2-1.4 (b, 12H), 0.90 (t, J = 7.5 Hz, 3H); MS (EI): m/z (%) 469.9 (100) [M⁺].

Synthesis of (5-bromo-3-octylthien-2-yl)(perfluorophenyl)methanone (12). MnO_2 (12 g) was suspended in a solution of alcohol 11 (8.99 g, 19.1 mmol) in 100 mL dichloromethane with stirring for 3 days. After removal of the solids by filtration and concentration, the oil was purified by column chromatography on silica gel, eluting with a 9:1 mixture of hexanes:diethyl ether, to give 8.52 g of a colorless oil (94% yield). Anal. Calcd. for $C_{19}H_{18}BrF_5OS$: C, 48.42; H, 4.28; Found: C, 48.35; H, 4.31; ¹H NMR (CDCl₃): δ 7.09 (s, 1H), 2.95 (t, J = 6.0 Hz, 2H), 1.2-1.4 (b, 12H), 0.89 (t, J = 7.5 Hz, 3H); MS (EI): m/z (%) 467.9 (100) [M⁺].

Synthesis of 5,5"'-bis(perfluorophenacyl)-4,4"'-dioctyl-2,2':5',2":5'',2"'quaterthiophene (4). A mixture of 12 (0.671 g, 1.43 mmol), 5,5'-bis(tributylstannyl)-2,2'dithiophene (0.532 g, 0.715 mmol), and tetrakis(triphenylphosphine)palladium(0) (25.0 mg, 0.0215 mmol) was then pump-backfill degassed with nitrogen 4 times before 8 mL anhydrous DMF was added. The reaction mixture was then heated to 80 °C for 10 h with stirring. Upon cooling, the reaction mixture was poured into 100 mL ether and extracted three times with 50 mL of water, once with 50 mL brine, and dried over MgSO₄. The red solid obtained upon filtration and concentration was purified by column chromatography on silica gel, eluting with a 5:1 mixture of hexanes:diethyl ether, to afford 0.185 g of **4** as a red solid (36% yield). Anal. Calcd. for $C_{30}H_6F_{10}O_2S_4$: C, 50.28; H, 0.84; Found: C, 50.14; H, 0.87; ¹H NMR (CDCl₃): δ 7.20 (d, J = 4.5 Hz, 2H), 7.18 (s, 2H), 7.15 (d, J = 5.0 Hz, 2H), 2.96 (t, J = 8.5 Hz, 4H), 1.64 (m, 4H), 1.2-1.4 (b, 10H), 0.85 (t, J = 8.5 Hz, 6H); m.p. 52 - 55°C; MS (EI): m/z (%) 715.8 (100) [M⁺].

Synthesis of 5-(5-(pinacolatoboryl)thien-2-yl)(perfluorophenyl)methanone (15). An 8 mL microwave reaction vessel was charged with (5-bromothien-2-yl)(perfluorophenyl)methanone 13 (0.536 g, 1.5 mmol), bis(pinacolato)diboron (0.419 g, 1.65 mmol), [Pd(dppf)Cl₂] (37 mg, 0.045 mmol), and powdered dry potassium acetate (0.442 g, 4.5 mmol) before it was evacuated and backfilled with nitrogen 4 times, and 5 mL toluene added. The reaction mixture was then irradiated with microwaves for 30 min at a temperature of 150 °C. This procedure was repeated five more times, and the combined reaction mixtures poured into 30 mL of ether, passed through a 3 cm plug of Celite, concentrated *in vacuuo*, and the resulting oil purified by Kugelrohr distillation (50 mT, 170 °C) to give 1.20 g of boronic ester **15** as a colorless solid (33% yield). Anal. Calcd. for $C_{17}H_{14}BF_5O_3S$: C, 50.52; H, 3.49; Found: C, 50.47; H, 3.40; ¹H NMR (CDCl₃): δ

7.98 (d, J = 4.0 Hz, 1H), 7.72 (d, J = 4.0 Hz, 1H), 1.38 (s, 12H); m.p. 53-55°C; MS (EI): m/z (%) 404.08 (100) [M⁺].

Synthesis of 5-(5-(pinacolatoboryl)thien-2-yl)(phenyl)methanone (16). An 8 mL microwave reaction vessel was charged with (5-bromothien-2-yl)(phenyl)methanone **14** (0.267 g, 1.00 mmol), bis(pinacolato)diboron (0.279 g, 1.10 mmol), [Pd(dppf)Cl₂] (25 mg, 0.030 mmol), and powdered dry potassium acetate (0.196 g, 2.00 mmol) before it was evacuated and backfilled with nitrogen 4 times, and 6 mL toluene added. The reaction mixture was irradiated with microwaves for 20 min at a temperature of 160 °C. This procedure was repeated two more times and the combined reaction mixtures poured into 30 mL of ether, passed through a 3 cm plug of Celite, concentrated *in vacuuo*, and the resulting dark oil purified by Kugelrohr distillation (50 mT, 190 °C) to give 0.074 g of boronic ester **16** as a light-yellow viscous oil (50% yield). Anal. Calcd. for C₁₇H₁₉BO₃S: C, 64.98; H, 6.09; Found: C, 64.81; H, 5.98; ¹H NMR (CDCl₃): δ 7.89 (d, J = 6.5 Hz, 2H), 7.73 (d, J = 4.0 Hz, 1H), 7.64 (d, J = 4.0 Hz, 1H), 7.60 (t, J = 7.0 Hz, 1H), 7.50 (t, J = 8.0 Hz, 2H), 1.38 (s, 12H); m.p. 78-81°C; MS (EI): m/z (%) 314.10 (100) [M⁺].

Synthesis of 3,3',5,5'-tetrabromo-2,2'-bithiophene (17). In a 1 L round bottom flask fitted with a reflux condenser, bromine (288 g, 1.8 mol) was added slowly over 1 h to a stirring solution of 2,2'-bithiophene (60.0 g, 0.361 mol) in 280 mL chloroform containing 120 mL glacial acetic acid (CAUTION: Addition of the first two equivalents of bromine produces a strongly exothermic reaction). The mixture was then stirred at reflux for 12 h. Upon cooling to room temperature, a colorless precipitate was isolated by filtration and washed with methanol. The filtrate was then concentrated and a second crop of tan precipitate was collected and also washed with methanol. The combined solids were dissolved in methylene chloride (500 mL), washed

four times with 200 mL water, once with 100 mL brine, and dried over anhydrous MgSO₄. The solution was then filtered, and the solvent removed by evaporation to give 157 g (90% yield) of a colorless powder. ¹H NMR (CDCl₃): δ 7.06 (s, 2H) ppm.

Synthesis of 3,3'-dibromo-2,2'-bithiophene (18). Zn powder (31.7 g, 0.485 mol) was added in portions to a vigorously stirred, refluxing mixture of bithiophene 17 (77.9 g, 0.162 mol) in 400 mL of ethanol containing 40 mL water, 100 mL glacial acetic acid, and 8 mL of 3 M HCl (aq). After refluxing for 2 h, the mixture was filtered hot and upon cooling to 0 °C, the resulting yellow crystals were collected by filtration. The crystals were next dissolved in 500 mL diethyl ether, washed three times with 200 mL water, once with 100 mL brine, and dried over anhydrous MgSO₄. The solution was then filtered and the solvent removed by evaporation to afford 49.4 g (94% yield) of a light-yellow powder. Anal. Calcd. for C₈H₄Br₂S₂: C, 29.65; H, 1.24; Found: C, 29.59; H, 1.14; ¹H NMR (CDCl₃): δ 7.41 (d, J = 5.3 Hz, 2H), 7.09 (d, J = 5.3 Hz, 2H) ppm.

Synthesis of 2,2'-bithiophene-3,3'-dicarbaldehyde (19). A solution of bithiophene 18 (8.39 g, 25.9 mmol) in 50 mL THF was added dropwise over 1 h to a stirring solution of n-BuLi (82.5 mL, 1.6 M in hexanes) in 200 mL THF at -78 °C. The reaction mixture allowed to stir for an additional 2 h at -78 °C before dry DMF (4.17 g, 57.0 mmol) in 50 mL THF was added dropwise to the reaction mixture over the course of 30 min. The reaction mixture was then allowed to stir for an additional 30 min before it was quenched with 50 mL of 5% HCl (aq), allowed to warm to room temperature, washed three times with 200 mL water, once with 100 mL brine, and dried over anhydrous MgSO₄. The red solid obtained upon filtration and concentration was purified by column chromatography on silica gel, eluting with a 6:1 mixture of hexanes:chloroform ether, to afford 3.19 g of **19** as a red solid that was dried *in vacuuo* and used immediately in the next reaction. Anal. Calcd. for $C_{10}H_6O_2S_2$: C, 54.03; H, 2.72; Found: C,

53.90; H, 2.64; ¹H NMR (CDCl₃): δ 9.86 (s, 1H), 7.65 (d, J = 5.5 Hz, 2H) , 7.50 (d, J = 5.5 Hz, 2H); MS (EI): m/z (%) 222.1 (100) [M⁺].

Synthesis of 2,2'-bithiophene-3,3'-oxalaldehyde (20). The precatalyst 3,4-dimethyl-5-(2-hydroxyethyl)thiazolium iodide (1.70 g, 6.74 mmol) was suspended in 180 mL dry DMF before 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1.02 g, 6.70 mmol) was slowly added and the solution allowed to stir for 5 min. Dialdehyde **19** was then added and the reaction mixture allowed to stir for 2 h under nitrogen, before being opened to air and allowed to stir overnight. The dark red reaction mixture was then poured into 500 mL of chloroform, extracted seven times with 200 mL of water, once with 200 mL brine, and dried over MgSO₄. A dark colored solid was obtained upon filtration, concentration, and was purified by sublimation under vacuum (138 °C / 100 mTorr) to afford 4.61 g (94% yield). Anal. Calcd. for C₁₀H₄O₂S₂: C, 54.53; H, 1.83; Found: C, 54.48; H, 1.76; ¹H NMR (CDCl₃): δ 7.62 (d, J = 5.0 Hz, 2H), 7.44 (d, J = 5.0 Hz, 2H); m.p. 221-223 °C; MS (EI): m/z (%) 220.0 (100) [M⁺].

Synthesis of 5,5'-diiodo-2,2'-bithiophene-3,3'-oxalaldehyde (21). N-iodosuccinimide (4.56 g, 20.2 mmol) was slowly added to a stirring suspension of quinone 20 (2.23 g, 10.1 mmol) in 20 mL BF₃·Me₂O and allowed to stir under air in a Nalgene beaker for 4 h before being poured into 100 mL of water, the crude product was collected by filtration, washed with 20 mL NaHSO₄ (aq, 5% w/v), and recrystallized from xylenes to afford 2.68 g dark purple crystalline material (61% yield). Anal. Calcd. for C₁₀H₂I₂O₂S₂: C, 25.44; H, 0.43; Found: C, 25.36; H, 0.49; ¹H NMR (DMSO-d6): δ 7.70 (s, 2H); m.p. 315-318 °C; MS (EI): m/z (%) 471.8 (100) [M⁺].

Synthesis of 2,7-diiodo-9,10-phenanthrenequinone (22). Iodine (14.6 g, 57.5 mmol) and potassium permanganate (10.3 g, 65.0 mmol) were suspended in a mixture of 100 mL glacial

acetic acid and 30 mL acetic anhydride that had been stirring for 5 h. The suspension was stirred vigorously with a magnetic stirbar and maintained at 5 °C while H_2SO_4 (aq, conc., 40 mL) was added dropwise (CAUTION: Addition of concentrated H_2SO_4 can produce a vigorous exotherm if not performed slowly). The slurry was then allowed to warm to room temperature before phenanthrenequinone (10.4 g, 50.0 mmol) added and the reaction mixture stirred for 2 days. The product solids were isolated by filtration, washed with 30 mL hexane, 50 mL methanol, 100 mL NaHSO₄ (aq, 5% w/v), 50 mL acetone, and then recrystallized from hot xylenes to afford 6.31 g orange solid (27% yield). Anal. Calcd. for $C_{14}H_6I_2O_2$: C, 36.55; H, 1.31; Found: C, 36.52; H, 1.25; ¹H NMR (DMSO-d₆): δ 8.25 (s, 2H), 8.11 (d, J = 7.5 Hz, 2H), 8.10 (d, J = 8.0 Hz, 2H); m.p. 302-305 °C; MS (EI): m/z (%) 459.9 (100) [M⁺].

Synthesis of 2,7-bis((5-perfluorophenacyl)thiophen-2-yl)-9,10-phenanthrenequinone (5). A 25 mL Schlenk flask with an attached condenser was charged with boronic ester 15 (0.848 g, 2.10 mmol), aryl iodide 22 (0.460 g, 1.00 mmol), $[Pd_2(dba)_3]$ (183 mg, 0.200 mmol), tri-*o*-tolylphosphine (122 mg, 0.400 mmol), and evacuated then backfilled with nitrogen five times before 13 mL toluene and 3.1 mL Na₂CO₃ (aq, degassed, 1.5 M) were added. The reaction mixture was next heated at reflux overnight and the solids collected by filtration upon cooling, washed with 10 mL acetone, 10 mL methanol, and purified by multiple gradient sublimations (307 °C/< 10⁻⁶ mT) to give 0.190 g of **5** as a dark-brown crystalline solid (26% yield). Anal. Calcd. for C₃₆H₁₀F₁₀O₄S₂: C, 56.85; H, 1.33; Found: C, 56.78; H, 1.21; ¹H NMR (DMSO-d6): δ 8.51 (d, J = 8.0 Hz, 2H), 8.40 (s, 2H), 8.27 (d, J = 7.5 Hz, 2H), 8.06 (d, J = 4.0 Hz, 2H), 8.02 (d, J = 4.5 Hz, 2H); m.p. 351-354 °C; MS (EI): m/z (%) 760.0 (100) [M⁺].

Synthesis of 2,7-bis((5-phenacyl)thiophen-2-yl)-9,10-phenanthrenequinone (6). A 25 mL Schlenk flask with an attached condenser was charged with boronic ester 16 (0.736 g, 2.34 mmol), aryl iodide 22 (0.513 g, degassed, 1.12 mmol), $[Pd_2(dba)_3]$ (428 mg, 0.47 mmol), tri-*o*-tolylphosphine (142 mg, 0.94 mmol), and evacuated then backfilled with nitrogen five times before 15 mL toluene and 3.1 mL Na₂CO₃ (aq, 1.5 M) were added. The reaction mixture was next heated at reflux overnight, and the solids collected by filtration upon cooling, washed with 10 mL acetone, 10 mL methanol, and recrystallized 5 times from boiling nitrobenzene to afford 0.214 g of **6** as a brown crystalline material (33% yield). Anal. Calcd. for C₃₆H₂₀O₄S₂: C, 74.46; H, 3.47; Found: C, 74.59; H, 3.58; ¹H NMR (DMSO-d₆): δ 8.51 (d, J = 8.0 Hz, 2H), 8.40 (s, 2H), 8.27 (d, J = 7.5 Hz, 2H), 8.06 (d, J = 4.0 Hz, 2H), 8.02 (d, J = 4.5 Hz, 2H); m.p. 312-315 °C; MS (EI): m/z (%) 580.2 (100) [M⁺].

Synthesis of 2,7-bis(thiophen-2-yl)-9,10-phenanthrenequinone (7). A 25 mL Schlenk flask with an attached condenser was charged with 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (0.441 g, 2.10 mmol), aryl iodide 20 (0.460 g, 1.00 mmol), $[Pd_2(dba)_3]$ (183 mg, 0.200 mmol), tri-*o*-tolylphosphine (122 mg, 0.400 mmol), and evacuated then backfilled with nitrogen five times before 13 mL toluene and 3.1 mL Na₂CO₃ (aq, 1.5 M) were added. The reaction mixture was then heated at reflux overnight and the resulting solids then collected by filtration upon cooling, washed with 10 mL acetone, 10 mL methanol, and purified by multiple gradient sublimations to give 0.145 g of **7** as a dark-brown crystalline solid (39% yield). Anal. Calcd. for C₂₂H₁₂O₂S₂: C, 70.94; H, 3.25; Found: C, 70.87; H, 3.17; ¹H NMR (DMSO-d₆): δ 8.35 (d, J = 8.0 Hz, 2H), 8.19 (s, 2H), 8.08 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 3.5 Hz, 2H), 7.69 (d, J = 5.0 Hz, 2H), 7.22 (t, J = 4.5 Hz, 2H); m.p. 295-298 °C; MS (EI): m/z (%) 372.1 (100) [M⁺].

Synthesis of pyrene-4,5,9,10-tetraone (23). Sodium metaperiodate (35.1 g, 164 mmol), water (100 mL), and RuCl₃·3H₂O (0.498 g, 2.40 mmol) were added to a solution of pyrene (4.05 g, 20.0 mmol) in a mixture of 80 mL dichloromethane and 80 mL acetonitrile. The reaction mixture was heated to 40 °C, allowed to stir overnight, and the resulting solids then collected by filtration upon cooling. The crude product was then recrystallized from xylenes to afford 0.632 g **21** as a black crystalline material (15% yield). Anal. Calcd. for C₁₆H₆O₄: C, 73.29; H, 2.31; Found: C, 73.26; H, 2.28; ¹H NMR (CDCl₃): δ 8.46 (d, J = 3.5 Hz, 2H), 8.20 (d, J = 2.0 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H); MS (EI): m/z (%) 262.0 (100) [M⁺].

Synthesis of 2,7-diiodopyrene-4,5,9,10-tetraone (24). N-iodosuccinimide (0.674 g, 3.00 mmol) dissolved in 1 mL H₂SO₄ (aq, conc.) was slowly added to a suspension of tetraone 23 (262 mg, 1.00 mmol) in a mixture of 2 mL trifluoroacetic acid and 5 mL H₂SO₄ (aq, conc.). The reaction mixture was allowed to stir for 2 days at 40 °C before being poured into 20 mL of water, and the crude product collected by filteration, washed with 20 mL NaHSO₄ (aq, 5% w/v), and recrystallized from nitrobenzene to give 295 mg of 22 as a black crystalline material (59% yield). Anal. Calcd. for C₁₆H₄I₂O₄: C, 37.39; H, 0.78; Found: C, 37.27; H, 0.69; ¹H NMR (DMSO-d6): δ 8.51 (s, 4H); MS (EI): m/z (%) 513.9 (100) [M⁺].

2.2.3 Polymer Molecular Weight Determination

GPC measurements were performed on a Polymer Laboratories PL-GPC 220 instrument using 1,2,4-trichlorobenzene solvent (stabilized with 125 ppm BHT) at 150 °C. A set of three PLgel 10 µm mixed columns was used. Samples were prepared at 160 °C. Molecular weights were determined by GPC using narrow polystyrene standards and are not further corrected.

2.2.4 Device Fabrication and Measurement

Prime grade p-doped silicon wafers (100) having 300 nm thermally grown oxide layer (Process Specialties Inc.) were used as device substrates. These were sonicated in methanol, acetone, propanol, and oxygen plasma cleaned before film deposition. Trimethylsilyl functionalization of the SiO₂ surface was carried out by exposing the cleaned silicon wafers to hexamethyldisilazane (HMDS) vapor under nitrogen at room temperature for 4 days. Vacuum-deposited films of oligomers were thermally evaporated onto temperature-controlled substrates under high-vacuum (< 3 x 10⁻⁶ Torr) at a QCM-monitored growth rate of 0.1 - 0.2 Å/s. Solution-deposited oligomer and oligomer-polymer blend films were drop-cast from 0.4 mL toluene or xylenes solutions onto a temperature-controlled substrate in a solvent-saturated air atmosphere. Films of polymer 3 were spin-coated and drop-cast from a 500 ppm solution in a xylenes/diethylamine mixture (9:1 v/v), dried at 120 °C in vacuuo for 12 h. Annealing was performed 150 °C and 250 °C with negligible effect on device performance. For FET device fabrication, top-contact gold electrodes (500 Å) were deposited by thermal evaporation through a shadow mask to define channels with dimensions 100 μ m (L) by 2.00 mm (W). The capacitance of the insulator is 1 x 10⁻⁸ F/cm² for 300 nm SiO₂, and mobility is measured in the saturation regome. TFT device measurements were carried out at 21 °C - 23 °C in a customized high-vacuum probe station ($< 1 \times 10^{-6}$ Torr) or in air. Coaxial and/or triaxial shielding was incorporated into Signaton probes to minimize the noise level. TFT characterization was performed with a Keithley 6430 sub-femtoampmeter (drain) and a Keithley 2400 (gate) source meter, operated by a locally written Labview program and GPIB

communication. Thin films were analyzed by wide-angle X-ray film diffractometry (WAXRD) on a Rikagu ATX-G instrument using standard θ -2 θ techniques and Cu K α_1 radiation. Scanning electron microscopy was performed on a Hitachi 4800 SEM with samples coated with a 2 nm Au/Pd sputtered film.

2.2.5 Electrochemistry

Cyclic voltammetry measurements were performed in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate in dry THF. Platinum electrodes were used as both working and counter electrodes, and Ag wire was used as the pseudo-reference electrode. A ferrocene/ferrocenium redox couple was used as an internal standard and potentials obtained in reference to the silver electrode were converted to the saturated calomel electrode (SCE) scale.

2.2.6 Thermal characterization

All materials were dried under vacuum for 3 d at 100 °C before thermal analysis. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TMA/SDTA841e instrument at a ramp rate of 10 °C/min using an aluminum oxide crucible under vacuum (5 T) for molecular materials or under nitrogen at atmospheric pressure for the polymer. Differential scanning calorimetry (DSC) was performed using a Mettler Toledo DSC823e instrumentat a ramp rate of 10 °C/min using aluminum pans under nitrogen.

2.2.7 Single-crystal X-ray diffraction

Crystals were was mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a CCD area detector with graphite monochromated MoK α radiation. See Section 2.6 for details of single crystal diffraction structure refinement.

2.2.8 Computational methodology

Equilibrium geometry optimizations were performed in QChem 2.1⁴⁷ at the density functional theory (DFT) level with a B3LYP functional and the 6-31G* basis set. Single point calculations using these geometries were then performed at the DFT/B3LYP/6-31+G* level of theory to obtain molecular orbital energy levels (QChem) and orbital electron density plots (Spartan '06). Energy levels were calibrated to the experimental HOMO/LUMO energies³⁹ of sexithiophene.

2.3 Results

2.3.1 Synthesis

The synthesis of all of the present semiconductors proceeds according to Scheme 2.1. Compounds 1 - 3 are obtained by Stille coupling of the appropriate phenacyl-thiophene bromide to bis-stannylated bithiophene.⁴⁵ Gel permeation chromatography (GPC) is used to determine polymer molecular weight versus polystyrene. Polymer **3** was found to have $M_w = 15,300$ D and PDI = 2.51. Model compound 4 is obtained by Stille coupling of 5-(5-(pinacolatoboryl)thien-2yl)(perfluorophenyl)methanone 15 and 5,5'-bis(tributylstannyl)-2,2'-bithiophene. Phenanthrenequinone-based compounds 5 - 7 are obtained by Suzuki coupling of the corresponding boronic esters and 2,7-diiodophenanthrenequinone (22). Purification of 5 and 7 is achieved by multiple gradient high-vacuum sublimations, and 6 is purified by multiple recrystallizations from nitrobenzene. The two other quinone compounds, 5,5'-diiodo-2,2'bithiophene-3,3'-oxalaldehyde (21) and 2,7-diiodopyrene-4,5,9,10-tetraone (24), are synthesized in five and two steps, respectively, from commercially-available starting reagents. Couplings of bithiophene quinone 21 with 15 or 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane yield the desired products (confirmed by EI-MS), however the reaction mixtures decompose below 250 °C, precluding product isolation by sublimation, and are intracTable 2.(even in refluxing nitrobenzene or trichlorobenzene). Suzuki coupling of boronic ester 15 or 4,4,5,5tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane with 24 yields intracTable 2.solids, and the EI-MS spectra of these materials does not indicate the presence of the desired products.

All semiconductor building blocks 12 - 16, 21, 22, and 24 were synthesized from commercially available materials as shown in Scheme 2.2. The *n*-octyl functionalized aryl



Scheme 2.1. Synthesis of semiconductors 1 - 7.



Scheme 2.2. Synthesis of precursor materials.

bromide 12, precursor of semiconductor 4, was synthesized in four steps. First, 3-octylthiophene was brominated to give compound 8, which was then formylated by quenching the Grignard reagent with DMF. The lithium salt of pentafluorobenzene was next reacted with the 2-carboxythiophene 9 to give alcohol 10, which was brominated with NBS then oxidized with MnO_2 to afford 12. After purification via column chromatography, compound 12 was coupled with 5,5'-bis(tributylstannyl)-2,2'-bithiophene to give the new material 4 in 36% yield, after purification by column chromatography and Kugelrohr distillation (Scheme 2.2).

Catalytic borylation^{48, 49} is employed in the synthesis of intermediates **15** and **16**, precursors to semiconductors **5** and **6**, since both the π -deficient quinone core **22** and phenacyl-thiophene units in **13** and **14** are unstable under conventional metallation conditions. As borylation and acetal protection of quinones **21** and **22** was unsuccessful, efforts focused on catalytic borylations of the phenacyl-thiophene bromides **13** and **14**. Since borylation of **13** performed in the standard solvent DMF^{48, 50} affords the *para*-hydroxyl substituted pentafluorophenyl derivative, anhydrous toluene is used as the reaction solvent. Note that the reactions performed using conventional heating occur in low yields (< 5% in this case), however, microwave irradiation results in yields of 33% and 50% for **15** and **16**, respectively, after purification by sublimation in a Kugelrohr apparatus.

