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Probing the Relationship between Structure and Function of Self-Assembling Conjugated Molecules

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ABSTRACT

Probing the Relationship between Structure and Function of Self-Assembling Conjugated Molecules

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This thesis discusses the synthesis, self-assembly, and conductivity properties of novel oligothiophene derivatives with an emphasis on how molecular structure affects the assembly. In order to facilitate self-assembly in conjugated molecules, specific non-covenant forces were included into the molecular design of several derivatives. First, an amphiphilic oligothiophene derivative consisting of a quater- and quinquethiophene moiety attached to a poly(ethylene glycol) tail was synthesized. At high concentrations in polar solvents, a self-supporting gel forms consisting of molecules ordered into interdigitated bilayers. The number of thiophene repeat units and the length of the poly(ethylene glycol) polymer direct effects the molecular ordering in the gel state. The longer PEG tails disrupt the lamellar ordering due to the crystallization of the polymer. The disruption of the ordering by the longer PEG chain causes a decrease in the measured conductivity. Next, a symmetric oligothiophene derivative containing a hydrogen bond forming segment was synthesized. This symmetric derivative was found to form a gel consisting of self-assembled 1D nanostructures at low concentrations in organic solvents. Hydrogen bond formation was found to be essential for the formation of nanostructures. Conductivity values in the semiconducting range were observed for a quinquethiophene derivative when self-assembled while no conductivity was observed for a quaterthiophene derivative. A peptide-based quinquethiophene amphiphile was synthesized for assembly in aqueous conditions. 1D nanostructures were observed to form upon gel formation aqueous conditions. The composition

of the peptidic segment was found to dictate the ordering of the thiophene segment of the molecules in the supramolecular structures. Furthermore, only when a flexible spacer between the hydrogen bonding and π - π stacking segments was included, were both forces able to be balanced in the same assembly. Finally, conjugated surfactants were synthesized to direct the formation of ordered organic/inorganic hybrid materials. Hybrid materials of silicon dioxide and zinc oxide with conjugated surfactants were successfully synthesized using either evaporation induced self-assembly or electrodeposition. Direct inclusion of the conjugated molecules in the deposition process allowed for high dye loading in the hybrid structures. By tuning the molecular structure, conjugated molecules are able to assemble into highly ordered materials in a wide variety of conditions.

For my family and friends

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DDTC	1:1 complex of p-toluenesulfonic acid and 4-
DP15	dimethylaminopyridine
DSC	Differential Scanning Calorimetry
EDC	1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride
EDX	Energy Dispersive X-Ray
EISA	Evaporation Induced Self-Assembly
ESI	Electron spray ionization
GIXS	Grazing Incidence X-Ray Scattering
HC1	Hydrochloric acid
HWE	Horner-Wadsworth-Emmons
I-V	Current- Voltage
LAH	Lithium Aluminum Hydride
LC	Liquid crystal
Leu (L)	Leucine
Lys (K)	Lysine
NaH	Sodium Hydride
<i>n</i> -BuLi	<i>n</i> -butyl lithium
nm	Nanometer
NMR	Nuclear magnetic resonance
Pd(PPh ₃) ₄	tetrakistriphenylphosphine palladium (0)
PEG	Poly(ethylene glycol)
P3HT	Poly(3-hexylthiophene)
РуВА	Pyrene butyric acid
RP-HPLC	Reverse phase high performance liquid chromatography
S/cm	Siemens per centimeter
SAXS	Small Angle X-ray Scattering
SDS	Sodium dodecylsulfate
SIMS	Secondary Ion Mass Spectrometry

STEM	Scanning Transmission Electron Microscopy
Т	Temperature
<i>t</i> Bu	<i>Tert</i> butyl
TEM	Transmission Electron Microscopy
TEOS	Tetraethyl orthosilicate
TGA	Thermogravimetric analysis
THF	Tetrahydropyran
TiO ₂	Titanium Dioxide
T _m	Melting Temperature
Val (V)	Valine
ZnO	Zinc Oxide
λ_{max}	Wavelength maximum

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Chapter 1

Introduction and Background

Chapter 1. Introduction and Background

1.1 Objective and Significance

Molecular self-assembly is the organization of molecules into defined, well-ordered aggregates with minimal human intervention through the use of non-covalent interactions.¹⁻³ In biology, self-assembly is particularly important because it regulates many functions within a cell.⁴ The most famous example of biological self-assembly is the DNA duplex, but self-assembly is also ubiquitous in peptides.⁵⁻⁸ The secondary and tertiary structure of a protein can often determine the function of a protein in a cell.⁹⁻¹² A structural change in a protein can often cause a loss of function and adverse effects to an organism, such as the case with Alzheimer's disease.^{13, 14} Understanding how forces such as hydrogen bonding, electrostatic forces, metalligand interactions, and hydrophobic collapse affect structural change in molecules has become a large and active research field.¹⁵ Inspired by nature, self assembly has also become a particularly attractive field for soft organic materials because organic synthetic chemistry offers a facile method to add functional groups to induce self assembly to a wide variety of substrates.¹⁶⁻¹⁹