Iodo-functionalized quinone cores are used here since the aryl-bromide derivatives are unreactive under Suzuki Coupling conditions. Quinone **21** is synthesized in five steps from 2,2'bithiophene. First, 2,2'-bithiophene is tetrabrominated by refluxing with Br_2 in a mixture of chloroform and acetic acid to afford 3,5,3',5'-tetrabromo-2,2'-bithiophene **17**, which was then selectively debrominated with Zn to yield 3,3'-dibromo-2,2'-bithiophene **18**. Compound 3,3'-dicarboxy-2,2'-bithiophene (**19**) was obtained by slowly adding compound **18** to a dilute solution of n-BuLi, followed by reacting the dilithium salt with DMF. The resulting dialdehyde undergoes benzoin condensation⁵¹ in the presence of 3,4-dimethyl-5-(2-hydroxyethyl)thiazolium iodide to afford the corresponding cyclized α -hydroxy ketone, which is then oxidized in air to afford quinone **20** in 94% yield, after purification by sublimation. Aryl-diiodide **21** is obtained in 61% yield by BF₃•(CH₃)₂O-catalyzed iodination of **20** with *N*-iodo-succinimide. Finally, commercially-available phenanthrenequinone is iodinated by I₂/KMnO₄ to give intermediate **22** in 27% yield after recrystallization from xylenes. Diiodinated pyrenetetraone **24** is obtained by RuCl₃-catalyzed oxidation of pyrene with sodium metaperiodate, then iodination with I₂/KMnO₄.

2.3.2 OSC thermal properties

Thermogravimetric analysis (TGA) is used to evaluate the thermal stability of semiconductors 1 - 7 (Figure 2.2a, Table 2.1). A mass loss of 5% is defined as the threshold for sublimation (1, 2, 5, 6, 7) or decomposition (3, 4). The TGA of molecules for use in vacuum deposition (1, 2, 5, 6, 7) is measured at a pressure of 5 Torr (with a N₂ purge) and the TGA of materials only processed from solution (3, 4) is performed under N₂ at atmospheric pressure. All molecular materials demonstrate good thermal stability and volatility, with the onset of sublimation at 295 °C and 342 °C for compounds 1 and 2, respectively, and at 375 °C, 404 °C, and 309 °C for quinone-based 5, 6, and 7, respectively. Polymer 3 and solution-castable molecule 4 decompose at 425 °C and 363 °C, respectively. Differential scanning calorimetry (DSC) is employed to characterize thermal transitions of 1 - 7 under N₂. DSC plots reveal reversible melting transitions at 294 °C (1), 306 °C (2), 352 °C (5), 316 °C (6), and 297 °C (7) for vacuum-deposited materials (Figure 2.2b and Table 2.1). Polymer 3 exhibits no thermal transitions in the experimental window, while material 4 undergoes a liquid crystalline transition at 51 °C and melting at 99 °C.



Figure 2.2. Thermogravimetric analysis (TGA, a) and differential scanning calorimetry (DSC, b) plots of materials 1 - 7. Data are collected in Table 2.1.

compound	m.p. (°C) -	T _{DSC}		
		heating	cooling	$\mathbf{I}_{\mathbf{IGA}}(\mathbf{C})$
1	291 - 194	294	257	295
2	302 - 307	306	277	342
3				425
4	95 - 99	51, 99		363
5	350 - 353	352	333	375
6	309 - 316	316	281	404
7	294 - 297	297	254	309

 Table 2.1. Thermal properties of oligomers and polymers.

2.3.3 Optical properties

Solution and thin-film optical absorption spectra of the present oligomers and polymer are shown in Figure 2.3, and optical data summarized in Table 2.2. In THF solution, molecules 1, 2, and polymer **3** exhibit absorption maxima at 458 nm, 442 nm, and 460 nm, respectively. The spectra of **1** and **2** as thin films reveal hypsochromic shifts of 23 nm and 38 nm, respectively, while the absorption maximum of compound **3** shifts bathochromically by 16 nm. Compound **4** exhibits similar behavior to polymer **3**, with a solution absorption maximum at 453 nm and a bathochromic shift for the film to 457 nm. Quinone-based materials **5**, **6**, and **7** are significantly blue-shifted, having their solution absorption maxima located at 369 nm, 370 nm, and 318 nm, respectively. As thin films, these materials exhibit slight peak broadening with absorption maxima at 371 nm, 365 nm, and 329 nm, respectively.

2.3.4 Electrochemical properties

The redox behavior of compounds 1 - 7 was investigated in THF solution using cyclic voltammetry (Figure 2.4 and Table 2.3). Oligomers 1 and 2 exhibit an onset of reduction at -0.81 V and -0.97 V with first reduction half-wave potentials of -1.03 V and -1.31 V, respectively. Two irreversible oxidation events are observed in 1 at +1.07 and +1.22 V, while no oxidations are observed in 2. Polymer 3 exhibits three reversible reductions with reductive onset at -1.05 V and half-wave potentials located at -1.12 V, -1.24 V, and -1.79 V. Two irreversible oxidations are observed for compound 3 at +0.96 V and +1.13 V. Model compound 4 exhibits a 0.2 V anodic shift in reduction potential compared to 1, with onset at -1.16 V, and the reduction half-wave located at -1.23 V. Two irreversible oxidations are observed for 4 at +1.04 V and +1.40 V. The new quinone-containing molecules exhibit significant ~ +0.6 V cathodic shifts in their completely reversible reduction behavior.



Figure 2.3. Optical absorbtion spectra of compounds **1** - **7** in THF solution (**a**) and as thin films on glass (**b**). Data are collected in Table 2.2.

	λ_{\max}^{soln} (nm)	$\lambda_{ ext{shoulder}}^{ ext{ soln}} onumber \ (nm)$	$\lambda_{\max}^{ \ \ film} (nm)$	$\lambda_{ ext{shoulder}}^{ ext{film}} onumber (nm)$	E _{gap} ^{opt a} (eV)	HOMO ^b (eV)	LUMO ^c (eV)
1	458		435	495, 373	2.40	5.99	-3.59
2	442		404	462	2.47	5.90	-3.43
3	460		476	522	2.37	5.72	-3.35
4	453		457	469	2.41	5.88	-3.47
5	369	374, 322	371		2.62	6.64	-4.03
6	370	382	365		2.54	6.56	-4.02
7	318	340, 354	329	370	2.56	6.53	-3.97

 Table 2.2. Summary of optical absorbtion data for materials 1 - 7.

^aOptical band gap calculated from the red edge of the S_0 - S_1 absorbtion band at 1/10 of the maximum intensity. ^bHOMO energy estimated by subtracting the optical gap from LUMO energy. ^cEstimated from the onset of the first electrochemical reduction using the correction factor -4.4 V to convert the SCE reference to vacuum.⁵²



Figure 2.4. Cyclic voltammograms of compounds **1** - **7** in THF solution. Data are collected in Table 2.3.

	Oxid	ation ^a	Reduction								
	cathodic		cathodic			anodic			half-wave		
compound	E _{c1}	E_{c2}	E _{c1}	E_{c2}	E_{c3}	E _{a1}	E_{a2}	E_{a3}	$E_1^{1/2}$	$E_2^{1/2}$	$E_{3}^{1/2}$
1	1.07	1.22	-0.99	-1.12		-1.07	-1.18		-1.03	-1.15	
2			-1.27			-1.35			-1.31		
3	0.96	1.13	-1.08	-1.15	-1.88	-1.17	-1.32	-2.06	-1.12	-1.24	-1.97
4	1.04	1.40	-1.13			-1.34			-1.23		
5	1.60		-0.40	-0.86	-1.69	-0.50	-1.18	-1.79	-0.45	-1.02	-1.74
6			-0.41	-0.91	-1.74	-0.51	-1.25	-1.89	-0.46	-1.08	-1.82
7			-0.44	-1.04	-1.27	-0.64	-1.12	-1.47	-0.54	-1.08	-1.37

Table 2.3. Anodic (E_a), cathodic (E_c), and half-wave ($E^{1/2}$) potentials (V vs. SCE) from cyclic voltammetry of compounds **1** - **7** in THF solution.

^aOxidation events are irreversible.

Reduction onset occurs at -0.37 V, -0.39 V, and -0.43 V; first half-wave potentials are located at -0.45 V, -0.46 V, and -0.54 V; second half-wave potentials are located at -1.02 V, -1.08 V, and - 1.08 V; and third half-wave potentials are located at -1.74 V, -1.82 V, and -1.37 V for compounds **5**, **6**, and **7**, respectively. One irreversible oxidation event is observed for compound **5** at +1.60 V. It is interesting that the quaterthiophene-based materials exhibit a +0.3 V cathodic shift upon fluorination while the quinone-based materials have onset and reduction half-wave potentials that are largely independent of ancillary substitution.

2.3.5 Thin-film X-ray diffraction and surface microstructure analysis

Thin-film wide angle X-ray diffraction (WAXRD) θ -2 θ scans of materials **1** - **7** were performed to investigate the degree of film crystallinity and molecule/polymer chain orientation with respect to the substrate plane. Scanning electron microscopy (SEM) was employed to characterize film surface morphology and uniformity. OSC films were vacuum-deposited or drop-cast onto the same substrates (HMDS treated p⁺⁺-Si-300 nm SiO₂) used to fabricate TFTs. Oligomers **1**, **2**, **5**, and **6** thin films exhibit pronounced Bragg diffraction features (Figure 2.5), while the films of molecules **4**, **7**, and polymer **3** do exhibit detecTable 2.reflections in the WAXRD scans. SEM imaging revealed primarily homogenous films with crystallites and ribbons protruding from the surface (Figures 2.6 and 2.8). Thin films of oligomers **1** and **2** exhibit prominent Bragg reflections in θ -2 θ scans up to 10th and 8th order, respectively. The scans indicate single-phase films with d-spacings of 26.6 ± 0.1 Å (**1**) and 26.31 ± 0.1 Å (**2**). As the substrate deposition temperature (T_D) in increased, higher intensity and narrower reflections are observed for both films. The θ -2 θ diffraction patterns of quinone-based materials **5** and **6** evidence similar crystallinity trends with T_D.



Figure 2.5. X-ray diffraction θ -2 θ plots of semiconductors 1 (a), 2 (b), 5 (a), and 6 (b) as thin vapor-deposited films (unless otherwise indicated) onto substrates at the indicated temperature, T_D .

Thus, oligomer **5** exhibits a single family of Bragg reflections up to 9th order with a d-spacing of 27.9 \pm 0.1 Å, indicating a single-phase film. Films of **6** exhibit reflections up to 7th order with a primary d-spacing of 25.90 \pm 0.08 Å, a second phase is also present at T_D = 150 °C and having a d-spacing of 27.05 \pm 0.04 Å.

SEM imaging of vapor-deposited oligomers **1** and **2** reveals crystallites protruding from a smooth underlying film (Figures 2.6a-f). Crystallite size increases with T_D for both materials from ~ 100 nm at $T_D = 25$ °C to ribbons > 1 µm long at $T_D = 90$ °C. Solution-cast films of **1** exhibit large crystalline plates having flat surfaces and dimensions > 50 µm in SEM images (Figure 2.6g) and obvious birefringence in optical micrographs (Figure 2.7a). Blends of oligomer **1** and polymer **3** also exhibit film surfaces with crystalline plates having dimensions of ~ 50 µm SEM images (Figure 2.6h) and birefringence in optical micrographs (Figure 2.7b).

SEM imaging of vapor-deposited compound **5** films reveals similar surface morphologies to **1** and **2**. Crystallites ~ 100 nm long dominate the surface of films grown at $T_D = 25$ °C, while longer, > 1 µm ribbons protrude from otherwise smooth films at higher T_D (Figure 2.8a-c). Oligomer **6** exhibits a surface with fewer crystallites at $T_D = 25$ °C, which grow and coalesce into smooth films at intermediate T_D values before gaps begin to appear in the film at $T_D = 150$ °C (Figure, 7d-f). Films of **7**, which do not exhibit X-ray diffraction, also have markedly different surface morphology from the other materials. Films grown at $T_D = 25$ °C are amorphous and become discontinuous as T_D increases with large gaps forming between islands of **7** (Figures 2.8g-h).



Figure 2.6. SEM micrographs of semiconductor 1 and 2 thin-films vapor-deposited onto substrates at temperatures of 25 °C (\mathbf{a} , \mathbf{d}), 70 °C (\mathbf{b} , \mathbf{e}), or 90 °C (\mathbf{c} , \mathbf{f}), or as solution-cast films of 1 (\mathbf{g} , toluene, 500 ppm) and a 1:3 blend (\mathbf{h} , toluene, 1:1, 500 ppm).



Figure 2.7. Optical micrographs of drop-cast films of oligomer 1 (a) and a blend of 1 and 3 (b).



Figure 2.8. SEM micrographs of semiconductor **5** (**a**, **b**, **c**) and **6** (**d**, **e**, **f**) thin films vapordeposited onto substrates at temperatures of 25 °C (**a**, **d**,), 120 °C (**b**, **e**), or 150 °C (**c**, **f**), as well as micrographs of **7** thin films vapor-deposited onto substrates at temperatures of $T_D = 50$ °C (**g**), 50 °C (**h**), or 90 °C (**i**).

2.3.6 Transistor fabrication and optimization

Thin-film transistors were fabricated with films of OSCs **1** - **7** as the semiconducting layer. Oligomers **1**, **2** and **4** - **7** were vacuum-deposited (**1**, **2**, and **4** were also drop-cast), while polymer **3** was spin-cast and drop-cast. A minimum of 10 devices for all FETs were tested under highvacuum and once fully characterized, their operational stability in air was also evaluated. Oligomers **1**, **3**, **5**, and **6** exhibited exclusively n-type transport in top-contact bottom-gate FET geometries (Figures 2.9, 2.10, and 2.11), while **2** exhibits exclusively p-type behavior. Oligomer and polymer film microstructure was adjusted to optimize device performance by varying the substrate temperature (T_D) during vacuum deposition and drop-casting. Solution-cast films of OSCs **1** - **4** were additionally annealed at 75 °C, 150 °C, and 250 °C with negligible effect on FET performance. The FET performance of **1** is enhanced as T_D is increased (Table 2.4), from 25 °C ($\mu_e = 0.18 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, I_{on:off} = 3 x 10⁵, V_T = +68 V at T_D = 25 °C), to a maximum at T_D = 80 °C ($\mu_e = 0.45 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, I_{on:off} = 1 x 10⁸, V_T = +35 V). Under the optimized conditions, **1** exhibits low contact resistance and excellent saturation behavior in the output plot (Figure 2.9b), but does not exhibit FET activity under air. The FET response of **2** also increases with T_D, from $\mu_h = 0.012 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at 25 °C (I_{on:off} = 10⁵, V_T = -33 V), to a maximum μ_h of 0.043 cm² V⁻¹ \text{s}^{-1} at T_D = 90 °C (I_{on:off} = 10⁶, V_T = -19 V). Films of **2** exhibit ideal saturation behavior with only slight contact resistance (Figure 2.9d) and completely air-stable operation.

Solution-cast films of **1** and **2** exhibit excellent FET performance (Figure 2.10). The average μ_e for drop-cast **1** films is 0.21 (8) cm²V⁻¹s⁻¹ (0.27 cm²V⁻¹s⁻¹ maximum) with a large I_{on:off} of 4 x 10⁵ figures of merit similar to the vapor-deposited films. Drop-cast films of **2** exhibit an average μ_h of 8 (4) x 10⁻⁴ cm²V⁻¹s⁻¹ with an I_{on:off} of ~ 10⁴. Spin-cast and drop-cast films of polymer **3** exhibit a mobility of 1.7 (6) x 10⁻⁶ with an I_{on:off} of 2 (1) x 10² and V_T = +52 (10) V (Figure 2.10b). Blends of **1** and **3** were also drop-cast to enhance FET performance while maintaining the favorable solution rheology of the polymer (500 ppm concentration at a 1:1 wt. ratio from xylenes), resulting in films exhibiting $\mu_e = 0.02$ (1) cm²V⁻¹s⁻¹ with I_{on:off} = 3 x 10⁴ and V_T = +68 V (Figure 2.10c).



Figure 2.9. FET transfer (a) and output (b) plots of vacuum-deposited films of 1 ($T_D = 80$ °C) and 2 (c and d, respectively, $T_D = 90$ °C).



Figure 2.10. FET transfer plots measured under vacuum for 1 drop-cast (a), 3 spin-cast (b), and a 1:3 blend drop-cast (c).

	Semiconductor								
$T_D(^{\circ}C)$		1		2					
	$\mu_{e} (cm^{2}V^{-1}s^{-1})$	$V_{T}(V)$	I _{on:off}	$\mu_{h} (cm^{2}V^{-1}s^{-1})$	$\mathbf{V}_{\mathbf{T}}\left(\mathbf{V}\right)$	$\mathbf{I}_{\mathrm{on:off}}$			
25	0.18 (3)	68 (12)	3 (1) x 10 ⁵	1.2 (3) x 10 ⁻²	-33 (9)	2 (1) x 10 ⁵			
50	0.17 (2)	47 (9)	3 (2) x 10 ⁵	1.4 (5) x 10 ⁻²	-27 (4)	5 (2) x 10 ⁵			
70	0.31 (3)	45 (7)	8 (2) x 10 ⁵	2.8 (8) x 10 ⁻²	-22 (5)	7 (2) x 10 ⁵			
80	0.45 (5)	35 (5)	1 (1) x 10 ⁸	3.9 (4) x 10 ⁻²	-17 (3)	2 (2) x 10 ⁶			
90	0.17 (5)	34 (4)	2 (1) x 10 ⁷	4.3 (7) x 10 ⁻²	-19 (5)	3 (1) x 10 ⁶			
Soln. Cast	0.21 (8)	66 (4)	4 (3) x 10 ⁵	0.8 (4) x 10 ⁻³	-32 (6)	$5(3) \times 10^3$			

 Table 2.4. FET performance of vacuum-deposited 1- and 2-derived films measured under vacuum. Standard deviations are given in parentheses.

Films of 5 and 6 were vacuum-deposited at T_Ds ranging from 25 °C - 150 °C. Material 5 exhibits n-channel FET activity with performance increasing with T_D from $\mu_e = 5.3$ (2) x 10⁻³ $cm^{2}V^{-1}s^{-1}$ (I_{on:off} = 8 x 10⁵, V_T = +33 (8) V) at 25 °C to μ_{e} = 0.017 (2) $cm^{2}V^{-1}s^{-1}$ (I_{on:off} = 2 x 10⁸, V_T = +28 (8) V) at 150 °C (Figure 2.11 and Table 2.5). The air stability of 5-derived n-channel FETs was evaluated over 3 months (Figure 2.11a) revealing stable performance of $\mu_e = 0.015$ (3) $cm^2V^{-1}s^{-1}$ (I_{on:off} = 1 x 10⁶, V_T = +26 (5) V) after the initial the device break-in (the performance of $T_D = 150$ °C devices was unchanged after > 1 year in air). The output plot for 5-based devices in Figure 2.11b reveals negligible contact resistance and excellent saturation behavior. Oligomer 6also exhibits n-channel FET activity for $T_D > 90$ °C (Figures 2.11c, d and Table 2.5). Performance increases slightly with $T_{\rm D}$ to a maximum μ_e = 1.2 (2) x $10^{\text{-5}}\ \text{cm}^2 V^{\text{-1}} \text{s}^{\text{-1}}$ (I_{on:off} = 2 x 10⁴, $V_T = +94$ (13) V) at 150 °C. The output plot of **6**-derived films reveals excellent saturation behavior and only slight contact resistance. Due to the very high sublimation temperatures of 5 and $\mathbf{6}$, the chemical composition of both the evaporation source and the thin films was confirmed after deposition by 'H NMR and elemental analysis and found to be consistent with the pure oligomers.



Figure 2.11. FET transfer (a) and output (b) plots measured under vacuum (and after 1 year in air for a) of vacuum-deposited films of compounds 5 ($T_D = 150$ °C) and 6 (c and d, respectively, $T_D = 150$ °C).

	Semiconductor									
$T_D(^{\circ}C)$		5		6						
-	$\mu_{e} (cm^{2}V^{-1}s^{-1})$	$\mathbf{V}_{\mathbf{T}}\left(\mathbf{V}\right)$	I _{on:off}	$\mu_{e} (cm^{2}V^{-1}s^{-1})$	$\mathbf{V}_{\mathrm{T}}\left(\mathbf{V}\right)$	$I_{on:off}$				
25	5.3 (2) x 10 ⁻³	33 (8)	8 (2) x 10 ⁵							
50	9.0 (4) x 10 ⁻³	34 (6)	6 (1) x 10 ⁶							
90	1.2 (2) x 10 ⁻²	31 (6)	$1(1) \ge 10^7$	7.9 (3) x 10 ⁻⁶	120 (18)	$1(1) \times 10^3$				
120	1.8 (4) x 10 ⁻²	32 (5)	8 (2) x 10 ⁷	8.7 (5) x 10 ⁻⁶	112 (22)	$4(2) \times 10^3$				
150	1.7 (2) x 10 ⁻²	28 (8)	$2(1) \ge 10^8$	1.2 (2) x 10 ⁻⁵	94 (13)	2 (1) x 10 ⁴				

 Table 2.5. FET performance of vacuum-deposited 5- and 6-derived films measured under vacuum. Standard deviations are given in parentheses.
Crystal packing. The crystal structures of oligomers 1 and 2 as well as model compound 7 were determined by X-ray diffraction of single crystals grown by slow sublimation (refer to Section 2.6 refinement parameters). Oligomer 1 crystallizes in a monoclinic cell with a space group C2/c (Figures 2.12a, c). Unit cell dimensions are a = 53.617(12) Å, b = 7.4030(17) Å, c =6.5735(15) Å, and $\beta = 94.259(4)^{\circ}$. The quaterthiophene cores orient in a typical herringbone packing motif at an angle of 33°, with a π - π stacking distance of 3.50 Å (C14 - C15') and a maximum inter-thiophene torsion angle of 4°. The ancillary phenyl groups are twisted at an angle of 53° with respect to the thiophene π -core, and the carbonyl is oriented at a 6° dihedral angle with respect to the adjacent thiophene subunit plane. One molecular layer is 26.77 Å thick with the fluorophenyl rings not interdigitated. Molecule 2 crystallizes in a monoclinic cell with a P2(1)/n space group (Figures 12b, d). The unit cell dimensions are a = 6.0174(8) Å, b =7.4293(10) Å, c = 52.685(7) Å, $\beta = 93.137(2)^\circ$. The quaterthiophene cores of 2 are also packed in a herringbone motif at a slightly decreased 26.5° angle, with the π - π stacking distance being 3.43 Å (C14 - C16') and a larger maximum inter-thiophene torsion angle of 13°. The ancillary phenyl substituents are also twisted with respect to the thiophene π -core by an angle of 49°, and the carbonyl lies 17° out-of of the adjacent thiophene subunit plane. One molecular layer is 26.51 Å thick with the phenyl rings not interdigitated.

Quinone-based oligomer 7 crystallizes in an orthorhombic cell having the *Pbca* space group (Figures 10e,f). Unit cell dimensions are a = 12.5516(9) Å, b = 12.9708(9) Å, and c = 20.2613(14) Å (see Section 2.6 for further details). The phenanthrenequinone core exhibits a slight 4.7° (C9-C8:C12-C13) torsion angle with the carbonyl carbons displaced slightly out of the anthracene plane, and the ancillary thiophenes tilted at 8.4° relative the phenanthrenequinone



Figure 2.12. Crystal structures semiconductors of 1, 2, and 3. Structures 1 and 2 are viewed perpendicular to the long axis of the unit cell (a and b, respectively) and along the long axis (c and d, respectively). The structure of semiconductor 7 is viewed along the *a* axis (e) and *b* axis (f).

core. The molecules are π -stacked in a cofacial orientation with the quinones aligned antiparallel and at an interplanar π - π distance of 3.47 Å (S2-C9). These π -stacks align along the *b* axis and make an acute angle of 64.3° relative to each other (Figure 2.12e). A donor-acceptor packing motif is also observed in **7**, with the molecules slipped 5.7 Å along the long axis of the molecule, overlapping the π -deficient quinone moiety with the electron-rich thiophene fragment.

2.3.7 Quantum chemical modeling

The molecular orbital (MO) energy levels and geometries are calculated using the DFToptimized structures of **1**, **2**, **5**, **6**, and **7** (Figure 2.13). The π -conjugated quaterthiophene cores of **1** and **2** exhibit minimal inter-ring torsion, and the phenyl rings are twisted at 53° and 44°, respectively. MO electron density plots reveal that the HOMO and LUMO are completely delocalized across the quaterthiophene core and the carbonyls, with minimal contribution from the phenyl substitutents. The calculated HOMO energy for both **1** and **2** is -6.0 eV while the LUMO energies are -3.6 eV and -3.4 eV, respectively. For OSCs **5** - **7**, there is < 5° thiophenephenanthrenequinone interring torsion, and the phenyl rings are twisted with respect to the π core in **5** and **6**. MO plots reveal that the HOMO is delocalized across the phenanthrenequinone and thiophene subunits. Interestingly, the LUMO in **5** - **7** is localized to the phenanthrenequinone subunit (Figure 2.13c-e). HOMO energies are -6.6 eV, -6.6 eV, and -6.5 V for **5**, **6**, and **7**, respectively, while the LUMO energies are all -4.0 eV for **5** - **7**.

2.4 Discussion

The correlations between thin-film morphology and FET performance for the present materials will first be discussed in the context of the SEM, WAXRD, and FET measurements. Detailed molecular-level analysis to examine the effect of molecular modifications and to interpret the



Figure 2.13. Structures and molecular orbital electron density plots of oligomers 1 (a), 2 (b), 5 (c), 6 (d), and 7 (e) viewed normal to the planar π -conjugated cores.

observed FET device response will follow. This analysis will utilize information from the single crystal X-ray structure determinations, thermal analysis, optical spectroscopy, electrochemistry, and DFT-level MO analysis.

FET device performance of each material was optimized by varying T_D for both vapordeposited and drop-cast films. Spin-cast films optimized by varying the solvent and solvent mixtures were also utilized. A wide range of FET device performance characteristics and film microstructures result from the film optimization experiments. Materials **1**, **3**, **5**, and **6** are found to exhibit n-channel FET activity under high-vacuum, and **5** also exhibits air-stable operation over a period greater than one year (Figure 2.14). Oligomer **2** exhibits p-channel behavior under both high-vacuum and air, while no FET activity is observed in this study for model compounds **4**- and **7**-derived films.

2.4.1 Thin-film microstructure and field-effect transistor device optimization

Top-contact bottom-gate FETs fabricated with vapor-deposited films of semiconductors **1**, **2**, **5**, and **6** were initially measured under vacuum. The performance of **1**-based devices increases with T_D (Figures 2.8a, b and 2.14a), from $\mu_e = 0.18$ (3) cm²V⁻¹s⁻¹ ($V_T = 68$ (12) V, $I_{on:off} = 3$ (1) x 10⁵) at $T_D = 25$ °C to $\mu_e = 0.45$ (5) cm²V⁻¹s⁻¹ ($V_T = 35$ (5) V, $I_{on:off} = 1$ (1) x 10⁸) at $T_D = 80$ °C, before diminishing slightly at $T_D = 90$ °C (Table 2.4). This performance enhancement corresponds to an increase in crystallite grain size observed in SEM images from ~100 nm at $T_D = 25$ °C to > 1 μ m at $T_D = 90$ °C (Figures 2.5a-c). WAXRD of the films indicates that the overall crystallinity also increases with T_D , although reflections from a second phase begin to appear at $T_D = 90$ °C (Figure 2.4a). Such a phase-impurity can diminish μ , as observed in this study, by creating defect sites in the film that scatter or trap charge carriers.^{15,41}



Figure 2.14. Plot of the FET μ vs. T_D for oligomers 1, 2, 5, and 6 (a) and μ_e vs. the number of weeks of storage in air for 5-derived films deposited at the indicated T_D (b). Dashed lines are a guide for the eye.

The d-spacing of the dominant phase, 26.6 ± 0.1 Å, corresponds well with the thickness of one molecular layer determined from the single-crystal structure determination, 26.77 Å, indicating that the long axes of the molecules are aligned along the substrate plane normal.

Fluorine-free oligomer **2** exhibits p-channel FET behavior that also increases with T_D (Figures 2.8c, d and 2.14a) from $\mu_h = 0.012$ (3) cm²V⁻¹s⁻¹ ($V_T = -33$ (9) V, $I_{on.off} = 2$ (1) x 10⁵) at $T_D = 25$ °C to $\mu_h = 0.043$ (7) cm²V⁻¹s⁻¹ ($V_T = -19$ (5) V, $I_{on.off} = 3$ (1) x 10⁶) at $T_D = 90$ °C (Table 2.4). Importantly, the FET performance is unchanged when measured in air. As with the fluorocarbon analog **1**, this performance enhancement coincides with an increase in average crystallite size observed in the SEM images of **2**-derived films from ~ 100 nm at $T_D = 25$ °C to ~ 1 μ m at $T_D = 90$ °C (Figure 2.5d-f). WAXRD reflection intensity from **2** films also increases with T_D , indicating that the overall film crystallinity is enhanced (Figure 2.6). The 26.31 ± 0.1 Å d-spacing calculated from the Bragg progression corresponds well with the thickness of one molecular layer determined from the single-crystal diffraction structure, 26.51 Å, indicating that the long axes of the molecules are aligned parallel to the substrate plane normal.

Quinone-containing oligomer **5** exhibits n-channel FET behavior when measured both in vacuum and under air (Figures 2.9a, b and 2.14). The FET performance when measured under vacuum increases with T_D from $\mu_e = 5.3$ (2) x 10^{-3} cm²V⁻¹s⁻¹ ($V_T = 33$ (8) V, $I_{ontoff} = 8$ (2) x 10^5) at $T_D = 25$ °C to $\mu_e = 0.018$ (4) cm²V⁻¹s⁻¹ ($V_T = 28$ (8) V, $I_{ontoff} = 2$ (1) x 10^8) at $T_D = 150$ °C (Table 2.5). When measured in air, V_T exhibits negligible change and μ_e exhibits a slight decrease in magnitude to 0.015 (3) cm²V⁻¹s⁻¹ ($V_T = 31$ (12) V, $I_{ontoff} = 5$ (1) x 10^6) at $T_D = 150$ °C (Figure 2.14b), which is stable for greater than one year when stored and measured under laboratory air. The WAXRD data indicate phase-pure films having a d-spacing of 27.9 ± 0.1 Å, which

corresponds closely with the 28.0 Å thickness of one molecular layer (determined from the DFT geometry plus a 0.3 Å interlayer spacing estimated from that observed in the crystal structure of **1**). This indicates that the long axes of the molecule are aligned normal to the substrate surface, in a motif similar to that of **1** and **2**.

Oligomer 6 also exhibits n-channel FET activity under vacuum for $T_D > 90$ °C (Figures 2.9c, d, and 2.14a). The performance increases with T_D from $\mu_e = 7.9$ (3) x 10^{-6} cm²V⁻¹s⁻¹ (V_T = 120 (18) V, $I_{\text{on:off}} = 1$ (1) x 10³) at $T_{\text{D}} = 90$ °C to $\mu_{\text{e}} = 1.2$ (2) x 10⁻⁵ cm²V⁻¹s⁻¹ (V_T = 94 (13) V, $I_{\text{on:off}} = 2$ (1) x 10⁴) at T_D = 150 °C (Table 2.5). This diminished μ_e relative to the other vapor-deposited oligomers 1, 2, and 5 can likely be attributed to the different thin-film crystal phase that is revealed by WAXRD. Note that no decomposition is observed upon sublimation of 6. Also, the experimental and DFT-computed frontier MO energies reveal that 5 and 6 are isoenergetic and isogeometric (Table 2.2 and Figure 2.13), so the difference in performance is not intrinsically MO-based. The dominant family of Bragg reflections corresponds to a d-spacing of 25.90 ± 0.08 Å, indicating that the molecules are tilted $\sim 70^{\circ}$ relative to the substrate plane (calculated using the DFT-optimized geometry plus an assumed 0.3 Å interlayer spacing). This tilt angle is similar to the $\sim 65^{\circ}$ angle made by the slipped dimers in the single-crystal diffraction structure of 7 (Figure 2.12), suggesting that the molecules of compound 7 may pack in a similar slipped structure. Such a slipped structure can potentially decrease the efficiency of π - π coupling compared to completely overlapped oligomers, as in the structures of 1, 2, and 5. There is a second, minority phase detected in 6-derived films grown at $T_D = 150$ °C having a 27.05 ± 0.04 Å d-spacing, which corresponds to a more upright molecular orientation. While this second phase may exhibit stronger intermolecular π - π coupling, the dominant, tilted phase likely limits

FET response. The SEM images of **6**-derived films also reveal a morphology different from the other oligomers, with a more homogenous surface that begins to exhibit void spaces of ~ 1 μ m at $T_D = 150$ °C. Model compound **7** does not exhibit FET activity or show evidence of thin-film crystallinity.

Materials **1** - **3** yield uniform films when drop-cast from common organic solvents, while spincasting of **3** also yields highly-uniform films. Drop-cast films of oligomers **1** and **2** exhibit outstanding FET response (Figure 2.10a) with $\mu_e = 0.21$ (8) cm²V⁻¹s⁻¹ ($V_T = 66$ (4) V, $I_{on:off} = 4$ (3) x 10⁵) and $\mu_h = 8$ (4) x 10⁻⁴ cm²V⁻¹s⁻¹ ($V_T = -32$ (6) V, $I_{on:off} = 5$ (30) x 10³), respectively. The performance of **1** is one of the highest reported to date for a solution-cast organic semiconductor. Films of both materials exhibit the same crystal phase as the vapor-deposited films, as assessed by WAXRD data (Figure 2.4), while SEM and optical microscopy of **1** drop-cast films reveal large crystalline plates with dimensions up to 0.1 mm (Figures 2.5g and 2.7a, respectively).

Films of polymer **3** drop-cast and spin cast exhibit a mobility of 1.7 (6) x 10⁻⁶. While **1**- and **2**derived films exhibit very strong Bragg reflections, **3** films do not, indicating poor film crystallinity that likely compromises charge carrier mobility. To enhance the film FET performance while maintaining favorable solution processing rheology, solutions of **1** and **3** were blended. An equal weight ratio of molecule:polymer yields films exhibiting $\mu_e = 0.02$ (1) cm²V⁻ ¹s⁻¹ with I_{on:off} = 3 x 10⁴ and V_T = +68 V. This unique polymer-oligomer blend solution combines the favorable rheological characteristics of the polymer solution with the extremely-high FET performance of molecule **1** to give a more processable solution that yields excellent semiconductor films for FETs. Molecule **4** was designed to assess whether repositioning the *n*alkyl solubilizing groups from the inner two thiophenes of the quaterthiophene core in **3** to the outer thiophenes would result in higher crystallinity and therefore enhanced FET performance. Interestingly, films of **4**, either vacuum-deposited or drop-cast, do not exhibit Bragg reflections, indicating that the substitutent repositioning does not enhance thin-film crystallinity.

2.4.2 Electronic properties, molecular modeling, and crystal packing

While thin-film microstructure can significantly impact FET device response, the intrinsic molecular properties of an organic semiconductor ultimately determine the performance limits.⁵³⁻⁵⁵ The primary molecular-level considerations are crystal packing and frontier orbital delocalization/energetics. In this study, optical spectroscopy, single crystal X-ray structure determination, electrochemistry, and DFT-level computational modeling are employed to probe these properties both experimentally and theoretically.

Since charge is transported through the frontier molecular orbitals of organic semiconductors, their geometry and extent of delocalization directly affect carrier stability and the intermolecular hopping rate.⁵⁶ Ideally, the HOMO and LUMO are delocalized over the entire π -core of the semiconductor for p- and n-channel transport, respectively.⁵⁷ Indeed, this complete delocalization is observed in the DFT-derived MO plots of **1** and **2**, enhancing charge transfer rates by increasing charge stabilization and intermolecular π -overlap (Figure 2.13a, b). Interestingly, although the HOMOs of **5** - **7** are well-delocalized, the LUMOs are localized on the phenanthrenequinone subunits (Figures 13c-e). Such highly localized LUMOs are expected to reduce intermolecular π -overlap compared to the ideal delocalization present in **1** and **2** and may favor electron trapping at the quinone site. This localization may be a contributing factor diminishing the μ_e of **5** and **6** compared to **1**, despite the greater electron affinity.

The MO energies affect charge carrier stability and are a key parameters majority charge carrier type in standard FETs. In materials 1 - 4, the phenacyl ancillary substitutents stabilize the

LUMO, diminishing the susceptibility of a mobile electron to trap states (Table 2.2).^{13, 42, 58} In the case of **1** and **3**, this stabilization lowers the LUMOs to -3.6 eV and -3.4 eV, respectively, and is sufficient to enable n-channel activity on HMDS-treated SiO₂. These energy levels are below that postulated for n-channel activity in the presence of surface hydroxyl groups,^{15, 59, 60} but insufficient for n-channel activity in the presence of air-based trapping species.^{16, 37}

In this study, quinone moieties are introduced into the π -core to further stabilize the LUMO and enable air-stable n-channel FET operation. Previous reports on NDI-F^{16, 29} and CuF₁₆Pc^{27, 30.32} have postulated that LUMO energies below -3.9 eV are sufficient to enable air-stable n-channel FET operation for perfluoroalkyl-substituted semiconductors. Computational modeling reveals that introduction of either bithiophene-quinone (**21**), phenanthrenequinone, or pyrene-4,5,9,10-tetraone (**24**) can lower the LUMO energy below this -3.9 eV threshold. Although all of the proposed quinone-containing cores (**21**, **22**, **24**) were successfully synthesized in this work, only the Suzuki coupling reactions involving 2,7-diiodo-9,10-phenanthrenequinone (**22**) were successful, yielding materials **5** - **7**.

As predicted, fluorinated oligomer **5** exhibits air-stable n-channel operation, while the nonfluorinated analog **6** does not. The ambient stability of **5** is likely the result of the more tightly packed perfluorophenyl vs. phenyl ancillary substitutents since the LUMO energies of **5** (-4.03 eV) and **6** (-4.02 eV) as well as their geometries are very similar. This result is in agreement with previous studies suggesting that fluorocarbon substitution of a semiconductor with a LUMO energy below -3.9 eV creates an O₂-barrier, preventing O₂ from trapping mobile electrons in the FET channel.¹⁶ Additionally, compound **5** maintains a high $I_{on:off} = 10^6$ since the LUMO energy (-4.03 eV) is above the -4.2 eV level at which ambient doping has previously been observed in extremely-high electron affinity organic semiconductors.^{26, 37} The crystal packing motifs of **1** and **2** are similar, with the quaterthiophene cores herringbonepacked at distances of 3.50 Å and 3.43 Å, respectively (Figure 2.12). This type of herringbone π stacking motif has been shown experimentally and theoretically to afford optimal π -overlap in quaterthiophene-based semiconductors.^{44, 56} The structures of both materials reveal two layers of π -stacked molecules per unit cell, with the out-of-plane phenyl substitutents locking the π stacked molecules into an orientation normal to the *bc*- or *ab*-face, respectively. In polymer **3**, introduction of the *n*-octyl solubilizing group, in combination with the phenyl-thiophene dihedral angle along the polymer backbone, likely disrupts the herringbone π -stacked layers and results in the observed decreased thin-film crystallinity and diminuted FET performance. Model compound **4** was synthesized to evaluate how crystallinity is affected when the alkyl substitutents are moved toward the edge of the π -core. The crystal lattice is also disrupted with the substituents in this skeletal position, resulting in **4** being extremely-soluble and producing amorphous films.

The X-ray diffraction-derived crystal structure of quinone model compound 7 reveals a highlyplanar π -core with adjacent molecules cofacially π -stacked (Figures 12e, f). The stacked molecules are slipped ~ 5.7 Å along the long molecular axis making a 64 ° angle from one π stack to the next. This packing motif is likely induced by a π -donor-acceptor interaction between the electron-rich thiophene and the electron-deficient quinone subunits. The quinone moieties also stack antiparallel due to stabilizing dipole-dipole interactions. This slipped structure, which diminishes intermolecular π - π coupling, is likely similar to the dominant phase of the **6**-derived films, where the long molecular axes are tilted at 69.0 ° relative to the substrate plane. This structure of **7** provides evidence for the high crystal packing affinity of quinone-containing materials and also insight into the diminuted carrier mobility of **6**-derived films.

2.5 Conclusions

The present family of phenacyl-thiophene and quinone based semiconductors exhibits rich relationships between molecular-level electronic/structural properties, solution processability, thin-film morphology, and p-/n-channel FET device characteristics. The design strategy implemented here to concurrently enhance solubility and crystal packing has yielded highperformance solution-processable n-channel FET materials with μ_e up to ~ 0.3 cm²V⁻¹s⁻¹ for solution cast films of 1 and one of the first n-channel polymers (3). Blending 1 with the 3 enhances both solution rheology and FET device performance from $\mu_e \approx 10^{\text{-6}} \text{ cm}^2 V^{\text{-1}} \text{s}^{\text{-1}}$ for neat 3based films to $\sim 0.02 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for blend films. A computational study of additional LUMO stabilization reveals that introduction of quinone subunits into the π -conjugated core enables airstable n-channel operation. Introduction of phenanthrenequinone, one of the three quinones identified here, affords oligomer $\boldsymbol{5}$ exhibiting air-stable n-channel FET operation with $\mu_e\approx 0.02$ and a high $I_{on:off} = 10^6$ under ambient conditions. The fluorine-free $cm^2V^{-1}s^{-1}$ phenanthrenequinone analog, 6, exhibits diminished $\mu_e \approx 10^{-5} \text{ cm}^2 V^{-1} \text{s}^{-1}$ and air-unstable FET operation, in agreement with the O_2 -barrier model proposed in previously. Films of **6** also exhibit a different thin-film phase from that of the other oligomers, likely with diminished intermolecular π - π coupling which results in a depressed μ_{e} . The crystal structures of quaterthiophenes 1 and 2 reveal that both pack in a herringbone motif with short π -stacking distances and layered structures. The first crystal structure of a quinone-containing thiophenebased semiconductor, 7, reveals anti-parallel dipole alignment and cofacial packing with a short

3.48 Å π - π stacking distance. This work demonstrates that rational design can yield extremely π electron deficient monomer units for implementation in air-stable n-channel FET molecules and polymeric semiconductors.

2.6 Single crystal X-ray structure determination

2.6.1 5,5"'-bis(perfluorophenacyl)-2,2':5',2":5",2"'-quaterthiophene

Data Collection (for compound 1)

A orange plate crystal of C_{30} H₈ F₁₀ O₂ S₄ having approximate dimensions of 0.430 x 0.300 x 0.024 mm was mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a CCD area detector with graphite monochromated MoK\ α radiation. Cell constants and an orientation matrix for data collection corresponded to a Monoclinic cell with dimensions:

a = 53.617(12) Å
b = 7.4030(17) Å
$$\beta$$
 = 94.259(4)°
c = 6.5735(15) Å
V = 2602.0(10) Å³

For Z = 4 and F.W. = 718.60, the calculated density is 1.834 g/cm³. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

C2/c

The data were collected at a temperature of 153(2) K with a theta range for data collection of 1.52 to 28.68°. Data were collected in 0.3° oscillations with 20 second exposures. The crystal-to-detector distance was 50.00 mm with the detector at the 28° swing position.

Data Reduction (for compound 1)

Of the 11225 reflections which were collected, 3146 were unique (Rint = 0.1645). Data were collected using Bruker SMART detector and processed using SAINT-NT from Bruker. The linear absorption coefficient, mu, for MoK\ α radiation is 0.470 mm⁻¹. An analytical absorption correction was applied. Minimum and maximum transmission factors were: 0.8314 and 0.9885, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement (for compound 1)

The structure was solved by direct methods¹ and expanded using Fourier techniques². The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included in "idealized" positions, but not refined. The final cycle of full-matrix least-squares refinement³ on F2 was based on 3146 reflections and 208 variable parameters and converged (largest parameter shift was 0.000 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.0860$$

$$wR^{2} = \{\Sigma[w(F_{o}^{2}-F_{c}^{2})^{2}]/\Sigma[w(F_{o}^{2})^{2}]\}^{1/2} = 0.1630$$

The weighting Scheme was calc.

calc w=1/[$\sigma^2(F_o^2)$ +(0.0597P)²+13.1648P] where P=(F_o^2 +2 F_c^2)/3

The standard deviation of an observation of unit weight⁴ was 1.048. The weighting Scheme was based on counting statistics and included a factor to downweight the intense reflections. Plots of $\Sigma \text{ w} (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.755 and -0.381 e⁻/Å³, respectively. Neutral atom scattering factors were taken from Cromer and Waber⁵. Anomalous dispersion effects were included in Fcalc⁶; the values for Df⁴ and Df⁴ were those of Creagh and McAuley⁷. The values for the mass attenuation coefficients are those of Creagh and Hubbell⁸. All calculations were performed using the Bruker SHELXTL⁹ crystallographic software package.

 Table 2.6.
 Crystal data and structure refinement for 1.

Identification code	s49p1m			
Empirical formula	$C_{30} \ H_8 \ F_{10} \ O_2 \ S_4$			
Formula weight	718.60			
Temperature	153(2) K			
Wavelength	0.71073 Å			
Crystal system, space group	Monoclinic, C2/c			
Unit cell dimensions	a = 53.617(12) Å			
	$b = 7.4030(17) \text{ Å} \beta = 94.259(4) \text{ °}$			
	c = 6.5735(15) Å			
Volume	2602.0(10) Å ³			
Z, Calculated density	4, 1.834 mg/m^3			
Absorption coefficient	0.470 mm ⁻¹			
F(000)	1432			
Crystal size	0.430 x 0.300 x 0.024 mm			
Theta range for data collection	1.52 to 28.68°			
Limiting indices	-71<=h<=70, -9<=k<=9, -8<=l<=8			
Reflections collected / unique	11225 / 3146 [R(int) = 0.1645]			
Completeness to theta =	28.68 93.7 %			
Absorption correction	Integration			
Max. and min. transmission	0.9885 and 0.8314			
Refinement method	Full-matrix least-squares on F2			
Data / restraints / parameters	3146 / 0 / 208			
Goodness-of-fit on F^2	0.991			
Final R indices [I>2sigma(I)]	R1 = 0.0680, wR2 = 0.1630			
R indices (all data)	R1 = 0.0967, wR2 = 0.1791			
Largest diff. peak and hole	$0.755 \text{ and } -0.381 \text{ e}^{-}/\text{Å}^{3}$			



Figure 2.15. ORTEP structure of 1.

S(1) 0.161324(14) 0.19972(12) -0.08722(12) 32(1) $S(2) 0.209857(14) 0.31085(11) 0.46249(12) 31(1)$ $F(1) 0.08875(3) 0.5291(3) -0.0652(3) 38(1)$ $F(2) 0.03999(3) 0.5672(3) -0.0108(3) 43(1)$
S(2) 0.209857(14) $0.31085(11)$ $0.46249(12)$ $31(1)$ $F(1) 0.08875(3)$ $0.5291(3)$ $-0.0652(3)$ $38(1)$ $F(2) 0.03999(3)$ $0.5672(3)$ $-0.0108(3)$ $43(1)$
F(1)0.08875(3)0.5291(3)-0.0652(3)38(1) $F(2)$ 0.03999(3)0.5672(3)-0.0108(3)43(1)
F(2) = 0.03999(3) = 0.5672(3) = -0.0108(3) = -0.43(1)
(2) 0.00000(0) 0.0002(0) 0.0000(0) 10(1)
$F(3) 0.00902(3) 0.2771(3) -0.0384(3) \qquad 47(1)$
F(4) 0.02702(3) -0.0518(3) -0.1394(3) 45(1)
F(5) 0.07552(3) -0.0917(3) -0.2008(3) 37(1)
O(1) 0.11503(4) 0.1400(3) -0.3581(4) 37(1)
C(1) 0.08388(6) 0.2178(4) -0.1379(4) 26(1)
C(2) 0.07411(6) 0.3812(4) -0.0826(5) 30(1)
C(3) 0.04894(6) 0.4031(4) -0.0518(5) 33(1)
C(4) 0.03305(6) 0.2571(5) -0.0699(5) 35(1)
C(5) 0.04232(6) 0.0913(5) -0.1227(5) 34(1)
C(6) 0.06729(6) 0.0727(4) -0.1548(5) 32(1)
$C(7) 0.11091(6) 0.1941(4) -0.1892(5) \qquad 29(1)$
$C(8) 0.13065(6) 0.2340(4) -0.0317(5) \qquad 29(1)$
C(9) 0.12901(6) 0.2821(4) 0.1669(5) 32(1)
C(10) 0.15256(6) 0.2947(4) 0.2772(5) 33(1)
C(11) 0.17191(6) 0.2522(4) 0.1592(5) 27(1)
C(12) 0.19826(6) 0.2370(4) 0.2233(5) 28(1)
C(13) 0.21706(6) 0.1642(4) 0.1191(5) 30(1)
C(14) 0.24056(6) 0.1643(4) 0.2330(5) 31(1)
C(15) 0.23980(5) 0.2383(4) 0.4213(5) 27(1)

Table 2.7. Atomic coordinates and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for **1**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

2.6.2 5,5"'-bis(phenacyl)-2,2':5',2":5",2"'-quaterthiophene

Data Collection (for compound 2)

A orange plate crystal of C_{30} H₁₈ O₂ S₄ having approximate dimensions of 0.200 x 0.120 x 0.016 mm was mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a CCD area detector with graphite monochromated MoK\ α radiation. Cell constants and an orientation matrix for data collection corresponded to a Monoclinic cell with dimensions:

a =
$$6.0174(8)$$
 Å
b = $7.4293(10)$ Å $\beta = 93.137(2)^{\circ}$
c = $52.685(7)$ Å
V = $2351.8(5)$ Å³

For Z = 4 and F.W. = 538.68, the calculated density is 1.521 g/cm³. Based on systematic absences, and the successful solution and refinement of the structure, the space group was determined to be:

P2(1)/n

The data were collected at a temperature of 153(2) K with a theta range for data collection of 0.77 to 25.00° . Data were collected in 0.3° oscillations with 25 second exposures. The crystal-to-detector distance was 50.00 mm with the detector at the 28° swing position.

Data Reduction (for compound 2)

Of the 16978 reflections which were collected, 4131 were unique (Rint = 0.1391). Data were collected using Bruker SMART detector and processed using SAINT-NT from Bruker. The linear absorption coefficient, mu, for MoK\ α radiation is 0.434 mm⁻¹. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement (for compound 2)

The structure was solved by direct methods¹ and expanded using Fourier techniques². The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions, but not refined. The final cycle of full-matrix least-squares refinement³ on F2 was based on 4131 reflections and 325 variable parameters and converged (largest parameter shift was 0.000 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.0860$$

$$wR^{2} = \{\Sigma[w(F_{o}^{2}-F_{c}^{2})^{2}]/\Sigma[w(F_{o}^{2})^{2}]\}^{1/2} = 0.1883$$

The weighting Scheme was calc.

calc w=1/[
$$\sigma^2(F_o^2)$$
+(0.0597P)²+13.1648P] where P=(F_o^2 +2 F_c^2)/3

The standard deviation of an observation of unit weight⁴ was 1.048. The weighting Scheme was based on counting statistics and included a factor to downweight the intense reflections. Plots of $\Sigma \text{ w} (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.668 and -1.157 e⁻/Å³, respectively. Neutral atom scattering factors were taken from Cromer and Waber⁵. Anomalous dispersion effects were included in Fcalc⁶; the values for Df and Df'' were those of Creagh and McAuley⁷. The values for the mass attenuation coefficients are those of Creagh and Hubbell⁸. All calculations were performed using the Bruker SHELXTL⁹ crystallographic software package.

2				
Identification code	s22q			
Empirical formula	C30 H18 O2 S4			
Formula weight	538.68			
Temperature	153(2) K			
Wavelength	0.71073 Å			
Crystal system, space group	Monoclinic, P2(1)/n			
Unit cell dimensions	a = 6.0174(8) Å			
	$b = 7.4293(10) \text{ Å} \qquad \beta = 93.137(2)^{\circ}$			
	c = 52.685(7) Å			
Volume	2351.8(5) Å ³			
Z, Calculated density	4, 1.521 Mg/m ³			
Absorption coefficient	0.434 mm ⁻¹			
F(000)	1112			
Crystal size	0.200 x 0.120 x 0.016 mm			
Theta range for data collection	0.77 to 25.00 °			
Limiting indices	-7<=h<=7, -8<=k<=8, -60<=l<=62			
Reflections collected / unique	16978 / 4131 [R(int) = 0.1391]			
Completeness to theta =	25.00 100.0 %			
Absorption correction	Integration			
Max. and min. transmission	0.9930 and 0.9355			
Refinement method	Full-matrix least-squares on F2			
Data / restraints / parameters	4131 / 0 / 325			
Goodness-of-fit on F ²	1.048			
Final R indices [I>2sigma(I)]	R1 = 0.0860, wR2 = 0.1883			
R indices (all data)	R1 = 0.1362, wR2 = 0.2112			
Largest diff. peak and hole	0.668 and -1.157 e^{-1}/A^{3}			

 Table 2.8. Crystal data and structure refinement for 2.



Figure 2.16. ORTEP structure of 2.

U(eq) Х у Z S(1) 0.4636(3)0.5137(2)0.15345(3)22(1)S(2) -0.0298(3)0.20842(3)21(1) 0.6513(2)0.0348(3)0.28971(3) S(3) 0.5187(2)20(1)-0.4601(3)S(4) 0.6488(2)0.34483(3)22(1)0.10568(9)O(1) 0.6979(7)0.5182(7)31(1)O(2) -0.6928(8) 0.6398(7)0.39285(9)32(1) C(1) 0.1877(11) 0.4995(9) 0.06875(13)23(2)C(2) 0.1126(12) 0.4959(10) 0.04346(13)30(2)C(3) 0.2433(12) 0.5628(10) 0.02470(13)30(2)C(4) 0.4516(12) 0.6316(9) 0.03175(13) 30(2)C(5) 0.5302(11) 0.6326(9)0.05679(13)24(2)0.5664(8) 0.07534(12)20(1)C(6) 0.3989(11) 23(2) $C(7) \quad 0.4988(11)$ 0.5528(9) 0.10198(13)23(2)C(8) 0.3607(11) 0.5779(9) 0.12349(12)C(9) 0.1539(10) 0.6562(9) 0.12471(12)21(2)C(10) 0.0785(10) 0.6642(9) 0.14948(12) 21(2)C(11) 0.2279(10) 0.5909(8) 0.16717(12) 19(1)C(12) 0.2053(10) 0.5721(8) 0.19428(12)17(1)C(13) 0.3483(10)0.4911(8) 0.21199(12)20(1)0.4957(8) 0.23680(12) 17(1)C(14) 0.2720(10)C(15) 0.0684(10) 0.5742(8) 0.23823(12)18(1)C(16) - 0.0625(10)0.5983(8) 0.26012(12)16(1)C(17) - 0.2647(10)0.6784(8) 0.26169(12)18(1)C(18) -0.3452(11) 0.6771(8)20(1)0.28641(12)C(19) - 0.1997(10)0.5958(8) 0.30387(11)16(1)C(20) -0.2245(10) 19(1) 0.5720(8)0.33096(12)C(21) - 0.0763(11)0.4979(9) 0.34844(12)22(2)C(22) -0.1501(10) 0.5023(9) 0.37337(12)20(2)C(23) -0.3554(11) 0.5799(9)0.37451(12)21(2)C(24) -0.4953(11) 0.6038(9)0.39611(12)22(2)C(25) -0.3954(11) 0.5793(9) 0.42239(12)23(2)

0.6447(9) 0.42996(13)

0.6337(9) 0.45505(13)

0.5555(10) 0.47295(13)

0.4860(10) 0.46559(13)

0.4999(9) 0.44077(12)

24(2)

27(2)

27(2)

31(2)

25(2)

C(26) -0.1823(11)

C(27) -0.1051(11)

C(28) -0.2370(11)

C(29) - 0.4433(12)

C(30) -0.5238(11)

Table 2.9. Atomic coordinates and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for **2**.U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

2.6.3 2,7-bis(thiophen-2-yl)-9,10-phenanthrenequinone

Data Collection (for compound 7)

A orange cube crystal of $C_{22}H_{12}O_2S_2$ having approximate dimensions of 0.157 x 0.063 x 0.057 mm was mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a CCD area detector with graphite monochromated MoK\ α radiation. Cell constants and an orientation matrix for data collection corresponded to a Trigonal cell with dimensions:

a = 12.5516(9) Å
$$\alpha = 90^{\circ}$$

b = 12.9708(9) Å $\beta = 90^{\circ}$
c = 20.2613(14) Å $\gamma = 90^{\circ}$
V = 3298.6(4) Å³

For Z = 8 and F.W. = 372.42, the calculated density is 1.492 g/cm³. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be Pbca. The data were collected at a temperature of 153(2) K with a theta range for data collection of 2.01 to 28.89 °. Data were collected in 0.3° oscillations with 20 second exposures. The crystal-to-detector distance was 50.00 mm with the detector at the 28° swing position.

Of the 29125 reflections which were collected, 4096 were unique (Rint = 0.0774). Data were collected using Bruker SMART detector and processed using SAINT-NT from Bruker. The linear absorption coefficient, mu, for MoK\ α radiation is 0.470 mm⁻¹. An analytical absorption correction was applied. Minimum and maximum transmission factors were: 0.8314 and 0.9885, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement (for compound 7)

The structure was solved by direct methods and expanded using Fourier techniques. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included in "idealized" positions, but not refined. The final cycle of full-matrix least-squares refinement on F2 was based on 4096 reflections, 0 restraints, and 236 variable parameters and converged (largest parameter shift was 0.000 times its esd with unweighted and weighted agreement factors of:

 $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.1122$

$$wR^{2} = \{\Sigma[w(F_{o}^{2}-F_{c}^{2})^{2}]/\Sigma[w(F_{o}^{2})^{2}]\}^{1/2} = 0.3345$$

The weighting Scheme was calc.

calc w=1/[$\sigma^2(F_o^2)$ +(0.0597P)²+13.1648P] where P=(F_o^2 +2 F_c^2)/3

The standard deviation of an observation of unit weight was 1.048. The weighting Scheme was based on counting statistics and included a factor to downweight the intense reflections. Plots of $\Sigma \text{ w} (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 5.552 and -1.086 e⁻/Å³, respectively. Neutral atom scattering factors were taken from Cromer and Waber. Anomalous dispersion effects were included in Fcalc; the values for Df and Df' were those of Creagh and McAuley. The values for the mass attenuation coefficients are those of Creagh and Hubbell. All calculations were performed using the Bruker SHELXTL crystallographic software package.

 Table 2.10. Crystal data and structure refinement for 7.

Identification code	s71tm-face			
Empirical formula	C22 H12 O2 S2			
Formula weight	372.44			
Temperature	153(2) K			
Wavelength	0.71073 A			
Crystal system, space group	Orthorhombic, Pbca			
Unit cell dimensions				
	a = 12.5516(9) Å	alpha = 90 deg.		
	b = 12.9708(9) Å	beta = 90 deg.		
	c = 20.2613(14) Å	gamma = 90 deg.		
Volume	3298.6(4) Å^3			
Z, Calculated density	8, 1.492 Mg/m^3			
Absorption coefficient	0.295 mm^-1			
F(000)	1344			
Crystal size	0.157 x 0.063 x 0.057	7 mm		
Theta range for data collection	2.01 to 28.89 deg.			
Limiting indices	-16<=h<=16, -17<=k<=17, -27<=l<=27			
Reflections collected / unique	29125 / 4096 [R(int) = 0.0774]			
Completeness to theta = 28.89	94.3 %			
Refinement method	Full-matrix least-squares on F^2			
Data / restraints / parameters	4096 / 0 / 236			
Goodness-of-fit on F ^A 2	1.434			
Final R indices [I>2sigma(I)]	R1 = 0.1122, wR2 =	0.3345		
R indices (all data)	R1 = 0.1499, wR2 = 0.3494			
Largest diff. peak and hole	5.552 and -1.086 e. Å^-3			



Figure 2.17. ORTEP structure of 7.

	x y	Z	U(eq)			
C(1)	6750(4)	6191(4)	6862(3)	34(1)		
C(2)	7808(4)	6070(4)	6851(3)	28(1)		
C(3)	8262(4)	5114(3)	7217(2)	16(1)		
C(4)	7166(3)	4624(3)	7463(2)	20(1)		
C(5)	7116(3)	3667(3)	7843(2)	19(1)		
C(6)	8058(4)	3209(4)	8069(2)	19(1)		
C(7)	8041(3)	2300(4)	8426(2)	18(1)		
C(8)	9079(4)	1869(4)	8632(2)	22(1)		
C(9)	9082(4)	817(4)	8979(2)	23(1)		
C(10)	6153(4)	3179(4)	8013(3)	26(1)		
C(11)	6141(4)	2279(4)	8376(3)	25(1)		
C(12)	7081(3)	1798(4)	8595(2)	19(1)		
C(13)	7079(3)	841(3)	8976(2)	19(1)		
C(14)	6127(4)	348(4)	9174(2)	23(1)		
C(15)	6147(4)	-557(4)	9541(2)	25(1)		
C(16)	7102(4)	-1025(4)	9739(2)	20(1)		
C(17)	8052(4)	-544(4)	9542(2)	21(1)		
C(18)	8040(4)	360(3)	9170(2)	19(1)		
C(19)	7136(4)	-1981(4)	10123(2)	23(1)		
C(20)	8051(3)	-2472(3)	10408(2)	13(1)		
C(21)	7728(5)	-3367(4)	10766(3)	34(1)		
C(22)	6666(5)	-3564(4)	10730(3)	35(1)		
O(1)	9920(3)	2306(3)	8540(2)	36(1)		
O(2)	9931(3)	390(3)	9080(2)	39(1)		
S(1)	6062(1)	5301(1)	7248(1)	50(1)		
S(2)	6003(1)	-2674(1)	10286(1)	31(1)		

Table 2.11. Atomic coordinates ($x \ 10^4$) and equivalent isotropic displacement parameters (A² x 10³) for **7**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Chapter Three

n-Channel Polymers by Design: Optimizing the Interplay of Solubilizing Substituents, Crystal Packing, and Field-Effect Transistor Characteristics in Polymeric Bithiophene-Imide Semiconductors

3.1 Introduction

Interest in organic electronics is inspired by the promise of low-cost printed electronics and the significant scientific challenges that must be overcome for this goal to be realized. Potential applications enabled by the lower-cost processing methods and unique mechanical properties of organics include lightweight flexible displays, RFID tags, and sensors.¹⁻³ Many of these applications demand dielectrics, conductors, and semiconductors that are solution-processable under ambient conditions using conventional printing techniques.⁴⁻¹⁴ In addition to these processability requirements, important fundamental questions remain about long-range charge transport in organic solids, especially for polymeric semiconductors used in field-effect transistors (FETs).

Recent studies have demonstrated robust, air-stable performance in p-channel FETs using thiophene-based polymeric semiconductors (Figure 3.1).¹⁵⁻²³ Unfortunately, there is a lack of polymeric semiconductors with comparable processing and performance characteristics for n-channel FETs. This is important since both hole (p-type) and electron (n-type) materials and devices are required to achieve low-power consumption complementary organic circuitry (CMOS).²⁴⁻²⁶ In addition to such logic and switching applications, polymers exhibiting efficient electron transport and high electron affinities should also be useful as acceptor materials in organic photovoltaics and electron transporting materials in polymer-based light-emitting diodes.²⁷⁻³⁰

Limited progress has been made in developing polymer-based n-channel FETs. The first report of a n-channel FET-active polymer was BBL, a ladder-type polymer processed from methane sulfonic acid.³¹ Here, an electron mobility (μ_e) of 0.03 cm²V⁻¹s⁻¹ and current on-off ratio ($I_{on:off}$) of



Figure 3.1. Representative semiconducting polymers.

10⁵ was achieved once residual acid was leached out (after annealing $\mu_e = 0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, $I_{onoff} \approx$ 5). More recently, a perylene diimide-based copolymer (structure in Figure 3.1) FET using aluminum electrodes was reported to exhibit $\mu_e = 1.3 \times 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and $I_{on:off} = 10^4$ under inert atmosphere.³² Other researchers achieved n-channel FET performance using poly(3-hexylthiophene) (P3HT) having a mobility of $6 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ by employing hydrophobic dielectric coatings (to minimize charge carrier trapping at the dielectric surface) and alkali metal electrodes to reduce contact resistance. These FETs were also fabricated and characterized under inert atmosphere.³³ Polymer-oligomer blends have also been explored with reported performance as high as $\mu_e = 0.01 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and $I_{on:off} > 10^4$.³⁴ These reports and others³⁵ have advanced the limits of n-channel polymer performance via the synthesis of novel materials and/or implementation of unconventional and inert atmosphere device fabrication techniques.

High-performance polymeric semiconductors must maintain a delicate balance between solubility and close, efficient π - π stacking for efficient charge transport. While several p-channel polymers for OFETs meet these requirements,^{15, 17-19, 22, 23, 36} achieving such performance in electron transporting polymers has proven to be significantly more challenging. Previous efforts to enable n-channel polymer charge transport using environmentally-sensitive materials and contacts or hazardous acidic solvents are not compatible with the low-cost, ambient-condition solution processing requirements essential for the realization of practical organic electronics. These studies have highlighted the need for materials having appreciable electron mobilities, that are soluble in conventional organic solvents, exhibit appropriate solution rheology for printing and spin casting, and have a sufficiently high electron affinity to avoid electron trapping^{33, 37} by ambient species and surface states (O₂, H₂O, -OH).

The realization of n-channel polymers having the aforementioned characteristics remains a significant challenge for organic electronics, since aromatic systems with appropriate electron affinity and crystallinity are typically poorly soluble, lack open positions for further substitution, and are not readily polymerizable.^{24, 25} To develop innovative materials that surpass such limitations, an original materials-design methodology is devised to validate favorable properties of candidate materials and evaluate structural modification options, resulting in more informed design decisions. Here we demonstrate this novel computationally-aided design strategy through the development of a new class of electron transporting polymers (Figure 3.2) by incorporating highly-tailorable solubilizing groups into an electron-deficient core based upon the *N*-alkyl-2,2'- bithiophene-3,3'-dicarboximide unit (**BTI**).

The combination of bithiophene planarity and efficient π - π stacking with the electronwithdrawing capacity of the imide functionality, serves as the foundation for this new class of materials. The pre-synthesis DFT-level computational analysis reveals that introduction of the π electron deficient imide moiety significantly increases monomer electron affinity, reducing the sensitivity of mobile electrons to trap states. Furthermore, the geometry optimization reveals that substitution at the imide nitrogen allows introduction of functionalities with varying degrees of steric bulk while not impinging on critical intermolecular π - π stacking characteristics. This motif also leaves the bithiophene 5 and 5' positions available for polymerization. Finally, the dipole moment introduced by the imide moiety stabilizes cofacial anti-parallel intra- and inter-chain monomer orientations, planarizing the polymer chain, enhancing π - π stacking, and minimizing steric crowding by situating solubilizing groups on opposite sides of π -stacked chains.



Figure 3.2. Structures of the BTI-based homopolymers and copolymers.

It will be seen that these unique molecular characteristics enable a balance of excellent crystallinity and efficient π - π overlap with highly-tunable solubility.

In the present contribution, the synthesis of these materials is achieved using the key intermediate, bithiophene anhydride, followed by imide condensation and polymerization. Introduction of the solubilizing substituent near the end of the synthetic progression allows expeditious generation of diverse homo- and co-polymer libraries, to evaluate the interplay of solubility, crystallinity, and charge transport. Two solution-processable polymers are obtained via this approach, which yield smooth films upon casting with extraordinarily high crystallinity and a high tolerance for film deposition conditions. The annealed homopolymer exhibits excellent solubility and $\mu_e > 0.01 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ with a current on-off ratio of 10⁷. The annealed copolymer exhibits a hole mobility (μ_h) of ~ 0.01 cm² V⁻¹ \text{s}^{-1} with an air-stable current on-off ratio of 10⁷.

3.2 Experimental

3.2.1 Materials and methods

All reagents were purchased from commercial sources and used without further purification unless otherwise noted. Anhydrous diethyl ether and THF were distilled from Na/benzophenone and toluene was distilled from Na. CO₂ gas was obtained by warming dry ice and dried with P₂O₅ before use. The Stille reagent 5,5'-bis(tributylstannyl)-2,2'-bithiophene was synthesized according to a published procedure.³⁸ Conventional Schlenk techniques were used and reactions were carried out under N₂ unless otherwise noted. Microwave-assisted reactions were run in sealed vessels using a CEM Discover microwave reactor in temperature-controlled mode. UV-visible spectra were recorded on a Cary Model 1 UV-visible spectrophotometer. NMR spectra

were recorded on a Varian Unity Plus 500 spectrometer (¹H, 500 MHz). Electrochemistry was performed on a C3 Cell Stand electrochemical station equipped with BAS Epsilon software (Bioanalytical Systems, Inc., Lafayette, IN).

3.2.2 Synthesis

Synthesis of 3,3',5,5'-tetrabromo-2,2'-bithiophene (1). Bromine (288 g, 1.8 mol) was added slowly over 1 h to a stirred solution of 2,2'-bithiophene (60.0 g, 0.361 mol) in 280 mL chloroform containing 120 mL glacial acetic acid in a 1 L round bottom flask fitted with a reflux condenser (CAUTION: addition of the first two equivalents of bromine produces a strongly exothermic reaction). The mixture was then stirred at reflux for 12 h. Upon cooling to room temperature, a colorless precipitate was isolated by filtration and washed with methanol. The filtrate was then concentrated and a second crop of tan precipitate was collected and washed with methanol. The combined solids were dissolved in methylene chloride (500 mL), washed four times with 200 mL water, once with 100 mL brine, and dried over anhydrous MgSO₄. The organic solution was then filtered, and the solvent removed by evaporation to give 157 g (90% yield) of a colorless powder. ¹H NMR (CDCl₃): δ 7.06 (s, 2H) ppm.

Synthesis of 3,3'-dibromo-2,2'-bithiophene (2). Zn powder (31.7 g, 0.485 mol) was added in portions to a vigorously stirred refluxing mixture of bithiophene 1 (77.9 g, 0.162 mol) in 400 mL of ethanol containing 40 mL water, 100 mL glacial acetic acid, and 8 mL of 3 M HCl (aq). After refluxing for 2 h, the mixture was filtered hot and upon cooling to 0 °C, yellow crystals were collected by filtration. The crystals were dissolved in diethyl ether, washed three times with 200 mL water, once with 100 mL brine, and dried over anhydrous MgSO₄. The organics were filtered and the solvent removed by evaporation to give 49.4 g (94% yield) of a light yellow powder.
Anal. Calcd. for C₈H₄Br₂S₂: C, 29.65; H, 1.24; Found: C, 29.59; H, 1.14; ¹H NMR (CDCl₃): 7.41 (d, J = 5.3 Hz, 2H), 7.09 (d, J = 5.3 Hz, 2H) ppm.

Synthesis of 2,2'-bithiophene-3,3'-dicarboxylic acid (3). A solution of bithiophene 2 (19.44 g, 60.0 mmol) in 150 mL diethyl ether was added dropwise over 1 h to a stirring solution of n-BuLi (82.5 mL, 1.6 M in hexanes) in 900 mL ethyl ether at -78 °C. The reaction allowed to stir for 1h at -78 °C before dry CO₂ was bubbled into the reaction mixturefor 30 min. The reaction mixture was then allowed to stir for an additional 30 min before 1 mL methanol was added and the reaction filtered cold to afford a colorless solid. The solid was dried overnight *in vacuuo* at 100 °C, dissolved in 200 mL water, acidified with 6 M HCl (aq), and the resulting colorless precipitate isolated by filtration. This diacid was dried overnight *in vacuuo* at 100 °C to yield 14.1 g (92% yield) of a colorless powder. Anal. Calcd. for C₁₀H₆O₄S₂: C, 47.23; H, 2.38; Found: C, 47.19; H, 2.45; ¹H NMR (CDCl₃): 7.45 (d, J = 4.0 Hz, 2H), 7.10 (d, J = 4.5 Hz, 2H); m.p. 194-198 °C; MS (EI): m/z (%) 253.79 (100) [M⁺].

Synthesis of 2,2'-bithiophene-3,3'-dicarboxylic anhydride (4). Diacid 3 (12.6 g, 49.4 mmol) was stirred in 100 mL acetic anhydride at reflux for 6 h. Upon cooling to 0 °C, the solid was collected by filtration, washed with 20 mL cold acetic anhydride, and dried *in vacuuo* at 120 °C overnight. The resulting light yellow crystals (11.4 g, 98% yield) were used without further purification. Anal. Calcd. for $C_{10}H_4O_2S_2$: C, 50.84; H, 1.71; Found: C, 50.78; H, 1.66; 1H NMR (CDCl₃): 7.68 (d, J = 4.0 Hz, 2H), 7.40 (d, J = 5.0 Hz, 2H); m.p. 260-263 °C; MS (EI): m/z (%) 235.96 (100) [M⁺].

Synthesis of 1-iodo-2-octyldodecane (5). Iodine (6.06 g, 23.9 mmol) was added to a solution of 2-octyl-1-dodecanol (6.20 g, 20.8 mmol), triphenylphosphine (6.53 g, 24.9 mmol), and

imidazole (1.69 g, 24.9 mmol) in 40 mL dichloromethane at 0 °C. After stirring for 15 min, the reaction mixture was allowed to warm to room temperature over 2 h before 5 mL sat. Na₂SO₃ (aq) was added. The organics were concentrated by evaporation and the mixture taken up in 200 mL pentane, washed three times with 100 mL water, once with 70 mL brine, passed through a 3 cm silica gel plug, and dried over Mg₂SO₄. The organics were concentrated by evaporation to give a light yellow oil (8.22 g, 97% yield). Anal. Calcd. for C₂₀H₄₁I: C, 58.81; H, 10.12; Found: C, 58.70; H, 9.97; ¹H NMR (CDCl₃): 2.60 (d, J = 5.0 Hz, 2H), 2.00 (t, J = 5.0 Hz, 1H), 1.30-1.20 (b, 32H), 0.89 (t, J = 7.5 Hz, 6H); MS (EI): m/z (%) 408.23 (100) [M⁺].

Synthesis of 2-octyldodecylamine (6). Iodoalkane 5 (5.90 g, 14.5 mmol) and potassium phthalimide (2.94 g, 15.9 mmol) were taken up in 25 mL DMF and vigorously stirred for 72 h at 25 °C. The reaction mixture was then taken up in 200 mL pentane, washed four times with 100 mL water, passed through a 3 cm silica gel plug, and concentrated to give a colorless oil. The oil was next taken up in 150 mL ethanol, 4 mL hydrazine hydrate was added, and the mixture refluxed overnight. The resulting precipitate was collected by filtration, dissolved in 100 mL water, and the solution made alkaline by addition of 6 M NaOH (aq). The resulting mixture was then taken up in 200 mL pentane, washed four times with 100 mL water, once with 70 mL brine, and concentrated to give a colorless oil (3.08 g, 72% yield). Anal. Calcd. for $C_{20}H_{43}N$: C, 80.73; H, 14.57; Found: C, 80.78; H, 14.52; ¹H NMR (CDCl₃): 2.60 (d, J = 5.0 Hz, 2H), 2.00 (t, J = 5.0 Hz, 1H), 1.30-1.20 (b, 32H), 0.89 (t, J = 7.5 Hz, 6H); MS (EI): m/z (%) 297.34 (100) [M⁺].

Synthesis of *N*-(2-octyldodecyl)-2,2'-bithiophene-3,3'-dicarboximide (7). A dry 8 mL microwave reaction tube was charged with a micro-stirbar, anhydride 4 (354 mg, 1.50 mmol), 4-(dimethylamino)pyridine (61 mg, 0.50 mmol), and 5 mL toluene. Next, 2-octyldodecylamine (446 mg, 1.5 mmol) was added dropwise to the suspension over 15 min and the reaction allowed

to stir for an additional 15 min until no solid remained. The reaction tube was then irradiated with microwaves ($P_{MAX} = 300$ W) for 2 h at a constant temperature of 220 °C. This procedure was repeated four more times and the five reaction mixtures were combined in 250 mL diethyl ether, washed six times with 150 mL water, one time with 100 mL brine, and the organics dried over Mg₂SO₄. After filtration, the solvent was removed by evaporation to afford a yellow oil (90% pure by ¹H NMR) that was purified by column chromatography on silica gel with a mixture of diethyl ether (10%) and hexane (90%) as the eluent. A light yellow oil (1.45 g, 37% yield) was obtained upon concentration of the main fractions. Anal. Calcd. for C₃₀H₄₅NO₂S₂: C, 69.85; H, 8.79; Found: C, 69.79; H, 8.71; ¹H NMR (CDCl₃): 7.76 (d, J = 5.5 Hz, 2H), 7.24 (d, J = 5.5 Hz, 2H), 4.20 (t, J = 7.5 Hz, 2H), 1.71 (m, 1H), 1.37 (m, 4H), 1.26 (b, 28H), 0.89 (t, J = 7.0 Hz, 6H); MS (EI): m/z (%) 515.29 (100) [M⁺]. The same procedure was followed for the synthesis of compounds **8-12** as described below.

Synthesis of *N***-hexyl-2,2'-bithiophene-3,3'-dicarboximide (8).** A light yellow solid (1.65 g, 69% yield) was obtained upon concentration of the main fractions. Anal. Calcd. for $C_{16}H_{17}NO_2S_2$: C, 60.16; H, 5.36; Found: C, 60.05; H, 5.41; ¹H NMR (CDCl₃): 7.76 (d, J = 4.5 Hz, 2H), 7.24 (d, J = 5.5 Hz, 2H), 4.20 (t, J = 7.5 Hz, 2H), 1.71 (m, J = 8.0 Hz, 2H), 1.40 (m, 2H), 1.34 (m, 4H), 0.90 (t, J = 7.5 Hz, 3H); m.p. 90-91 °C; MS (EI): m/z (%) 319.4 (100) [M⁺].

Synthesis of *N***-octyl-2,2'-bithiophene-3,3'-dicarboximide (9).** A light yellow solid (1.87 g, 72% yield) was obtained upon concentration of the main fractions. Anal. Calcd. for $C_{18}H_{21}NO_2S_2$: C, 62.21; H, 6.09; Found: C, 62.18; H, 3.90; ¹H NMR (CDCl₃): 7.76 (d, J = 4.5 Hz, 2H), 7.24 (d, J = 5.5 Hz, 2H), 4.20 (t, J = 7.5 Hz, 2H), 1.71 (m, J = 8.0 Hz, 2H), 1.40 (m, 2H), 1.36-1.28 (b, 10H), 0.89 (t, J = 7.5 Hz, 3H); m.p. 71-72 °C; MS (EI): m/z (%) 346.9 (100) [M⁺].

Synthesis of N-dodecyl-2,2'-bithiophene-3,3'-dicarboximide (10). A light yellow solid (1.79 g, 59% yield) was obtained upon concentration of the main fractions. Anal. Calcd. for $C_{22}H_{29}NO_2S_2$: C, 65.47; H, 7.24; Found: C, 65.31; H, 7.41; ¹H NMR (CDCl₃): 7.76 (d, J = 5.5 Hz, 2H), 7.24 (d, J = 5.5 Hz, 2H), 4.24 (m, 2H), 1.69 (m, 2H), 1.56 (m, 4H), 1.37 (m, 2H), 1.26 (b, 2H), 1.17 (m, 2H), 1.00 (d, J = 6.5 Hz, 3H), 0.87 (d, J = 6.5 Hz, 6H); m.p. 60-61 °C; MS (EI): m/z (%) 403.3 (100) [M⁺].

Synthesis of *N*-(4,8-dimethylnonyl)-2,2'-bithiophene-3,3'-dicarboximide (11). A light yellow solid (1.78 g, 61% yield) was obtained upon concentration of the main fractions. Anal. Calcd. for $C_{21}H_{27}NO_2S_2$: C, 64.74; H, 6.99; Found: C, 64.68; H, 7.01; ¹H NMR (CDCl₃): 7.76 (d, J = 5.5 Hz, 2H), 7.25 (d, J = 5.5 Hz, 2H) , 4.20 (t, J = 7.5 Hz, 2H), 1.71 (m, 1H), 1.37 (m, 2H), 1.26 (b, 16H), 0.89 (t, J = 7.0 Hz, 9H); m.p. 52-54 °C; MS (EI): m/z (%) 389.3 (100) [M⁺].

Synthesis of *N*-(2-ethylhexyl)-2,2'-bithiophene-3,3'-dicarboximide (M1, 12). A light yellow solid (1.10 g, 42% yield) was obtained upon concentration of the main fractions. Anal. Calcd. for $C_{19}H_{21}NO_2S_2$: C, 62.21; H, 6.09; Found: C, 62.09; H, 6.02; ¹H NMR (CDCl₃): 7.69 (d, J = 5.5 Hz, 2H), 7.25 (d, J = 5.5 Hz, 2H), 4.20 (t, J = 7.5 Hz, 2H), 1.80 (m, J = 8.0 Hz, 1H), 1.29 (b, 8H), 0.89 (t, J = 7.5 Hz, 6H); m.p. 54-56 °C; MS (EI): m/z (%) 347.1 (100) [M⁺].

Synthesis of *N*-(2-octyldodecyl)-5-5'dibromo-2,2'-bithiophene-3,3'-dicarboximide (13). Bromine (1.41 g, 8.84 mmol) was added to a solution of imide 7 (1.14 g, 2.21 mmol) in 30 mL dichloromethane followed by the addition of ferric chloride (7.2 mg, 0.044 mmol). The reaction mixture was allowed to stir in the dark for 6h before 5 mL sat. Na₂SO₃ (aq) was added and stirring continued for 0.5 h. The reaction mixture was then poured into 150 mL dichloromethane, washed three times with 100 mL water, once with 70 mL brine, and dried over Mg₂SO₄. The organics were next concentrated by evaporation to give a light yellow solid (1.40, 94% yield). Anal. Calcd. for $C_{30}H_{43}Br_2NO_2S_2$: 53.49; H, 6.43; Found: C, 53.36; H, 6.40; ¹H NMR (CDCl₃): 7.68 (s, 2H), 4.18 (d, J = 7.5 Hz, 2H), 1.86 (m, 1H), 1.34-1.20 (b, 32H), 0.89 (t, J = 7.5 Hz, 6H); m.p. 44-46 °C; MS (EI): m/z (%) XX(100) [M⁺]. The same procedure was followed for compounds **14-18** as described below.

Synthesis of *N***-hexyl-5-5'dibromo-2,2'-bithiophene-3,3'-dicarboximide (14).** A light yellow solid (84% yield) was obtained upon concentration. Anal. Calcd. for C₁₆H₁₅Br₂NO₂S₂: C, 40.27; H, 3.17; Found: C, 40.30; H, 3.13; ¹H NMR (CDCl₃): 7.72 (s, 2H), 4.16 (t, J = 7.0 Hz, 2H), 1.69 (m, J = 7.0 Hz, 2H), 1.33-1.27 (b, 6H), 0.89 (t, J = 7.5 Hz, 3H); m.p. 149-150 °C; MS (EI): m/z (%) 319.0 (100) [M⁺].

Synthesis of *N*-octyl-5-5'dibromo-2,2'-bithiophene-3,3'-dicarboximide (15). A light yellow solid (95% yield) was obtained upon concentration. Anal. Calcd. for $C_{18}H_{19}Br_2NO_2S_2$: C, 42.79; H, 3.79; Found: C, 42.66; H, 3.82; ¹H NMR (CDCl₃): 7.70 (s, 2H), 4.15 (t, J = 7.0 Hz, 2H), 1.67 (m, J = 7.0 Hz, 2H), 1.35-1.25 (b, 10H), 0.89 (t, J = 7.5 Hz, 3H); m.p. 133-135 °C; MS (EI): m/z (%) 347.1 (100) [M⁺].

Synthesis of *N*-dodecyl-5-5'dibromo-2,2'-bithiophene-3,3'-dicarboximide (16). A light yellow solid (98% yield) was obtained upon concentration. Anal. Calcd. for $C_{22}H_{27}Br_2NO_2S_2$: C, 47.07; H, 4.85; Found: C, 47.05; H, 4.77; ¹H NMR (CDCl₃): 7.70 (s, 2H), 4.15 (t, J = 7.0 Hz, 2H), 1.66 (m, 2H), 1.35-1.27 (b, 18H), 0.89 (t, J = 7.0 Hz, 3H); m.p. 117-119 °C; MS (EI): m/z (%) 403.3 (100) [M⁺].

Synthesis of *N*-(4,8-dimethylnonyl)-5-5'dibromo-2,2'-bithiophene-3,3'-dicarboximide (17). A light yellow solid (92% yield) was obtained upon concentration. Anal. Calcd. for $C_{21}H_{25}Br_2NO_2S_2$: C, 46.08; H, 4.60; Found: C, 45.99; H, 4.65; ¹H NMR (CDCl₃): 7.71 (s, J = 5.5

Hz, 2H), 4.15 (t, J = 7.5 Hz, 2H), 1.73 (m, 1H), 1.34 (m, 2H), 1.29 (b, 16H), 0.89 (t, J = 7.0 Hz, 9H); m.p. 127-130 °C; MS (EI): m/z (%) 389.0 (100) [M⁺].

Synthesis of *N*-(2-ethylhexyl)-5-5'dibromo-2,2'-bithiophene-3,3'-dicarboximide (18). A light yellow solid (95% yield) was obtained upon concentration. Anal. Calcd. for $C_{19}H_{19}Br_2NO_2S_2$: C, 42.79; H, 3.79; Found: C, 42.57; H, 3.84; ¹H NMR (CDCl₃): 7.69 (s, 2H), 4.19 (d, J = 7.0 Hz, 2H), 1.90 (m, 1H), 1.36-1.22 (b, 8H), 0.89 (m, 6H); m.p. 154-147 °C; MS (EI): m/z (%) 347.1 (100) [M⁺].

Synthesis of poly(N-(2-octyldodecyl)-2,2'-bithiophene-3,3'-dicarboximide) (P1). A solution of imide 23 (1.21 g, 1.80 mmol) in 70 mL DMF was added to a solution of bis(1,5cyclooctadiene)nickel(0) (0.594 g, 2.16 mmol), 1,5-cyclooctadiene (0.195 g, 1.80 mmol), and 2,2'-bipyridine (0.337 g, 2.16 mmol) which had been stirring for 20 min in 10 mL DMF. The reaction mixture was then heated at 60 °C for 48 h before bromobenzene (2.83 g, 18.0 mmol) was added and the reaction mixture allowed to stir for an additional 12 h. The mixture was then allowed to cool to room temperature, poured into 200 mL methanol containing 20 mL 12 M HCl (aq), stirred for 6 h, the precipitate collected by filtration, and dried overnight *in vacuuo* at 120 °C to give 0.970g solid. The crude product was dissolved in 40 mL toluene, filtered through a 0.45 µm filter, precipitated with 400 mL methanol, collected by filtration, and dried as before to give 0.912 g of dark red powder. This precipitation procedure was repeated four more times to give 0.821 g dark red powder which was placed in a microscale Soxhlet extractor and extracted for 48 h with methanol, 24 h with pentane, and recovered by extraction with dichloromethane. The dichloromethane solution was filtered through a 0.22 µm filter and the polymer precipitated with 300 mL methanol to give 5 as a red powder (0.634 g,) after drying in vacuuo at 120 °C.

Anal. Calcd. for $C_{30}H_{43}NO_2S_2$: C, 70.13; H, 8.44; N, 2.73; Found: C, 69.94; H, 8.69; N, 2.89; ¹H NMR (CDCl₃): 7.71 (b, 2H), 4.25 (b, 2H), 1.88 (b, 1H), 1.4-1.2 (b, 32H), 0.89 (t, J = 7.5 Hz, 6H); GPC(150 °C, TCB, vs. PS): $M_W = 7.9 \times 10^3$; PDI = 2.2. Attempts to prepare homopolymers were carried out using the same Yamamoto polymerization conditions with monomers **15-18**, yielding insoluble products. Polymerizations of **15-18** were also performed under mild conditions (30 °C, 1 h to 2h), all resulting in intracTable 3.products.

poly(N-(2-octyldodecyl)-2,2':5',2'':5'',2'''-quaterthiophene-3,3'-**Synthesis** of dicarboximide) (P2). Imide 13 (0.674 g, 1.00 mmol), 2,5'-bis(tributlystannyl)-2,2'-bithiophene (0.744 g, 1.00 mmol), and Pd(PPh₃)₄ (0.045 g, 0.050 mmol) in anhydrous DMF (20 mL) were heated at 90 °C under nitrogen for 24 h. The reaction mixture was then allowed to cool to room temperature, poured into 300 mL methanol, and the precipitate collected by filtration to give 0.621 g black solid. The crude material was placed in a microscale Soxhlet extractor and extracted for 48 h with methanol, 24 h with pentane, and recovered by extraction with chlorobenzene. The chlorobenzene solution was passed through a 0.22 µm filter and the polymer precipitated with 200 mL methanol to give P2 as a purple solid (0.107 g, 16% yield) after drying in vacuuo at 120 °C. Anal. Calcd. for C₃₈H₄₇NO₂S₄: C, 67.31; H, 6.99; N, 2.07; Found: C, 67.04; H, 7.11; N, 1.99; ¹H NMR (C₂D₄Cl₄): 8.09 (b, 2H), 7.20 (b, 4H), 4.32 (b, 2H), 2.05 (b, 1H), 1.35 (b, 32H), 0.96 (b, 6H); GPC(150 °C, TCB, vs. PS): $M_w = 2.5 \times 10^3$; PDI = 1.38. Attempts to copolymerize 15-18 and 2,5'-bis(tributlystannyl)-2,2'-bithiophene carried out using the same procedure yielded insoluble products. Copolymerizations of 15-18 with 2,5'bis(tributlystannyl)-2,2'-bithiophene using milder conditions were also attempted (30 °C, 1 h to 12 h), all resulting in intracTable 3.products.

Synthesis of *N***-hexyl-2,2':5',2'':5'',2'''-quaterthiophene-4',3''-dicarboximide (19).** A dry 8 mL microwave reaction tube was charged with a micro-stirbar, imide **14** (0.416 g, 0.871 mmol), 2-(tributlystannyl)thiophene (0.650 g. 1.74 mmol), Pd(PPh₃)₄ (0.041 g, 0.045 mmol), and DMF (6mL) before being irradiated with microwaves ($P_{MAX} = 300$ W) for 5 min at a constant temperature of 120 °C. Upon cooling, the orange precipitate was collected by filtration, washed with methanol (10 mL), and dried *in vacuuo* at 120 °C. The solid was purified by column chromatography on silica gel with a mixture of diethyl ether (30%) and hexane (70%) as the eluent. Orange 0.153 g of needle-like crystals were obtained upon concentration of the main fractions. The crystals were further purified by sublimation under vacuum to give orange needle-like crystals (0.111 g, 26% yield) suiTable 3.for single crystal diffraction. Anal. Calcd. for C₂₄H₂₁NO₂S₄: C, 59.60; H, 4.38; Found: C, 59.53; H, 4.34; ¹H NMR (CDCl₃): 7.81 (s, 2H), 7.34 (d, 4.5 Hz, 2H), 7.26 (d, 4.0 Hz, 2H), 4.21 (t, J = 8.0 Hz, 2H), 1.72 (m, 2H), 1.43 (m, 2H), 1.36 (b, 6H), 0.91 (t, J = 7.0 Hz, 3H); m.p. 190-193 °C; MS (EI): m/z (%) 483.2 (100) [M⁺].

Synthesis of *N*-(2-ethylhexyl)-2,2':5',2'':5'',2'''-quaterthiophene-4',3''-dicarboximide (M2). A dry 8 mL microwave reaction tube was charged with a micro-stirbar, imide 18 (0.445 g, 0.871 mmol), 2-(tributlystannyl)thiophene (0.650 g. 1.74 mmol), Pd(PPh₃)₄ (0.041 g, 0.045 mmol), and DMF (6mL) before being irradiated with microwaves ($P_{MAX} = 300$ W) for 5 min at a constant temperature of 120 °C. Upon cooling an orange precipitate was collected by filtration, washed with methanol (10 mL), and dried *in vacuuo* at 120 °C. The solid was purified by column chromatography on silica gel with a mixture of diethyl ether (30%) and hexane (70%) as the eluent to yield 0.153 g of orange needle-like crystals upon concentration of the main fractions. The crystals were further purified by sublimation under vacuum to give orange needle-like crystals (0.136 g, 22% yield). Anal. Calcd. for C₂₆H₂₅NO₂S₄: C, 61.02; H, 4.92; Found: C, 60.89;

H, 4.78; ¹H NMR (CDCl₃): 7.82 (s, 2H), 7.35 (d, 4.5 Hz, 2H), 7.26 (b, 2H), 4.27 (m, 2H), 1.87 (m, 1H), 1.38-1.26 (m, 8H), 0.92 (m, 6H); m.p. 181-184 °C; MS (EI): m/z (%) 511.2 (100) [M⁺].

3.2.3 Polymer molecular weight determination

GPC measurements were performed on a Polymer Laboratories PL-GPC 220 instrument using 1,2,4-trichlorobenzeneas the solvent (stabilized with 125 ppm BHT) at 150 °C. A set of three PLgel 10 µm mixed columns was used. Samples were prepared at 160 °C. Molecular weights were determined by GPC using narrow polystyrene standards and are not corrected.

3.2.4 Electrochemistry

Cyclic voltammetry measurements were performed with a 0.1 M tetrabutylammonium hexafluorophosphate electrolyte in dry acetonitrile for polymer films and in THF for molecules in solution. Platinum electrodes were used as both working and counter electrodes, and Ag wire was used as the pseudo-reference electrode. A ferrocene/ferrocenium redox couple was used as an internal standard and potentials obtained in reference to the silver electrode were converted to the saturated calomel electrode (SCE) scale. Thin films of the polymers were coated onto the Pt working electrode by drop casting from 0.1 wt % THF or 1,2-dichlorobenzene solutions and dried under vacuum at 80 °C for 2 h.

3.2.5 Thermal characterization

Polymers were dried under vacuum for 3 d at 120 °C before thermal analysis. Thermogravimetric analysis (TGA) was performed on a TA instruments Q50 at a ramp rate of 10 °C/min under nitrogen at atmospheric pressure in an aluminum oxide crucible. Differential scanning calorimetry (DSC) was performed using a Mettler Toledo DSC823e instrument at a ramp rate of 10 °C/min using aluminum pans under nitrogen.

3.2.6 Device fabrication and measurement

Prime grade p-doped silicon wafers (100) having 300 nm thermally grown oxide (Process Specialties Inc.) were used as device substrates. These were sonicated in methanol, acetone, propanol, and oxygen plasma cleaned before film deposition. Trimethylsilyl functionalization of the SiO₂ surface was carried out by exposing the cleaned silicon wafers to hexamethyldisilazane (HMDS) vapor under nitrogen at room temperature for 4 days. Films of P1 were spin-coated from 0.5 % (w/v) THF, CHCl₃, or 1,2,4-trichlorobenzene solutions and films of P2 were spincoated from 0.5 % (w/v) 1,2-dichlorobenzene solutions at 50 °C. All films were dried at 120 °C in vacuuo for 12 h and, if annealed, heated under nitrogen at various temperatures from 180 °C to 300 °C for 30 min or 2 h, as specified in the text. Spin-coated polymer films were 20-37 nmthick as determined by profilometry. For FET device fabrication, top-contact gold electrodes (500 Å) were deposited by thermal evaporation through a shadow mask to define channels with dimensions 100 μ m (L) by 2.00 mm (W). The capacitance of the 300 nm SiO₂ insulator is 1 x 10⁻ ⁸ F/cm² and mobilities were calculated in the saturation regime. TFT device measurements were carried out at 21 °C - 23 °C in a customized high-vacuum probe station (1 x 10⁻⁶ Torr) or in air. Coaxial and/or triaxial shielding was incorporated into Signaton probes to minimize noise levels. TFT characterization was performed with a Keithley 6430 sub-femtoampmeter (drain) and a Keithley 2400 (gate) source meter, operated by a locally written Labview program and GPIB communication.

3.2.7 Thin-film characterization

Thin films were analyzed by wide-angle X-ray film diffractometry (WAXRD) on a Rikagu ATX-G instrument using standard θ -2 θ techniques, with Cu K α_1 radiation. Atomic force

microscopy was performed on a Jeol 5200 SPM instrument. Scanning electron microscopy was performed on a Hitachi 4800 SEM with samples having a 2 nm Au/Pd sputtered film.

3.2.8 Computational methodology

Equilibrium geometry optimizations were performed in QChem 2.1³⁹ using density functional theory DFT with a B3LYP functional and the 3-12G* basis set. Single point calculations using these geometries were then performed at the DFT/B3LYP/6-31+G* level of theory to obtain molecular orbital energy levels (QChem) and molecular orbital electron density plots (Spartan '06). Energy levels were calibrated to the experimental HOMO/LUMO energies⁴⁰ of sexithiophene. Dipole moments for **M1** and **M2** were calculated using UHF/6-31+G* with DFT optimized geometries.

3.3 Results

BTI materials are first evaluated by computational analysis and their optimized geometries, MO energy levels, and orbital electron density plots are reported. Next, the six-step monomer synthetic route is described followed by the synthesis of model compounds and polymers. The materials obtained are next characterized by GPC, electronic absorbtion spectroscopy, and electrochemistry. WAXRD, SEM, and AFM are then employed to characterize spin-cast polymer film microstructure, followed by FET device fabrication and optimization. Finally, the crystal structure of a molecular model compound is described in detail.

3.3.1 Quantum chemical modeling

The geometries of a **BTI** trimer, **BTI**-bithiophene-**BTI** co-oligomer, and sexithiophene were optimized at DFT/B3LYP/3-21G* level, revealing a highly planar **BTI** π -core, with negligible inter-monomer torsion (Figure 3.3). The imides are found to be oriented anti-parallel in both **BTI**

containing oligomers, and there is no interaction of the imide nitrogen substituent with neighboring monomers. Using the optimized geometries, the molecular orbital energies were calculated using the 6-31+G* basis. Energies reported in Figure 3.3 and summarized in Table 3.2 were obtained by correcting the DFT-derived eigenvalues to the HOMO and LUMO energies of sexithiophene,⁴⁰ estimated⁴¹ from electrochemical data. Molecular orbital plots reveal highly delocalized HOMOs and LUMOs having aromatic and quinodal configurations, respectively. The **BTI** trimer LUMO energy is lowest at -3.52 eV while that of the co-oligomer is at -3.18 eV, both lower than that of sexithiophene at -2.69 eV. Sexithiophene is found to have the highest lying HOMO at -5.38 eV, followed by the co-oligomer at -5.90 eV, and the **BTI** trimer at -6.25 eV. Finally, the dipole moments of **M1** and **M2** are calculated to be 2.27 Debye and 3.78 Debye, respectively, oriented toward the imide nitrogen atom.

3.3.2 Synthesis

The dibromo-functionalized **BTI** building blocks 13-18 were all prepared from commercially available 2,2'-bithiophene according to Scheme 3.1. Model molecular compounds 19 and M2 were obtained according to Scheme 3.2 by Stille coupling of 2-(tributylstannyl)thiophene with reagents 14 and 18, respectively, and were purified by column chromatography and sublimation. Crystals of 19 suiTable 3.for single crystal diffraction were obtained by slow sublimation at 50 mTorr onto a cold finger. Yamamoto and Stille coupling polymerizations were employed to synthesize the homopolymers and bithiophene copolymers, respectively, as shown in Scheme 3.3. The key intermediate, bithiophene anhydride (4), was synthesized in four steps from 2,2'bithiophene. First, 2,2'-bithiophene was tetrabrominated by refluxing with Br₂ in a mixture of chloroform and acetic acid to give 3,5,3',5'-tetrabromo-2,2'-bithiophene 1, which was then debrominated 3,3'-dibromo-2,2'-bithiophene selectively with Zn to vield 2.



Figure 3.3. DFT optimized geometries, frontier orbitals, and orbital energies (eV vs. vacuum) of sexithiophene (**a**) and the indicated oligomers having two (**b**) or three (**c**) imide units.

To obtain the corresponding dicarboxylic acid, 2 was slowly added to a dilute solution of n-BuLi followed by quenching of the dilithium salt with dry carbon dioxide to afford the dilithium salt of 3,3'-dicarboxylate-2,2'-bithiophene. Diacid 3 was obtained upon acidification of the solid and was used without further purification. Condensation/cyclization of 3 was carried out in refluxing acetic anhydride to yield the novel key intermediate 2,2'-bithiophene-3,3'-dicarboxylic anhydride 4 in 77% overall yield from 2,2'-bithiophene. Six imides were then synthesized by condensation of 4 with primary amines. Of the amines used, only 2-octyldodecylamine was synthesized, while the remaining are commercially available. The reagent 2-octyldodecylamine amine was obtained in 70% overall yield via iodination of the commercially available alcohol to 5, followed by a Gabriel synthesis to yield 2-octyldodecylamine (6).

Imide condensations of the novel seven-membered anhydride **4** with primary alkyl amines were initially performed in molten imidazole. However, the required temperature of 200 °C and reaction times over 12 h resulted in significant decomposition of the imide to the corresponding diamide, resulting in < 5% yields when sterically hindered amines were used.⁴² Other imide condensation conditions were explored without success, including removal of water by azeotroping, and condensation in refluxing propionic acid.⁴³ The most efficient method found for synthesizing the unique seven-membered N-akyl-2,2'-bithiophene-3,3'-dicarboximides **7-12** was by microwave irradiation for 2 hours in toluene with a catalytic amount of 4- (dimethylamino)pyridine at a temperature of 220 °C. The crude products were purified by column chromatography to afford the pure imides in yields ranging from 72% for *n*-alkyl amines to 37% for branched-alkyl primary amines. Finally, the dibromo-functionalized monomers **13-18** were synthesized in quantitative yield by addition of Br₂ to a solution of the imides in dichloromethane containing a catalytic amount of ferric chloride.



Scheme 3.1. General synthetic route to 2,2'-bithiophene-3,3'-dicarboximide monomers.



Scheme 3.2. Synthesis of molecular model compounds N-hexyl-2,2':5',2'':5'',2'''quaterthiophene-4',3''-dicarboximide (19) and N-(2-ethylhexyl)- 2,2':5',2'':5'',2'''quaterthiophene-4',3''-dicarboximide (M2).



Scheme 3.3. Synthesis of BTI homopolymers and copolymers.

Polymers were synthesized according to Scheme 3.3 from the dibromo-functionalized imides 13, 15-17, and 5,5'-bis(tributylstannyl)-2,2'-bithiophene. Homopolymers were obtained by Yamamoto polycondensation of 13 or 15-18 for 48 h in DMF at 60 °C in a procedure similar to previous reports using electron-deficient bromo-functionalized heterocycles.⁴⁴ Polymers were isolated by filtration after quenching the reaction mixture with acidic methanol, and the soluble homopolymer P1 was purified by multiple precipitations from chloroform with methanol. Products obtained from reactions using the less bulky imides 15-18 were found to be insoluble. To reduce molecular weights, polymerizations were also carried out under milder conditions (30 °C, 1-2 h). Attempts to isolate tracTable 3.materials by Soxhlet extraction were unfruitful with only 1-2% of the crude products extracted using 1,2-dichlorobenzene, after washing with methanol and pentane. Copolymers of 13 and 15-18 with bithiophene were synthesized by Stille coupling using either standard polymerization conditions (90 °C, 24 h) or milder reaction conditions (30 °C, 1 h - 12 h). Crude reaction precipitates were isolated by filtration, and solubility was evaluated by Soxhlet extraction with methanol (48 h) and pentane (24 h), followed by redissolution of the polymer in chlorobenzene. Polymer **P2** was isolated by this method, followed by precipitation from chlorobenzene with methanol. Copolymers synthesized with 15-18, even under mild conditions, were found to be intractable. The structures of the π -conjugated monomers and polymers synthesized and characterized in this study, M1, M2, P1, and P2, are shown in Figure 3.4.



Figure 3.4. Structures of π -conjugated monomers and polymers M1, M2, P1, and P2.

3.3.3 Polymer molecular weight

Gel permeation chromatography (GPC) was used to determine polymer molecular weight versus polystyrene. **P1** was found to have $M_w = 7900$ D and PDI = 2.2, and **P2** to have $M_w = 2500$ D and PDI = 1.4.

3.3.4 Polymer thermal properties

Thermogravimetric analysis (TGA) was used to evaluate the thermal stability of purified polymers **P1** and **P2** (Figure 3.5a). A mass loss of 5% is defined as the threshold for thermal decomposition. Both materials demonstrate good thermal stability with the onset of decomposition at 401 °C for **P1** and 424 °C for **P2**.

Differential scanning calorimetry (DSC) was used to characterize the thermal transitions in the polymers (Figure 3.5b). Homopolymer **P1** exhibits a glass transition-like feature at 201 °C and a broad endothermic transition at 295 °C on the forward sweep of the first DSC cycle. No features are observed on the reverse sweep or in any of four subsequent cycles. Copolymer **P2** undergoes two reversible endothermic transitions at 127 °C and 196 °C. Both of these transitions are reversible with exotherms at 197 °C and 120 °C in the reverse sweeps over four cycles.

3.3.5 Polymer optical properties

Solution and thin-film UV-visible absorbtion spectra of the present monomers and the corresponding polymers are shown in Figure 3.6, and the optical spectroscopic data are summarized in Table 3.1. In chlorobenzene solution, molecules **M1** and **M2** exhibit absorption maxima at 348 nm and 432 nm, respectively, with a shoulder on the red side of the band ~20 nm from the peak maximum. **M1** thin films exhibit a maximum absorption at 351 nm and a shoulder at 371 nm (similar to that in solution), while **M2** films have a maximum at 455 nm and shoulders



Figure 3.5. Thermogravimetric analysis (TGA, a) and differential scanning calorimetry (DSC, b) plots for homopolymer P1 (red) and copolymer P2 (purple.) The first DSC cycle is shown for P1 while the second cycle is shown for P2.



Figure 3.6. Optical absorbtion spectra of monomers M1 (blue), M2 (green), homopolymer P1 (red), and copolymer P2 (purple) in chlorobenzene solution (a) and as thin films cast from chlorobenzene on quartz (b). Data are collected in Table 3.1.

 Table 3.1. Summary of optical absorption data for monomers M1, M2, homopolymer P1, and copolymer P2.

		Calculated ^d							
	λ_{\max}^{soln} (nm)	$\lambda_{\text{shoulder}}^{\text{sol}}$ (nm)	$\lambda_{\max}_{m}^{fil}$ (nm)	λ ^{fil} m (nm)	E _{gap} a (eV)	HOMO ^b (eV)	LUMO ° (eV)	HOMO (eV)	LUMO (eV)
M 1	348	367	351	371, 501, 602	3.2	-6.43 ^d	-3.23	-	-
Μ	432	454	455	428, 489	2.5	-5.94	-3.11	-	-
P1	535	503, 578	524	498, 564	2.0	-6.28	-3.47	-6.25	-3.52
P2	517	366, 553, 607	615	390, 517, 569	1.9	-5.88	-3.04	-5.90	-3.18

^aOptical band gap calculated from the red edge of the S_0 - S_1 absorbtion band at 1/10 of the maximum intensity. ^bHOMO energy estimated by subtracting the optical gap from LUMO energy. ^cEstimated from the onset of the first reduction using the correction factor -4.4 V to convert SCE reference to vacuum.⁴¹ ^dCalculated using DFT for oligomers in Figure 3.3 and corrected with the HOMO/LUMO energies of sexithiophene⁴⁰ estimated from solution electrochemistry.

at 428 nm and 489 nm. Homopolymer **P1** exhibits an absorption maximum at 535 nm in chlorobenzene with shoulders at 503nm and 578 nm. The thin-film spectrum of this polymer is similar, with a maximum at 524 nm and shoulders at 498 nm and 564 nm. The solution absorbtion spectrum of **P2** has a maximum at 517 nm and shoulders at 336 nm, 553 nm, and 607 nm. Similar to the thiophene-substituted molecule, the **P2** red absorbtion bands are enhanced in the thin-film spectrum with a maximum at 615 nm and shoulders at 390 nm, 517 nm, and 569 nm.

3.3.6 Electrochemical properties

The redox behavior of **M1**, **M2**, **P1**, and **P2** was investigated using cyclic voltammetry (Figure 3.7, Table 3.2). All potentials are reported vs. SCE with the ferrocene/ferrocenium couple used as an internal standard. **M1** exhibits the onset of reduction at -1.17 V with a reversible reduction wave at -1.65 V. A significant oxidation wave is not observed for this material. Thiophene-substituted molecule **M2** shows the onset of reduction at -1.29 V with a reversible reduction wave at -1.65 V. The onset of oxidation is found to be at 1.39 V with two partially reversible events at 1.54 V and 1.77 V. Homopolymer **P1** films on Pt exhibit multiple reversible reduction waves with onset at -0.93 V and half-wave potentials of -1.11 V and -1.32 V. Oxidation of the homopolymer **P2** thin-films exhibit two reversible reduction events with onset at -1.36 V and half-wave potentials at -1.36 V. A model at -1.54 V. Oxidation of the homopolymer thin-films occurs with an onset at 1.19 V and three irreversible oxidations with half-wave potentials at 1.39 V, 1.48 V, and 1.92 V.



Figure 3.7. Cyclic voltammograms of M1 (blue), M2 (green), homopolymer P1 (red), and copolymer P2 (purple). Data are collected in Table 3.2.

	Oxidation			Reduction					
	cathodic ^a		cathodic		anodic		half-	half-wave	
compound	E _{c1}	E_{c2}	E_{c3}	E _{c1}	E_{c2}	E _{a1}	E_{a2}	$E_1^{1/2}$	$E_2^{1/2}$
M1 ^b				-1.47		-1.83		-1.65	
$M2^{b}$	1.54	1.77		-1.27		-1.48		-1.38	
P1 ^c	1.71	1.88	1.97	-1.01	-1.26	-1.21	-1.38	-1.11	-1.32
P2 ^c	1.48	1.67	2.00	-1.27	-1.44	-1.42	-1.64	-1.34	-1.54

Table 3.2. Anodic (E_a), cathodic (E_c), and half-wave ($E^{1/2}$) potentials (V vs SCE) from cyclic voltammetry of **M1**, **M2**, **P1**, and **P2**.

^a Oxidation events are irreversible. ^b Electrochemistry performed in THF solution. ^c Electrochemistry performed on films on Pt electrode.

3.3.7 Thin-film X-ray diffraction analysis

Thin-film wide angle X-ray diffraction (XRD) θ -2 θ scans of homopolymer **P1** and copolymer **P2** were performed to investigate the degree of film crystallinity and the polymer chain orientation with respect to the substrate surface. Films were cast on the same substrates (p⁺⁺-Si/300 nm SiO₂, untreated or HMDS treated) used to fabricate TFTs (vide infra) then dried, and then annealed between 120 °C and 300 °C as specified. **P1** films exhibit several strong Bragg reflections on the HMDS treated substrates (Figures 3.8, 3.9, and 3.10), while less intense reflections are observed from films on the untreated substrates. XRD intensities increase and higher-order peaks are observed in all films when the annealing time and/or the temperature is increased. In all films of the homopolymer, a single family of Bragg peaks is observed corresponding to a d-spacing of 25.1 ± 0.6 Å with up to 5th order reflections observed from films on hydrophobic substrates. This d-spacing corresponds to **P1** chains angled at ~69.0° relative to the substrate plane if the chains are not interdigitated from TCB.

Films of copolymer P2 also exhibit strong Bragg reflections (Figure 3.11). Copolymer films on untreated SiO₂ substrates exhibit broad first- and second-order reflections with the intensities increasing with annealing temperature. Films on HMDS treated substrates exhibit more intense diffraction features, having narrower peaks and reflections up to third-order for films annealed at higher temperatures. The Bragg reflections observed in all films indicate highly crystalline films with a d spacing of 21.7 ± 0.1 Å along the substrate normal. This d-spacing corresponds to the polymer chains angled at ~53.5° relative to the substrate plane if the chains are not interdigitated from one layer to the next. The estimated tilt angle relative to the plane will be less if the chains are interdigitated between layers.



Figure 3.8. X-ray diffraction θ -2 θ plots of homopolymer P1 films spin-cast from CHCl₃ onto hydrophilic SiO₂ (S) and hydrophobic HMDS treated (H) substrates, then annealed at the indicated temperatures for 30 minutes unless otherwise noted.



Figure 3.9. WAXRD θ -2 θ scans of P1 films cast from TCB.



Figure 3.10. WAXRD θ -2 θ scans of **P1** films cast from THF.



Figure 3.11. X-ray diffraction θ -2 θ plots of copolymer **P2** spin-cast film from 1,2dichlorobenzene onto hydrophilic SiO₂ (S) and hydrophobic HMDS treated (H) substrates then annealed at various temperatures for 30 minutes.

3.3.8 Film surface microstructure

Scanning electron microscopy (SEM) and tapping-mode atomic force microscopy (AFM) were employed to evaluate the polymer film continuity, surface morphology, and roughness. Films of **P1** cast from all solvents on HMDS treated substrates are continuous with the roughness and surface morphology being highly dependent on the casting solvent (Figures 3.12, 3.14, and 3.15). Casting from TCB yields films with 2.6 nm rms roughness (after drying at 120 °C, Figure 3.12). Additional annealing results in a slightly decreased 1.8 nm rms roughness and the appearance of terracing in the polymer films with a step height of 2.5 nm as determined from AFM height histograms (Figure 3.13c). Films cast from chloroform contain large circular holes in otherwise featureless films after drying (Figure 3.14). The holes disappear with annealing and SEM and AFM images reveal smooth, continuous, polycrystalline films with rms roughness increasing with annealing temperature from 1.8 nm at 240 °C to 4.4 nm at 300 °C. Films cast from THF exhibit the greatest rms roughnesses (29 nm) with irregularly-shaped solvent pockets in samples dried at 120 °C that decrease in size with annealing to yield a highly textured film when annealed at 240 °C for 2h or 300 °C for 30 min (Figure 3.15). All homopolymer films cast on untreated SiO₂ substrates are featureless without evidence of solvent bubbles or crystallization (Figures 3.16, 3.17, and 3.18).

Films of **P2** were spin-cast from DCB at 60 °C and evidence continuous surface coverage upon drying. Those cast on untreated SiO₂ surfaces have an initial rms roughness of 1.2 nm which decreases with annealing to 1.0 nm (Figure 3.20). Films cast onto HMDS treated substrates exhibit a greater initial rms roughness of 4.0 nm, which increases with annealing to 5.8 nm (180 °C) and 8.4 nm (240 °C) (Figures 3.19a-f). This increase in roughness corresponds to melting of the polymer followed by dewetting from the hydrophobic surface as evidenced by large gaps



Figure 3.12. SEM (top) and AFM (lower) images of P1 films on HMDS treated SiO_2 cast from TCB.



Figure 3.13. AFM images of **P1** films spin-cast from TCB and annealed at 120 °C for 30 min (a), 240 °C for 2 h (b), and a height histogram (c) for both images (120 °C in blue and 240 °C in red) revealing the formation of a terraced surface having a 2.50 nm step height.



Figure 3.14. SEM (upper) and AFM (lower) images of P1 films spin-cast from CHCl₃ then annealed at 120 °C for 30 min (a, d), 240 °C for 2 h (b, e), and 300 °C for 30 min (c, f, respectively).



Figure 3.15. SEM (top) and AFM (lower) images of P1 films on HMDS treated SiO_2 cast from THF.

120 °C 240 °C (30 min.) 240 °C (2 hr.) 300 °C


Figure 3.16. SEM (top) and AFM (lower) images of P1 films on untreated SiO_2 cast from CHCl₃.



Figure 3.17. SEM (top) and AFM (lower) images of P1 films on untreated SiO_2 cast from TCB.



Figure 3.18. SEM (top) and AFM (lower) images of P1 films on untreated SiO_2 cast from THF.



Figure 3.19. SEM (upper) and AFM (middle) images of **P2** films on HMDS treated substrates annealed for 30 min at 120 °C (**a**, **d**), 180 °C (**b**, **e**), and 240 °C (**c**, **f**) as well as polarized (90°) optical micrographs (lower) of **P2** on glass imaged at 120 °C (**g**) in the crystalline phase, 180 °C (**h**) as a liquid-crystal, and at 220 °C during the melting transition (**i**).



Figure 3.20. SEM (top) and AFM (lower) images of P2 films on untreated SiO_2 cast from DCB.

appearing in the film when annealed at 180 °C. Only islands of polymer are present once the sample is annealed at 240 °C (Figure 3.19c, f). Cross-polarized hot-stage optical microscopy of **P2** films cast on untreated glass reveal a crystalline phase at temperatures below a liquid crystalline transition at 127 °C (Figure 3.19g), the liquid crystalline phase (Figure 3.19h), and finally the melting transition of the **P2** film at 196 °C (Figure 3.19i).

3.3.9 Transistor fabrication and optimization

Thin film transistors were fabricated with spin-cast and drop-cast films of polymers P1 and P2 as the semiconducting component. FETs fabricated with either material were initially tested under vacuum. Homopolymer P1 exhibits exclusively n-type transport in this geometry, while copolymer P2 exhibits only p-type behavior under vacuum (Figure 3.21). When the devices are measured under air, the homopolymer does not exhibit FET activity and the copolymer accumulation regime p-channel FET behavior is unchanged. Semiconductors cast onto HMDS treated substrates exhibit superior performance, while those on untreated SiO₂ substrates exhibit diminished performance in the case of P2 or negligible FET activity in the case of P1.

Polymer film microstructure was adjusted to optimize device performance by casting from various solvents (CHCl₃, THF, TCB or DCB), employing different substrate functionalizations and thermal annealing protocols to enhance crystallinity. Annealing temperatures were optimized from the thermal transitions observed in the DSC. Homopolymer **P1** was spin-cast from CHCl₃, THF, and TCB onto both HMDS treated and untreated substrates. Films cast on the hydrophilic untreated substrates do not exhibit FET activity, while those cast onto hydrophobic substrates exhibit prototypical n-channel FET behavior (Table 3.3).



Figure 3.21. FET transfer (**a**) and output (**b**) plots of **P1** spin-cast onto an HMDS treated substrate and annealed at 240 °C for 2 h; and **P2** (**c** and **d**, respectively) spin-cast onto an HMDS treated substrate and annealed at 180 °C for 30 min.

Table 3.3. FET performance measured under vacuum for homopolymer **P1** films spin-cast or drop-cast (DC) from the indicated solvents onto HMDS treated substrates. Standard deviations are given in parentheses.

	chloroform			tetrahydrofuran			1,2,4-trichlorobenzene		
Anneal ^a (°C)	μ_{e} (cm ² V ⁻¹ s ⁻¹)	$V_{T}(V)$	I _{on:off}	$(\mathrm{cm}^{2}\mathrm{V}^{-1}\mathrm{s}^{-1})$	$V_{T}(V)$	I _{on:off}	$\frac{\mu_{e}}{(cm^{2}V^{-1}s^{-1})}$	$V_{T}(V)$	I _{on:off}
120	1.7 (1) x 10 ⁻³	77 (6)	4 (4) x 10 ⁶	5 (2) x 10 ⁻⁴	87 (6)	2 (1) x 10 ⁶	5 (2) x 10 ⁻⁴	90 (11)	2 (2) x 10 ⁴
240	7.8 (8) x 10 ⁻³	80 (5)	4 (1) x 10 ⁷	8 (2) x 10 ⁻⁴	80 (11)	8 (5) x 10 ⁶	5.8 (2) x 10 ⁻³	88 (8)	2 (1) x 10 ⁷
240 (2 h)	1.1 (3) x 10 ⁻²	75 (4)	2 (2) x 10 ⁷	6 (1) x 10 ⁻³	71 (3)	2 (2) x 10 ⁷	7.2 (1) x 10 ⁻³	78 (1)	2 (1) x 10 ⁷
300	1.8 (1) x 10 ⁻⁴	95 (2)	2 (1) x 10 ³	8 (2) x 10 ⁻⁵	93 (1)	3 (1) x 10 ⁵	1.7 (4) x 10 ⁻⁵	115 (2)	5 (1) x 10 ¹
DC	3.2 (5) x 10 ⁻³	70 (7)	2 (1) x 10 ⁷				6 (3) x 10 ⁻⁴	60 (32)	2 (3) x 10 ⁶
21-1-1	1 1 0	20							

^aFilms annealed for 30 min unless otherwise noted.

Film electron mobilities (μ_e) after the initial drying at 120 °C vary from ~5 x 10⁻⁴ cm²V⁻¹s⁻¹ for films from TCB and THF to 2 x 10⁻³ cm²V⁻¹s⁻¹ for films from CHCl₃. Upon annealing, μ_e and I_{on:off} increase, with the highest μ_e of 0.011 ± 0.003 cm²V⁻¹s⁻¹ observed in films cast from CHCl₃ and annealed at 240 °C for 2 h (I_{on:off} = 2 x 10⁷, V_T = +75 V). Device performance decreases in all samples when films are annealed at 300 °C. Drop-cast films exhibit performance similar to that of spin-cast films with mobilities of 0.003 cm²V⁻¹s⁻¹ when cast from CHCl₃ and annealed at 120 °C.

Since P2 only has adequate solubility in DCB, annealing and substrate treatment were the two variables that were varied during device optimization. All films of P2 cast on hydrophobic HMDS treated substrates exhibit hole mobilities two orders of magnitude greater than those on untreated hydrophilic SiO₂ (Table 3.4). When samples are annealed at 180 °C, the mobility increases on both substrates up to 0.008 cm²V⁻¹s⁻¹ (I_{on:off} = 10⁷, V_T = -12 V) for films on HMDS treated substrates. Upon annealing at 240 °C however, the response of devices on hydrophobic substrates decreases significantly.

3.3.10 Crystal Structure

Molecule **19** was designed to provide insight into the intermolecular packing of this new class of **BTI** based materials via a single-crystal structure determination. Crystals were obtained by slow sublimation under reduced pressure and the crystal structure was determined by x-ray diffraction. Compound **19** crystallizes in a trigonal lattice belonging to the *R-3* space group. The molecules are organized in a pseudo-micellular motif, with alkyl tails in the center and the conjugated cores pointing outwards (Figure 3.22). The conjugated cores exhibit excellent π - π stacking with the closest C···C distance in the direction of π - π stacking being 3.43 Å (C7-C15). The *n*-hexyl tails

Table 3.4. FET performance values measured under vacuum and under air for copolymer **P2** films spin-cast or drop-cast (DC) from 1,2-dichlorobenzene onto either HMDS treated or untreated SiO_2 substrates. Standard deviations are given in parentheses.

	HM					SiO ₂	
	Anneal ^a (°C)	μ_h (cm ² V ⁻¹ s ⁻¹)	$V_{T}(V)$	I _{on:off}	$(cm^2V^{-1}s^{-1})$	$V_{T}(V)$	I _{on:off}
	120	6 (1) x 10 ⁻³	-28 (2)	9 (8) x 10 ⁶	4 (1) x 10 ⁻⁶	-34 (4)	1 (1) x 10 ⁴
Vacuum	180	8 (2) x 10 ⁻³	-12 (7)	$2(3) \times 10^7$	2 (1) x 10 ⁻⁵	-11 (1)	3 (4) x 10 ⁴
	240	3 (2) x 10 ⁻⁵	-70 (15)	7 (3) x 10^3	9 (1) x 10 ⁻⁶	-4 (5)	$5(3) \times 10^3$
	DC	4 (3) x 10 ⁻³	-27 (13)	6 (5) x 10 ⁶	2 (1) x 10 ⁻⁵	-18 (2)	7 (6) x 10 ⁴
1	120	4 (1) x 10 ⁻³	-40 (6)	1 (1) x 10 ⁷	3 (2) x 10 ⁻⁶	-33 (7)	2 (1) x 10 ⁴
Air ^b	180	6 (1) x 10 ⁻³	-18 (4)	1 (2) x 10 ⁷	2 (1) x 10 ⁻⁵	-26 (17)	3 (3) x 10 ⁴
	240	7 (1) x 10 ⁻⁶	-82 (4)	$3(2) \times 10^3$	6 (1) x 10 ⁻⁶	-1 (3)	6 (1) x 10 ⁴
	DC	2 (1) x 10 ⁻³	-40 (6)	8 (1) x 10 ⁶	2 (1) x 10 ⁻⁵	-34 (21)	7 (3) x 10 ⁴
					. h= .		

^aFilms annealed for 30 min unless otherwise noted. ^bDevices measured after 1 week in air.



Figure 3.22. Crystal structure of the π -stacked 19 tetramer (**a**, **b**) and views along the *c* axis (**c**, **d**) displayed without hydrogen atoms and with only one *n*-hexyl group orientation for clarity. Carbon atoms are shown in gray, oxygen in red, sulfur in yellow, and nitrogen in blue.

are highly disordered beyond the third carbon atom (C21). Ring-strain in the planar 7-membered ring is compensated by a slight increase in all internal bond angles to result in minima l4.6 ° outof-plane imide torsion (C9-C10:C8-C11). The most significant bond angle enlargement of \sim 7.4 ° is centered at the imide nitrogen atom (C9-N1-C10) at an angle of 132.4 ° from a nominal angle of \sim 125 °. Other important metrical parameters are summarized in Tables 3.5 and 3.6.

3.4 Discussion

3.4.1 Molecular modeling and crystal packing

Knowledge of the molecular geometry as well as the frontier molecular orbital spacial characteristics and energetics is key to understanding charge transport efficiency, majority carrier type, and charge trapping in organic semiconductor-based devices. Moreover, the molecular geometry determines the extent of π -conjugation and crystal packing, both of which directly impact intra- and inter-chain charge transport. Before synthesis of any BTI polymers, these properties were evaluated for monomeric model structures using quantum chemical modeling, electrochemistry, optical spectroscopy, and X-ray diffraction single-crystal structure determination. The electronic structure and molecular geometry of several candidate structures was first investigated computationally using density functional theory (DFT) to determine if their properties were consistent with those required for efficient charge transport. This pre-synthesis theoretical study was undertaken to suggest the design of this new class of polymer semiconductors by confirming favorable molecular properties and evaluating the merit of the design choices. Since FET performance can also be influenced by phenomena that cannot be efficiently modeled at present (i.e., crystal packing, grain-boundary effects, dielectricsemiconductor interfacial interactions, and long-range film morphology), this methodology

focuses on those intrinsic factors required for efficient, long-range charge transport. The approach should be viewed as a means to validate favorable properties of candidate materials, evaluate structural modification options, and eliminate structures/options that have properties inconsistent with efficient charge transport. Such undesirable properties include non-planar intramonomer geometry, significant inter-monomer dihedral angles, highly localized frontier orbitals, and intrusion of functional groups in the area of π - π stacking. This novel design approach is fundamentally different from previous computational studies of organic semiconductors where materials were evaluated to understand charge transport behavior at a mechanistic level, post-synthesis.^{45,46}

Five key properties of these **BTI** materials were assessed: a) planarity of the π -conjugated portion of the monomer, b) inter-monomer dihedral angle, c) steric effects of the functional groups, d) frontier molecular orbital delocalization, and e) frontier orbital energies. Geometry optimizations performed using DFT-level theory on a **BTI** trimer and a **BTI**-bithiophene-**BTI** co-oligomer reveal negligible π -core and inter-core torsion (Figure 3). Such intra-/inter-monomer planarity is important since it allows efficient π - π stacking and charge delocalization/stabilization along the π -conjugated polymer backbone. The equilibrium structures also reveal that the substituent on the imide N atoms is electronically and spatially isolated from the π -orbitals. Separation from the frontier orbitals minimizes the electronic energetic effects of varying the imide substituent, limiting their influence on crystal packing and solubility. The spatial separation suggests a tolerance for sterically-demanding functional groups without spatial intrusion into the π - π stacking region.

The molecular orbital electron density plots reveal that the HOMO and LUMO are completely delocalized on the **BTI** trimer and co-oligomer (Figures 3.3b and 3.3c, respectively), indicating a propensity for both hole and electron stabilization. Molecular orbital energy levels were computed to predict the majority charge carrier type. The co-oligomer HOMO energy of -5.9 eV is consistent with that of polymers^{15, 18, 19} exhibiting air-stable p-channel FET operation while the LUMO lies somewhat higher than those of known n-channel materials.^{25, 45, 48} In contrast, the -3.5 eV LUMO energy of the **BTI** trimer is within the energetic regime for n-channel FET materials,^{16, 25, 45, 46, 48} while the HOMO lies below that of known p-channel materials. This energy level analysis suggests that **BTI** homopolymers should exhibit n-channel FET activity, while copolymers with bithiophene are better suited for p-channel behavior. Finally, the dipole moments of the **M1** and **M2** monomers are calculated to be 2.27 Debye and 3.78 Debye, respectively. For monomers aligned anti-parallel in the crystal lattice (as in the case of **19**), the magnitude of the dipole moment can be used to estimate the gas-phase dipole-dipole interaction

energy using eq. 1.49

$$V = \frac{\bar{\mu}_1 \bar{\mu}_2}{4\pi\varepsilon_0 r^3} \tag{1}$$

Here μ_1 and μ_2 are the dipole moment vectors of the monomers, ε_0 is the vacuum permittivity, and the distance between the dipoles *r* is taken to be 3.43 Å, the cofacial stacking distance observed in the crystal structure of **19**. The dipole-dipole interaction is estimated to be -1.84 kcal/mol for **M1**, which schould stabilize the formation anti-parallel dimers. The magnitude of this stabilization is sufficient to direct the crystal packing in **P1** but still allow solubilization under appropriate conditions. The larger dipole moment of **M2** results in a significantly stronger -5.11 kcal/mol dimer interaction energy, suggesting enhanced **P2** aggregation over **P1**. This significant increase in aggregation affinity is in accord with the diminished solubility and, hence, the lower average degree of polymerization achieved for **P2** vs. **P1**.

Since it is difficult to obtain precise structural information about this new class of materials from polymeric samples alone, model molecular compound 19 was also synthesized. This molecule is similar to M2 (a monomer for P2) except for the *n*-hexyl solubilizing group instead of the 2-branched alkyl moiety in M2 and P2. The single crystal X-ray structure of this compound (Figure 3.22) reveals a highly planar conjugated core with negligible torsion of the imide ring of 4.3° (C8-C7-C12-C11). The molecules assemble in tetramers packed antiparallel in a face-to-face fashion with a short π - π distance of 3.43 Å. These π -stacked tetramers organize into larger micelle-like formations with the lipophilic solubilizing groups pointed inwards, surrounded by the π -stacked clusters. The recent discovery of a similar secondary structure in another π -stacked semiconductor, rubrene, has sparked interest in potential uses for such unique small clusters of organic semiconductors.^{50, 51} Although this molecular crystal secondary structure is intriguing, it is unlikely that the target polymers can organize into an analogous micellular structure due to the order induced by the longer macromolecular chain length. Nonetheless, the short-range structural information obtained from this model compound is relevant since the important dipolar, steric, and π - π stacking forces that determine monomer-monomer packing are reasonably conserved in the polymers.

There is also significant free volume in the crystal lattice of **19** for conformational mobility of the alkyl solubilizing groups as evidenced by the observed disorder of the *n*-hexyl substituent beyond the third carbon atom (C21). As predicted, the intermolecular antiparallel imide orientation forces the solubilizing groups to opposite sides of π -stacked polymer chains, minimizing steric crowding from adjacent chains, which could impede intermolecular core stacking. In combination with computational results on branched alkanes, these findings suggest that it should be possible to maintain optimal polymer chain geometry and favorable π - π stacking even when sterically-demanding solubilizing groups are introduced. Importantly, these poly(**BTI**s) should exhibit significant solubilizing group tolerance while concurrently optimizing the synthesis, solubility, solution rheology, crystallinity, and device performance.

Optical absorption spectroscopic data for polymers P1 and P2 as well as for monomers M1 and M2 reveal informative optical properties when thiophenes are incorporated into the BTI framework (Figure 3.6 and Table 3.1). Absorbtion maxima (λ_{max}) in solution exhibit a bathochromic shift as conjugation length is increased from M1 to M2 to the corresponding homo-/co-polymers, with vibronic features significantly more pronounced in the polymers. There are minimal differences between the solution and thin-film absorbtion spectra of either M1 or P1, while the compounds with electron-rich unfunctionalized thiophenes exhibit significant bathochromic shifts of 23 nm for M2, and 98 nm for P2. This suggests that the excited states of the thiophene-substituted molecule and copolymer are better stabilized in the solid state than in solution, possibly by bithiophene-bithiopheneimide charge transfer.^{52, 53} The 9 nm hypsochromic shift observed in **P1** films indicates slight destabilization of S_1 in the solid state, likely a result of the highly antiparallel ground state dipole arrangement in the crystal lattice and absence of donor-acceptor stabilized charge separation. Finally, enhanced bathochromic vibronic features in the P2 films reflect the observed high degree of structural order of this material in the solid state.52,54

The redox properties of the present polymers were studied by cyclic voltammetry to investigate frontier MO energetics. Reversible reduction events are observed for all materials in

this study, with the polymers exhibiting multiple reversible reductions (Figure 3.7 and Table 3.2). P1 exhibits the most pronounced reduction events with half-wave potentials at -1.11 V and -1.32 V vs SCE, while the reductions for copolymer P2 occur at -1.34 V and -1.54 V. Previous work has shown that materials with reduction potentials greater than or equal to ~ -1.2 V vs SCE can exhibit efficient electron transport while those that are more difficult to reduce tend not to be active in conventional top-contact n-channel FETs.^{25, 37} It has been postulated that this phenomena is caused by trapping of mobile electrons by dielectric surface hydroxyl groups, which is avoided by decreasing the LUMO energy to provide sufficient charge carrier stabilization. Recent results also suggest that the reduction potential of P1, -1.11 V, is likely insufficient for n-channel FET operation in air.⁵⁵ Conversely, oxidation of copolymer P2 is 0.23 V easier at +1.48 V than is that of the homopolymer at +1.71 V. Oxidation potentials in this range are typical for polymers such as F8T2 ($E_{ox}^{1/2} = +1.4$ V) used in air-stable p-channel FETs.¹, ^{15, 18, 19, 56} These electrochemical data and the favorable crystal geometry suggest that homopolymer **P1** should exhibit electron transport under inert atmosphere while the copolymer **P2** is better suited for hole transport. The suppositions are found to be correct.

3.4.2 Polymer thin-film morphology and field-effect transistor device optimization

The FET performance of the polymers synthesized in this study is strongly correlated with the surface chemical functionalization and energy of the gate dielectric/substrate that they are cast onto. Thus, **P1** films on hydrophobic HMDS treated substrates exhibit outstanding n-channel FET performance, while those cast on untreated hydrophilic SiO_2 do not exhibit FET activity. Similarly, copolymer **P2** exhibits enhanced p-channel FET performance when cast on HMDS treated versus untreated substrates. To understand this variation in FET performance and the

Films of homopolymer **P1** were cast from three different solvents (CHCl₃, THF, and TCB) and then annealed at various temperatures (120 °C, 240 °C, and 300 °C) to evaluate the effect on surface morphology, roughness, film crystallinity, and most importantly FET response. As seen in Table 3.3 and Figure 3.23, n-channel FET performance after the 120 °C annealing process is a function of the casting solvent, with films from CHCl₃ solutions having the highest μ_e (1.7 x 10⁻³ cm²V⁻¹s⁻¹) and films from THF and TCB having slightly lower μ_e (5 x 10⁻⁴ cm²V⁻¹s⁻¹) and I_{on:off}, with a higher V_T. Interestingly, n-channel FET performance becomes less dependent on casting

solvent when films are annealed at 240 °C for 2 h. Under these conditions μ_e of all films

converges to ~10⁻² cm²V⁻¹s⁻¹ with V_T values of ~75 V and $I_{on:off} > 10^7$.

are used to understand polymer film surface and microstructure.

Since crystallinity is an important parameter in FET performance, WAXRD θ -2 θ diffraction data were used to evaluate film crystallinity in all samples. The resulting diffraction patterns indicate that films of **P1** cast onto untreated hydrophilic substrates have poor crystallinity even after annealing, with only broad first- and second-order Bragg peaks (Figures 3.9 and 3.10). This explains the lack of FET activity in these films since crystallinity is typically a critical property for efficient charge transport.^{36, 57,59} In marked contrast, films cast onto HMDS treated substrates exhibit pronounced diffraction features that generally increase with annealing temperature and duration. A single family of Bragg peaks (up to fifth-order) is observed in all samples revealing an extreme degree of crystallinity for polymer films (Figure 3.8).^{57, 58} Laue fringes at $2\theta < 4^{\circ}$ observed in some θ -2 θ patterns of films cast from TBC evidence very smooth and highly uniform films.^{60, 61}



Figure 3.23. Plots of measured FET charge carrier mobility versus annealing temperature for P1 films on HMDS treated substrates measured under vacuum for the indicated spin-coating solvents (a) and P2 films on untreated or HMDS treated substrates measured under vacuum and air (b).

The increase in crystallinity corresponds well with the n-channel FET performance enhancement observed as the film samples are annealed, with the exception of those annealed ≥ 300 °C. Diminished FET response is observed in these samples even though the crystallinity continues to increase. This fall in performance is not a result of chemical decomposition since the materials are stable to ~400 °C as determined by TGA (Figure 3.5a), but rather can be explained by changes in the film morphology as revealed in AFM and SEM images.

Although WAXRD is a powerful tool that probes overall film crystallinity, other crucial properties such as film uniformity and crystallite connectivity affect transistor performance. AFM and SEM images show that films cast from the low-boiling solvents exhibit irregular morphologies characterized by the circular voids as observed in Figure 3.14 for CHCl₃-cast films and in Figure 3.15 for THF-cast films. These irregularities disappear when the samples are annealed at 240 °C and 300 °C, resulting in more continuous films. For example, the rms roughness of CHCl₃-cast films decreases from 17 nm when annealed at 120 °C, to a smoother and more continuous polycrystalline surface having 2.6 nm rms roughness when annealed at 240 °C for 2 h. However, the surface rms roughness of all samples increases by 2 nm to 12 nm when the film annealing is performed at 300 °C, and imaging shows the emergence of individual crystallites. This observation suggests that the polymer begins to undergo aggregation into larger, discrete domains that are not well interconnected.⁶² Such a decrease in crystallite connectivity would impede charge hopping, resulting in lower observed FET mobility.⁶³

A unique feature discovered in **P1** films cast from TCB is terracing (Figure 3.13), a phenomenon typically observed in highly ordered polymers, such as poly(ethylene terephthalate),⁶⁴ poly(2-(perfluorooctyl)ethyl acrylate),⁶⁵ block copolymers,^{66, 67} and

polyhydroxyalkanoates.⁶⁸ It is rarely observed in organic semiconducting materials and then only in highly-crystalline molecular semiconductors.⁶⁹⁻⁷¹ Recently, terracing was observed for the first time in a semiconducting polymer by annealing p-channel poly(2,5-bis(3-hexadecylthiophene-2yl)thieno[3,2-b]thiophene) in the liquid crystalline phase, revealing a step height matching the WAXRD-derived d-spacing.²² AMF images of annealed **P1** films cast from TCB exhibit a highly-terraced surface having step heights of 2.50 nm, which can be accurately determined from the trimodal distribution of the AFM height histogram (Figure 3.13c). This height is in good agreement with the 25.2 Å d-spacing determined by WAXRD, which corresponds to the height of a polymer layer tilted at an angle of ~69.0° relative to the substrate plane (assuming negligible side chain interdigitation). This rare terraced structure emphasizes the exceptional degree of crystallinity that **P1** films can attain.

Copolymer **P2** exhibits air-stable p-channel FET performance that is a marked function of substrate surface energy and annealing temperature. Annealing temperatures of 120 °C, 180 °C, and 240 °C were chosen to correspond to the phase transitions observed in the DSC traces (Figure 3.5). FET performance on HMDS treated substrates initially increases from $\mu_h = 6 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ when annealed at 120 °C to 8 x 10⁻³ cm² V⁻¹ s⁻¹ when annealed at 180 °C, before declining precipitously for 240 °C annealing (Table 3.4 and Figure 3.23). The performance of devices fabricated on untreated hydrophilic substrates also exhibits a similar annealing trend although hole mobilities are two orders of magnitude lower. These p-channel FETs were originally characterized under high-vacuum and then again after exposure to air for one week, exhibiting no change in I_{on:off}, a 5 V - 10 V increase in V_T, and only a 20% decrease in hole mobility.

As in the case of the homopolymer, WAXRD reveals that **P2** films deposited on HMDS treated substrates have significantly greater crystallinity than those on untreated SiO₂. The reflection intensities increase and peak widths decrease when **P2** films on hydrophobic substrates are annealed at 180 °C and 240 °C, while and those on untreated substrates exhibit only moderately increased intensities. These observations demonstrate the enhanced crystallinity achieved with annealing and correlate with greater hole mobilities for films annealed at 180 °C. Interestingly, although the WAXRD of **P2** films on hydrophobic substrates annealed at 300 °C indicates very substantial crystallinity, the μ_h in these films decreases markedly.

Surface characterization with AFM and SEM provides additional understanding of the observed performance trends of **P2**-based FETs. Films cast on untreated SiO₂ substrates have an initial rms roughness of 1.2 nm that increases only slightly to 1.4 nm for annealing at 240 °C. Correspondingly, device performance and WAXRD diffraction patterns of films on these bare SiO₂ samples exhibit only modest changes with annealing. In contrast, the surface of **P2** on HMDS treated substrates changes dramatically from a continuous film having 4 nm surface rms roughness when annealed at 120 °C to a largely delaminated film for annealing at 240 °C. This film dewetting is observed in SEM images as polymer droplets (Figure 3.19f) and in the AFM images as increased roughness and the formation of the large islands in Figure 3.19c. Films annealed at 180 °C exhibit very smooth surface having an rms roughness of 1.3 nm (excluding voids), although ~1 µm voids revealed by both AFM and SEM imaging indicate initial dewetting. Cross-polarized optical microscopy of **P2** films cast on untreated glass reveals that at 180 °C (Figure 3.19h), **P2** has undergone a liquid crystalline transition at 127 °C but has not yet melted. Annealing above the 196 °C **P2** melting temperature (see image of the melting transition,

Figure 3.19i) is accompanied by complete dewetting of films on hydrophobic surfaces, resulting in significant diminution in p-channel FET performance for the 240 °C anneal.⁷²

3.5 Conclusions

This work demonstrates a novel approach to organic semiconductor development, where presynthesis computational modeling guides material design from initial conception to refinement of the final semiconductor structure. Through computational understanding of molecular geometry as well as frontier orbital symmetry and energetics, the novel building block 2,2'bithiophene-3,3'-dicarboximide is identified. Properties predicted by this modeling are confirmed by the crystal structure of the model molecule 19, which reveals π -core planarity, antiparallel **BTI** packing, a short cofacial π - π distance of 3.43 Å, and a favorable solubilizing group orientation. Upon the synthesis of a series of 10 homo-/co-polymers, two materials were identified as having favorable solubility and solution rheology in common organic solvents. Polymer films exhibit extremely high crystallinity with P1 displaying exceptional n-channel FET performance ($\mu_e = 0.011 \pm 0.003 \text{ cm}^2 V^{-1} \text{s}^{-1}$, $I_{\text{on:off}} > 10^7$) and P2, air-stable p-channel FET operation ($\mu_h = 0.008 \pm 0.002 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, $I_{\text{on:off}} = 10^7$). While the behavior of many highperformance semiconductors is sensitive to deposition conditions, BTI polymer films exhibit FET performance predominately independent of film casting conditions. The extraordinary degree of thin-film order in BTI-based materials is also revealed by topographical terracing of the annealed **P1** films, a phenomenon observed only once before for a polymer semiconductor. The excellent figures-of-merit of this new class of materials reveals the efficacy of the present novel and general computationally-aided materials design strategy, employed here for the first time in organic electronic materials.

3.6 Single crystal X-ray structure determination of N-hexyl-2,2':5',2'':5'',2'''-quaterthiophene-4',3''-dicarboximide

Data Collection (for compound 19)

A orange needle crystal of $C_{24}H_{12}NO_2S_4$ having approximate dimensions of 0.780 x 0.116 x 0.096 mm was mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a CCD area detector with graphite monochromated MoK\ α radiation. Cell constants and an orientation matrix for data collection corresponded to a Trigonal cell with dimensions:

a = 40.173(2) Å
$$\alpha = 9\tilde{0}^{\circ}$$

b = 40.173(2) Å $\beta = 90^{\circ}$
c = 7.1602(6) Å $\gamma = 120^{\circ}$
V = 10007.4(12) Å³

For Z = 18 and F.W. = 474.59, the calculated density is 1.417 g/cm³. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

R-3

The data were collected at a temperature of 153(2) K with a theta range for data collection of 1.01 to 28.91 °. Data were collected in 0.3° oscillations with 20 second exposures. The crystal-to-detector distance was 50.00 mm with the detector at the 28° swing position.

Data Reduction

Of the 31579 reflections which were collected, 5554 were unique (Rint = 0.1645). Data were collected using Bruker SMART detector and processed using SAINT-NT from Bruker. The linear absorption coefficient, mu, for MoK\ α radiation is 0.470 mm⁻¹. An analytical absorption

correction was applied. Minimum and maximum transmission factors were: 0.8314 and 0.9885, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods¹ and expanded using Fourier techniques². The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included in "idealized" positions, but not refined. The final cycle of full-matrix least-squares refinement³ on F2 was based on 5554 reflections, 5 restraints, and 278 variable parameters and converged (largest parameter shift was 0.000 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.0692$$

$$wR^{2} = \{\Sigma[w(F_{o}^{2}-F_{c}^{2})^{2}]/\Sigma[w(F_{o}^{2})^{2}]\}^{1/2} = 0.1971$$

The weighting Scheme 3.was calc.

calc w=1/[
$$\sigma^2(F_o^2)$$
+(0.0597P)²+13.1648P] where P=(F_o^2 +2 F_c^2)/3

The standard deviation of an observation of unit weight⁴ was 1.048. The weighting Scheme 3.was based on counting statistics and included a factor to downweight the intense reflections. Plots of Σ w ($|F_o| - |F_c|$)² versus $|F_o|$, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.575 and -0.724 e⁻/Å³, respectively. Neutral atom scattering factors were taken from Cromer and Waber⁵. Anomalous dispersion effects were included in Fcalc⁶; the values for Df⁴ and Df⁴ were those of Creagh and McAuley⁷. The values for the mass attenuation coefficients are those of Creagh and Hubbell⁸. All calculations were performed using the Bruker SHELXTL⁹ crystallographic software package.

Table 3.5. (Crystal c	lata and	structure	refinement	for 19 .
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Identification code	ss35face					
Empirical formula	C24 H12 N O2 S4					
Formula weight	474.59					
Temperature	153(2) K					
Wavelength	0.71073 A					
Crystal system, space group	Trigonal, R-3					
Unit cell dimensions						
	a = 40.173(2) A alpha = 90 deg.					
	b = 40.173(2) A beta = 90 deg.					
	c = 7.1602(6) A gamma = 120 deg.					
Volume	10007.4(12) A^3					
Z, Calculated density	18, 1.417 Mg/m^3					
Absorption coefficient	0.449 mm^-1					
F(000)	4374					
Crystal size	0.780 x 0.116 x 0.096 mm					
Theta range for data collection	1.01 to 28.91 deg.					
Limiting indices	-53<=h<=54, -51<=k<=51, -9<=l<=9					
Reflections collected / unique	31579 / 5554 [R(int) = 0.1233]					
Completeness to theta $= 28.91$	94.6 %					
Refinement method	Full-matrix least-squares on FA2					
Data / restraints / parameters	5554 / 5 / 278					
Goodness-of-fit on F^2	1.069					
Final R indices [I>2sigma(I)]	R1 = 0.0692, wR2 = 0.1971					
R indices (all data)	R1 = 0.0856, wR2 = 0.2132					
Largest diff. peak and hole	1.575 and -0.724 e.A^-3					



Figure 3.24. X-ray crystal structure of 19 shown without hydrogen atoms and only one hexyl group orientation.

	X	У	Z	U(eq)
C(1)	7385(1)	-97(1)	12536(4)	25(1)
C(2)	7154(1)	46(1)	12089(4)	26(1)
C(3)	7243(1)	245(1)	10307(4)	21(1)
C(4)	7564(1)	239(1)	9490(4)	20(1)
C(5)	7749(1)	412(1)	7730(4)	21(1)
C(6)	8047(1)	406(1)	6850(4)	21(1)
C(7)	7932(1)	778(1)	4720(4)	19(1)
C(8)	8158(1)	615(1)	5134(4)	20(1)
C(9)	8468(1)	612(1)	4055(4)	25(1)
C(10)	8534(1)	1053(1)	1298(4)	23(1)
C(11)	8193(1)	1094(1)	1602(4)	20(1)
C(12)	7942(1)	986(1)	3088(4)	19(1)
C(13)	8103(1)	1284(1)	188(4)	21(1)
C(14)	7788(1)	1318(1)	580(4)	19(1)
C(15)	7615(1)	1491(1)	-543(4)	20(1)
C(16)	7293(1)	1523(1)	-125(4)	25(1)
C(17)	7211(1)	1717(1)	-1563(5)	28(1)
C(18)	7461(1)	1824(1)	-3026(4)	25(1)
C(19)	8984(1)	828(1)	1789(5)	30(1)
C(20)	8877(1)	520(2)	306(6)	55(1)
C(21)	9233(2)	531(3)	-488(9)	106(3)
C(22)	9323(5)	616(8)	-2220(20)	243(7)
C(23)	9655(5)	566(8)	-2950(20)	243(7)
C(24)	9833(5)	822(7)	-4690(20)	243(7)
C(25)	9413(14)	339(18)	630(50)	243(7)
C(26)	9631(16)	220(20)	-770(70)	243(7)
C(27)	10152(16)	354(15)	180(100)	243(7)
N(1)	8643(1)	844(1)	2480(3)	22(1)
O(1)	8588(1)	403(1)	4595(4)	40(1)
O(2)	8733(1)	1209(1)	-72(3)	37(1)
S(1)	7728(1)	1(1)	10890(1)	26(1)
S(2)	7594(1)	675(1)	6444(1)	22(1)
S(3)	7601(1)	1122(1)	2749(1)	22(1)
S(4)	7803(1)	1694(1)	-2695(1)	24(1)

Table 3.6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A² x 10^3) for **19**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Chapter Four

General Trends in the Variable Temperature Behavior of n-Channel, p-Channel, and Ambipolar Organic Field Effect Transistors

4.1 Introduction

Advances in high-performance organic electronic devices have primarily been made through discovery of new materials and the development of novel processing/fabrication techniques. Many applications enabled by these advances utilizing organic field effect transistors (FETs) are organic light-emitting diode displays,¹⁻⁴ organic TFT-driven active-matrix display backplanes,⁵⁻⁷ ring-oscillators,⁸ and inverters.⁹⁻¹¹ Even though these new organic devices are driven by FETs, the community is still searching for a comprehensive understanding of charge transport in FETs. Understanding the charge transport mechanism involves fundamental questions of long-range interfacial charge transport in organics and can enable enlightened design/optimization of materials and devices.

The importance understanding charge transport phenomena in FETs has been highlighted by recent discoveries. Separate work by de Leeuw, et. al¹² and Katz, et. al¹³ suggest that the ambient instability of mobile electrons in FETs was a result of carrier trapping by H₂O and O₂. These ideas were recently employed to develop air-sTable 4.n-channel FET semiconductors not relying on an O₂ barrier.^{14, 15} Further work revealed that rigorous exclusion of surface-born trapping species (i.e. hydroxyl groups) can enhance n-channel FET performance for p-type and n-type semiconductors under inert atmosphere by eliminating deep electron traps with densities > 10¹³ cm⁻². While these energetically deep and very-high density charge traps are critical to overcome for efficient FET operation, it has been postulated that shallow, lower-density (~10¹⁰ cm⁻² to ~10¹² cm⁻²) traps limit the effective FET carrier mobility (μ_{eff}) for both p- and n-channel FET operation.¹⁶⁻²¹

The variable temperature behavior of FETs has been used to study the charge transport mechanism and generally reveals temperature activated charge transport, with activation energies (E_A) on the order of 10 - 100 meV. The most widely-accepted model for charge transport in organic semiconductors is multiple trapping and release (MTR).^{20, 22} The model proposes that the free carrier mobility (μ_0) is diminished by recurrent charge carrier trapping and thermal release from shallow trap states below the conduction band edge to give the observed μ_{eff} . Since μ_{eff} is dominated by this trapping and release behavior, the density of these traps (N_{T0} , cm⁻²) and their energy distribution in the band tail determines the temperature dependence of μ_{eff} . For simplicity, when modeling μ_{eff} , a discrete trap state is typically assumed at energy E_T , which captures electrons according to Fermi-Dirac statistics. The density of trapped charge (N_T) in units of cm⁻² is therefore given by Eq. 1 where E_F is the Fermi energy.^{16, 17, 20, 22}

$$N_T = N_{T0} \exp\left(\frac{-(E_T - E_F)}{kT}\right) \tag{1}$$

Using this single energy level trap model, μ_{eff} is given by Eq. 2, where the activation energy E_A is the energy difference between the trap state and the conduction band edge (E_C) .^{16-20, 22-24}

$$\mu_{eff} = \mu_0 \exp\left(\frac{-E_A}{kT}\right) \tag{2}$$

This interpretation of MTR predicts Arrhenius behavior for μ_{eff} and has been used to model temperature dependence of p-channel and n-channel FETs.¹¹⁻¹³

The variable temperature behavior of p-channel semiconductors generally reveals temperature activated μ_{eff} with behavior consistent with the Arrhenius relationship of Eq. 2 (Table 4.1). Pentacene-based FETs having $\mu_{eff} \approx 0.3 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ typically exhibit $E_A = 39 \pm 3 \text{ meV}$, although one report reveals that devices with exceptionally high-room temperature ($\mu_{eff} = 1.5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) exhibit temperature independent behavior.^{21, 25, 26} Sexithiophene-based (6T) p-channel FETs exhibit similar activated behavior with $E_A \approx 100 - 220$ meV for devices with $\mu_{eff} \approx 0.02 - 0.15$ cm²V⁻¹s⁻¹.^{20, 22, 27} In separate work, the E_A of poly-3-hexylthiohene-based FETs (P3HT) was found to be 85 meV for devices with $\mu_{eff} = 0.092$ cm²V⁻¹s⁻¹ and 29 meV for $\mu_{eff} = 0.7$ cm²V⁻¹s⁻¹.¹⁸ Several studies noted negative threshold voltage shifts with decreasing temperature and suggest that this may be a result of charge trapping, although since only a limited number of materials were studied in each work, no general trends were observed.^{22, 24, 29} While some studies find consistent behavior once FET fabrication is optimized, others report varying behavior both within and between studies (Table 4.1). Two reports find that E_A is a strong function of dielectric, substrate preparation, or other yet unknown parameters.^{21, 25} The results from thee studies suggest that the phenomenon(a) limiting charge transport is correlated to interfacial effects or film microstructure.

More recently n-channel dicyanomethylene-terthiophene (DCMT) and perylene-diimide (PDI) based FETs were found to exhibit Arrhenius-like temperature activated behavior (Table 4.1). DCMT exhibited $E_A = 35 \pm 10$ meV for a $\mu_{eff} \approx 0.12$ cm²V⁻¹s⁻¹ (estimated from plot) and an onset voltage shift of ~ + 40 V from room temperature to 80 K.²³ PDI derivatives exhibit $E_A = 60 - 90$ meV for devices having $\mu_{eff} \approx 0.07 - 1.05$ cm²V⁻¹s⁻¹ and also exhibit a positive onset voltage shift ~ 10 - 15 V.^{16, 17} Since the dominant trapping mechanism for mobile electrons is thought to be different that that of holes,^{12, 30} it is interesting that MTR (assuming a discrete energy level trap) is able to satisfactorily fit both n-channel and p-channel variable temperature μ_{eff} behavior.

Semiconductor	Carrier Type	$\begin{array}{c} \mu_{eff} \\ (cm^2 V^{\text{-1}} s^{\text{-1}}) \end{array}$	E _A (meV)	$\sim \Delta V_{T}^{a}$ (V)
n-C ₆ H ₁₃ S S S S S n-C ₆ H ₁₃ DH-6T ²⁰	р	0.04	220	
α -6T ²²	р	0.15	~ 100	-16
α -6 T^{27}	р	0.02	~ 100	
$ \begin{array}{c} & & & \\ & & & \\ $				
P3HT nanofibers ²⁴	р	0.06	65	- 30
P3HT ¹⁸	р	0.7	29	
P3HT ¹⁸	р	0.092	85	
Pentacene ²⁵	р	0.3	38	
Pentacene ²⁶	р	0.3	36	
Pentacene ²⁸	р	0.3	42	
Pentacene ²⁸	p	0.3	40	
$\begin{array}{c} n-C_4H_9 n-C_4H_9 \\ NC S S S CN \\ DMCT^{23} \end{array}$	n	0.11	35	40
$H_{2n+1}C_n - N$ $PDIn$ $PDIn$				
PDI5 ¹⁷	n	0.066	83	
PDI12 ¹⁶	n	0.55	44	11
PDI5 ¹⁶	n	0.39	91	15
PDI8 ¹⁶	n	1.05	50	12

Table 4.1. Summary previous reports of variable temperature thin film-based organic FET

 behavior fit using an Arrhenius relationship.

^aDifference in V_T between T = 300 K and T = \sim 80 K estimated for plots.

The work summarized above has demonstrated the utility of MTR to model variable temperature FET behavior for several families of materials. An analysis of fit parameters between studies and even within a single study reveals that μ_{eff} and E_A can vary dramatically based upon device fabrication parameters such as dielectric composition, dielectric surface treatment, and source/drain electrode work function. Unfortunately, the high-sensitivity of E_A to variations in experimental parameters prohibits the comparison of materials between studies and has limited the ability to observe general trends in the charge transport mechanism between different semiconductors. Additionally, each report has focused on a single oligomer/polymer or a family of molecules with only solublizing group variations. Given the central role of trapping predicted by MTR and emphasized by recent discoveries,³⁰⁻³² significant insights could be gained from the ability to compare variable temperature behavior of FETs based on diverse set of semiconductors.

This contribution enables the correlation of practical device performance to fundamental charge transport parameters such as E_A and the temperature dependence of trap density across a set of semiconductors fabricated under optimized and rigorously controlled conditions. Six semiconductors are rationally chosen to elucidate the relationship of charge carrier trapping to conduction state energies, dominant charge carrier type, room temperature μ_{eff} , and threshold voltage (V_T). Materials **1** - **5** are oligomers having varying π -core and ancillary substitution with frontier MO energy levels that cover a ~ 1 eV range as well as electron, hole, or ambipolar mobilities between ~ 0.01 - 0.4 cm²V⁻¹s⁻¹ (Table 4.2). Semiconductor **6** is one of the first n-channel polymers, exhibiting extreme crystallinity and high $\mu_{eff} = 0.011$ cm²V⁻¹s⁻¹. All devices will be fabricated using their optimized conditions and substrate preparation, contact electrodes, and measurement parameters will be identical.

 Table 4.2. Semiconductors, their FET properties, and first reduction potential studied in this contribution.

Semiconductor	Carrier Type	$(cm^2V^{-1}s^{-1})$	V _T (V)	E _{red1} (V vs. SCE)
	n	0.4	+28	-1.03
$\frac{1}{n-C_6F_{13}} \sqrt{\frac{1}{1}} \sqrt{\frac{1}{5}} $	n	0.3	+36	-0.88
$n - C_6 H_{13} \underbrace{ \left(\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \end{array} \right)} S \underbrace{ \left(\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \end{array} \right)} S \underbrace{ \left(\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{array} \right)} S \underbrace{ \left(\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	n, (p)	0.1 (0.01)	+42 (- 60)	-1.06
	р	0.04	-49	
$F \rightarrow F = 0$	n	0.02	+25	-0.45
$ \begin{array}{c} $	n	0.011	+67	-1.11

A general inverse correlation between μ_{eff} and E_A is revealed by this set of n-channel, pchannel, and ambipolar materials. Additionally, the calculated free carrier mobility (μ_0) is found to be similar for all materials even though the magnitude of μ_{eff} varies ~ 10² and the charge carrier sign changes across materials **1** - **6**. The relationship of conduction state energy level to shallow trapping events modeled by MTR is studied here for the first time in organic FETs revealing no correlation. Finally, this study reveals an intriguing and definitive relationship between V_T shift, trap density, MO/conduction state energies, and μ_{eff} .

4.2 Experimental

Semiconductors **1** - **6** were synthesized and purified according literature procedures.^{33:36} Prime grade p-doped silicon wafers (100) having 300 nm thermally grown oxide (Montco Silicon) were used as device substrates. These were sonicated in methanol, acetone, propanol, and oxygen plasma cleaned before film deposition. Trimethylsilyl functionalization of the SiO₂ surface next carried out by exposing the cleaned silicon wafers to hexamethyldisilazane (HMDS) vapor under nitrogen at room temperature for 4 days. Films of oligomers **1** - **5** were thermally evaporated onto substrates at their optimum deposition temperature (80 °C, 90 °C, 70 °C, 90 °C, and 150 °C, respectively)^{33:35} under high-vacuum (< 3 x 10⁻⁶ Torr) to a thickness of 50 nm at a QCM monitored rate of 0.1 - 0.2 Å/s. Films of **6** were spin-coated from 0.5 % (w/v) CHCl₃ solution, dried at 120 °C *in vacuuo* for 12 h, and annealed under nitrogen at 240 °C for 2 h.³⁶ Spin-coated polymer films were 43 ± 7 nm-thick as determined by profilometry. For FET device fabrication, top-contact gold electrodes (500 Å) were deposited by thermal evaporation at a rate of 0.1 - 0.3 Å/s through a shadow mask to define channels with dimensions 100 µm (L) by 5.00 mm (W). The capacitance (Cox)of the 300 nm SiO₂ insulator is 1 x 10⁻⁸ F/cm² and mobility (µ_{eff}) is
calculated in the saturation regime using to Eq. 3 within the V_G range 80 V - 100 V for n-channel FETs, -80 V - -100 V for p-channel FETs, or 110 V - 130 V for **6** to minimize the effect of varying V_G on μ_{eff} in this study. Subthreshold swing (S) was calculated using Eq. 4.

$$I_{D,sat} = \frac{W}{2L} C_{ox} \mu_{eff} \left(V_G - V_T \right)^2 \tag{3}$$

$$S = \left[\frac{d\log(I_D)}{dV_G}\right]^{-1} \tag{4}$$

A shielded Advanced Research Systems Helitran LT-3 open cycle cryostat was used with a Lakeshore Cryotronics Model 331 Temperature Controller equipped with dual calibrated silicon diode temperature sensors to control the temperature of the device during measurement. The cryostat was mounted in a customized high-vacuum probe station operated at pressures $< 1 \times 10^{-6}$ Torr. Devices and the silicon diode used to record the temperature were mounted on a 1 mmthick sapphire crystal, attached to the cryostat sample stage with indium. Coaxial and/or triaxial shielding was incorporated into Signaton probes to minimize noise levels. TFT characterization was performed with a Keithley 6430 sub-femtoampmeter (drain) and a Keithley 2400 (gate) source meter, operated by a locally written Labview program and GPIB communication. Variable temperature data was collected on a minimum of 10 devices for each semiconductor and their figures-of-merit averaged at each temperature. Standard deviations were < 15 % for all devices measured at a given temperature and data collected while cooling the device from 300 K to 79 K was indistinguishable from data collected while warming the device from 79 K to 300 K. A ramp rate of 2.0 K/min was used when changing temperature to minimize the effect of different coefficients of thermal expansion on device structure and post-run measurement confirmed negligible change in device performance for all FETs.

4.3 Results and Discussion

The temperature activated FET behavior for all compounds studied will first be presented. Fits of μ_{eff} data assuming a discrete trap energy MTR model (Eq. 2) will then be shown reveal Arrhenius behavior and E_A that scales inversely with room temperature μ_{eff} . Interestingly, the E_A is found to be independent of conduction state energy or carrier type, suggesting that hole and electron carriers encounter comparable traps irrespective of the conduction band energy and carrier charge. Next, the calculated μ_0 will be discussed and found to be largely independent of μ_{eff} , supporting a trap-limited mobility model. Finally, the effect of temperature on V_T will be analyzed (along with room temperature subthreshold swing measurements) to calculate trapped charge density (N_T) as a function of temperature and a striking correlation with u_{eff} is discovered. All of these results are discussed in the context of previous observations, found to be consistent, and add substantial understanding to FET charge transport phenomena.

4.3.1 Temperature activation of mobility

Plots of μ_{eff} vs. 1000/T reveal Arrhenius-like behavior and negligible deviation form linearity (Figure 4.1a). Plots of μ_{eff} vs. T^{0.5} to model delocalized charge transport or T^{0.25} to model variable range hopping exhibited curvature and increased errors in linear least squared fits compared to the Arrhenius plot. Linear fits to the Arrhenius plot reveal E_As of 21 ± 2 meV for n-channel 1, 22 ± 2 meV for n-channel 2, 27 ± 4 meV for n-channel 3, 39 ± 6 meV for p-channel 4, 70 ± 5 meV for n-channel 5, 75 ± 7 meV for n-channel 6, and 250 ± 20 meV for p-channel 3 (Table 4.3). These E_As reveal a trend of increasing activation energy as room tmeperature μ_{eff} diminishes across the series from $0.42 \pm 2 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for 1, $0.31 \pm 3 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for 2, $0.090 \pm 3 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for n-



Figure 4.1. Plots of FET μ_{eff} vs. inverse temperature with E_As indicated (**a**) and V_T as a function of temperature (**b**, $-V_T$ is plotted for p-channel materials). The dashed lines in **a** are least squares fits to the Arrhenius plot, while dotted lines in **b** are a guide for the eye.

channel **3**, 0.031 \pm 2 cm²V⁻¹s⁻¹ for **4**, 0.018 \pm 1 cm²V⁻¹s⁻¹ for **5**, 0.011 \pm 1 cm²V⁻¹s⁻¹ for **6**, and finally to 0.010 \pm 2 cm²V⁻¹s⁻¹ for p-channel **3** based FETs. This is the first time that a statistically significant correlation between room temperature μ_{eff} and E_A has been observed within one study of organic FETs. These results are indeed consistent with the majority of other reports employing Arrhenius models finding that for FETs with $\mu_{eff} \ge \sim 0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, $E_A < \sim 50 \text{ meV}$ (entries in the bottom half of Table 4.1) and that when $\mu_{eff} << 0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} E_A > \sim 50 \text{ meV}$ (entries an the top of Table 4.1).

Significantly, the calculated E_As do not correlate to the conduction band energies or charge carrier type, indicating that the MTR-modeled behavior is not intrinsically a characteristic of MO energy level, but rather arises from thin-film properties such as film microstructure, crystal strain/defect sites, grain boundaries, and/or quality of the semiconductor-dielectric interface. This is extremely insightful and in agreement with orthogonal studies,^{30, 31} suggesting that both n-channel and p-channel transport are prone to similar trapping states that are not necessarily a function of charge transport energy levels, but rather result from more general trapping/scattering phenomena in organic materials.

It is important know the origin and nature of such trap states that limit μ_{eff} for device design, fabrication, optimization, and operational stability. Indeed these trap states seem equally as important to achieve high room temperature μ_{eff} as a low-lying LUMO energy is to avoid O₂, H₂O, and surface hydroxyl trapping in n-channel FETs, and sufficiently-low HOMO energy is to ambient doping in p-channel FETs.^{12, 15, 37-39} This conclusion may also suggest why previous reports of FETs based on the same semiconductor exhibit differing variable temperature behavior, since parameters such as substrate cleaning/preparation, semiconductor purity,

Semiconductor (Carrier Type)	$\frac{{\mu_{\rm eff}}^a}{(cm^2V^{\text{-1}}s^{\text{-1}})}$	μ₀ ^b (cm ² V ⁻¹ s ⁻¹)	E _A ^b (meV)	S ^c (V decade ⁻¹)	$N_{SS}^{\max d}$ (cm ⁻²)	$\frac{\Delta N_{T}^{e}}{(cm^{-2})}$	E ^{1/2} _{red1} f (V)
1 (n)	0.42 (2)	0.83 (6)	21 (2)	6.3	6.8 x 10 ¹²	6.8 x 10 ¹²	-1.03
2 (n)	0.31 (3)	0.62 (4)	22 (2)	7.7	8.2 x 10 ¹²	8.2 x 10 ¹²	-0.88
3 (n)	0.090 (3)	0.28 (1)	27 (4)	7.5	9.4 x 10 ¹²	9.4 x 10 ¹²	-1.06
3 (p)	0.010(2)	160 (270)	248 (20)	10.4	1.1 x 10 ¹³	_g	
4 (p)	0.031 (2)	0.16 (2)	39 (6)	4.9	5.2 x 10 ¹²	5.2 x 10 ¹²	
5 (n)	0.018 (1)	0.27 (1)	70 (5)	3.9	4.2 x 10 ¹²	$4.2 \ge 10^{12}$	-0.45
6 (n)	0.011 (1)	0.19 (3)	75 (7)	14.7	1.8 x 10 ¹³	1.8 x 10 ¹³	-1.11

Table 4.3. Summary of fit parameters for FETs of 1 - 6 films with standard deviations in parentheses and first reduction potential of the semiconductor.

^aCalculated using Eq. 3. ^bCalculated using Eq. 2. ^cCalculated using Eq. 4. ^dCalculated using Eq. 5. ^eCalculated using Eq. 6. ^fElectrochemical half-wave potential vs. SCE of the first reduction event in THF. ^gDevice output below measurable limit at T = 79 K.

deposition conditions, and electrode contact can strongly influence variable temperature behavior.^{16-18, 20, 22, 25, 27, 28} Even though μ_{eff} at 300 K ranges from ~ 0.4 cm²V⁻¹s⁻¹ for **1** to ~ 0.01 cm²V⁻¹s⁻¹ for **6**, the calculated fit values for μ_0 reveal that in the absence of trapping, these materials would exhibit a $\mu = 0.2 - 0.8$ cm²V⁻¹s⁻¹. The narrower range of μ_0 for **1** - **6** reveals that the semiconductors have similar inherent charge transporting capabilities independent of charge carrier type but that device-level film/interface properties can dominate observed FET behavior. This finding that is consistent with recent studies showing that rigorous exclusion of charge traps and/or inclusion of gate dielectric interfacial layers can significantly enhance μ_{eff} in otherwise low-mobility FETs.^{30, 31} The large standard deviation in the E_A and μ_0 for p-channel operation of **3**-based FETs reveals that device performance is strongly impaired by trapping and the uncertainty in μ_0 precludes it from this part of the analysis.

4.3.2 Temperature dependence of V_T

Definitive evidence of charge trapping is observed in the temperature dependence of V_T . Semiconductors **1** - **6** exhibited a shift in threshold voltage (ΔV_T) ranging from 8 V to 54 V between 300K and 79 K (Figure 4.1b and Table 4.3). Such ΔV_T s have been observed previously with decreasing temperature for n-channel and p-channel FETs in the range of 11 V to 40 V.^{16, 22-24} In these studies however, the limited variety of semiconductors used and/or large device-to-device variation precluded a comprehensive analysis of the ΔV_T . In the present contribution, the breadth of semiconductors studied and the small standard deviations observed in V_T , reveal a clear correlation between ΔV_T and the trap-limited μ_{eff} at 300 K.



Figure 4.2. Plot of charge trap density (N_T) vs. temperature, calculated using Eq. 6 (**a**), and a plot of ΔN_T vs. temperature obtained from Eq. 6 (**b**). The dotted lines in **a** and **b** are a guide for the eye.

The trapped charge density at room temperature (N_{SS}^{max}) can be calculated using the subthreshold swing (S) according to the established relationship^{40, 41} in Eq. 5, where *e* is the natural number, *q* is the elementary charge and C_{ox} is the areal capacitance of the gate dielectric.

$$N_{SS}^{\max} = \left[\frac{S \cdot \log(e)}{kT/q} - 1\right] \frac{C_{ox}}{q}$$
(5)

The ΔV_T can be converted to the change in the trapped charge density ΔN_T using the previously developed relationship given in Eq. 6.^{17,42}

$$\Delta N_T = q \Delta V_T C_{ox} \tag{6}$$

These two relationships allow the trapped charge density N_T to be calculated at each temperature. This data allows analysis of the trapping behavior as temperature decreases and carriers cannot be thermally released from charge traps. In other words, shallow traps which contribute to diminished μ_{eff} according to the MTR model, are quantified by ΔN_T . Interestingly, the plots of ΔV_T and N_T vs. temperature suggest two regimes for charge trapping (Figures 4.1a and 4.2a, respectively). Similarity is seen in all curves for temperatures below 150 K where the N_T and V_T increase exponentially. This exponential behavior can be fit with the single level trap model given in Eq. 1 to model the filling of these shallow traps at low temperatures. Fits to the data below 125 C yield the trap depths of 28 meV - 40 meV for the n-channel FETs and 17 meV for p-channel **4** (Figure 4.3). These shallow trap energies correspond well with the shallow trap depth of ~ 50 meV estimated with a different method in the linear regime, utilizing the Meyer-Neldel relationship,⁴³ for PDI-based FETs.¹⁶ A grain boundary trap depth for p-channel operation of $\alpha 6T$ -based FETs has been identified to be ~ 15 meV,⁴⁴ comparable to the value obtained in this work for p-channel material **4**.



Figure 4.3. Plot of the natural log of $\Delta N_{T 125}$ ($\Delta N_{T 125} = N_T - N_{T 125}$) vs. inverse temperature from 79 K - 100 K. The dashed lines are fits to the data using Eq. 1, with the calculated trap depth indicated.

A second trapping regime is observed for temperatures above 150 K, where the two highestmobility semiconductors, **1** and **2**, exhibit negligible change in N_T and the semiconductors with lower mobility, **3** - **6** show evidence of significant charge trapping with increased curvature and $\Delta N_T \approx 2 \times 10^{12} \text{ cm}^{-2}$ at 150 K. Such divergent behavior is also evidenced in work by Frisbie, et. al, where PDI-based FETs with $\mu_{eff} = 0.055 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ exhibit V_T that increases as soon as temperatures fall below 300 K, while devices with $\mu_{eff} = 1.3 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ exhibit V_T that does not increase appreciably until ~ 170 K (estimated from plot).¹⁶ The three other sets of organic FET V_T vs. temperature data in the literature also exhibit similar behavior to the low mobility devices in this contribution, V_T begins to shift to higher potentials as soon as the temperature is decreased from 300 K for devices with $\mu_{eff} \leq ~ 0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.²²⁻²⁴ The ΔV_T behavior observed in this study is consistent with previous reports, although in this contribution, trends within the data set can be evaluated due to the greater breadth of semiconductors properties included and low device-to-device variability.

Interestingly, the high-mobility materials 1 and 2 do not show evidence of deep traps, while the materials with lower μ_{eff} do. This suggests for lower μ_{eff} materials 3 - 6 materials a second set of traps limits FET performance. Additionally, there is no correlation between the conduction state energy and the presence of these deeper traps since, e.g. the N_T curvature of 5 and 6 is very similar even though their LUMO energies differ by ~ 0.7 eV. Notably, the low temperature regime for all materials can be fit by Eq. 1 (Figure 4.2b), where the energetic parameter observed is the trap depth. The N_T calculated for the deep traps of ~ 2 x 10¹² in 3 - 6 is consistent with the density of grain boundary defect traps observed in previous work.⁴⁴

4.4 Conclusions

Temperature activated FET behavior is observed for a series of organic semiconductor-based FETs that were chosen for their unique and varied materials and device characteristics. Variable temperature characterization of FETs based on this set of materials revealed that there is no correlation between the conduction state energy level and E_A while there is an inverse relationship between E_A and μ_{eff} . Fits of μ_{eff} data assuming a discrete trap energy MTR model reveal low E_A for high mobility semiconductors 1 and 2 of 21 meV and 22 meV, respectively, while higher E_A values of 40 meV - 70 meV are exhibited by lower mobility FETs based on 3 -6. Analysis of the first ambipolar material revealed that although n-channel operation had an E_A = 27 meV, the p-channel regime exhibited evidence of significantly more trapping with an E_A = 250 meV. Interestingly, the calculated free carrier mobility (μ_0) is found to be 0.2 - 0.8 cm²V⁻¹s⁻¹ for all materials, largely independent of μ_{eff} , supporting a trap-limited mobility model. Finally, the effect of temperature on V_T revealed a two trapping regimes with N_T exhibiting a striking correlation with u_{eff} . The low-temperature regime reveals trapping by shallow states with an depth ~ 40 meV and density of ~ 10^{12} cm⁻², both consistent with previous orthogonal studies. This survey of the variable temperature behavior of several organic semiconductors reveals general trends in trapping for n-channel and p-channel operation and the ΔV_T data suggests that at least two trapping regimes can significantly influence room temperature FET performance.

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