Supramolecular chemists seek to understand how to use noncovalent forces to drive aggregation of molecules in large well-defined structures to access functionalities not otherwise accessible in a molecular system. While molecular chemistry frequently operates in the angstrom size scale and top-down approaches like lithography are best suited for the micron scale, supramolecular chemistry is most useful as a bottom-up approach to obtain structures in the nanometer size scale that is otherwise difficult to access.^{20, 21} Due to the need of long-range molecular ordering, self assembly is becoming important is electronic devices such as transistors,²²⁻²⁵ light emitting diodes,^{26, 27} and photovoltaic devices.²⁸⁻³¹ As the need for smaller,

more efficient computation devices grows, the need for a facile fabrication technique for devices on the nanometer scale becomes increasingly important as well. For large-scale applications, self-assembled systems are attractive because they allow spin casting and dip coating to be used to deposit the active layer in a device while keeping the molecular ordering required for high performing devices.³²⁻³⁴

Not only has self-assembly emerged an important component in purely organic systems, also in organic-inorganic hybrid systems.³⁵⁻³⁷ In the case of electronic materials, hybrid materials are often used to combine the low cost and mechanical flexibility of organic materials with the improved electrical and stability properties of inorganic materials.^{38, 39} As an example, in a photovoltaic cell the interface between the inorganic and organic phases, as well as the ordering of each phase, is particularly important because it not only affects the efficiency of charge separation and recombination, but also the role of charge trapping sites.^{40, 41} Each phase must be well ordered to allow the flow split excitons to reach their respective electrodes.^{30, 42} Close packing of the two phases within a highly ordered material that has well-defined linkages between phases is ideal for photovoltaic applications.

1.2 Supramolecular Chemistry

1.2.1 Supramolecular architectures

In 1987, the Nobel Prize in Chemistry was awarded for pioneering work in "chemistry beyond the molecule."^{43, 44} Since then, an explosion of work has been dedicated to the study of how to manipulate noncovalent interactions to assemble large ensembles of molecules into defined structures. In order to create supramolecular structures, researchers utilize hydrogen

bonding,⁴⁵⁻⁴⁷ π - π stacking,^{48,49} π -cation,^{50,51} hydrophobic,⁵²⁻⁵⁴ metal-ligand,⁵⁵⁻⁵⁷ Columbic^{58,59} and van der Waals interactions to hold together assemblies of molecules. While noncovalent forces are weak when compared to a covalent bond (see Table 1.1), the net interaction can become strong when considered as a whole in an aggregate of many interactions.⁶⁰ Because selfassembly is a thermodynamic process, there must be enough stabilization from the noncovalent interactions to overcome the loss of translation and conformational entropy to find a favorable energetic minimum.⁶¹ By synthesizing molecules preprogrammed to assemble in to discrete structures, a wide range of nanoobjects have been discovered by researches using a wide range of molecules. To date, these objects include (see figure 1.1) zero- and one dimensional objects,^{18,62, ⁶³ spherical micelles,^{64,65} cylindrical micelles,^{66,67} two-dimension sheets,⁶⁸ tubes,⁶⁹⁻⁷¹ and ribbons.^{72,73}}

In self-assembly, two of the most common secondary interactions are π - π stacking and hydrogen bonding. As a molecule becomes more conjugated, π - π interactions become increasingly important. The strength of interaction is mainly dependent on the amount of π -

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Type of interaction or bonding	Strength (kJ/mol)	
covalent Bond	100-400	
Coulomb	250	
hydrogen bond	10-65	
ion-dipole	50-200	
dipole-dipole	5-50	
cation-π	5-80	
π-π	0-50	
van der Waals forces	<5	
hydrophobic effects	Difficult to assess	
metal-ligand	0-400	

Table 1.1. List of noncovalent interactions and their associated strengths in the gas phase.(Adapted from Hoeben et al. Chem Rev. 2005, 105, 1491-1546.)



Figure 1.1. Examples of supramolecular architectures achieved through noncovalent forces. (Reproduced from Stupp et al. MRS Bull., **2000**, *25*, 42-48.)

orbital conjugation and the solvent.⁷⁴ As the extent of π -orbital conjugation increases, logically the strength of π - π interactions increases.⁷⁵ Furthermore, since extended π -orbital surfaces are hydrophobic in nature, solvents which solubilize hydrophobic surfaces will weaken the interaction, where hydrophilic solvents will strengthen π - π stacking due to hydrophobic collapse of the π surfaces.^{49, 76} Hydrogen bonding is an excellent choice for noncovalent interactions due to their directionality. By planning and synthetically installing hydrogen bonding units, the geometry of association can be controlled and manipulated.

1.2.2 Organogelators

Organogelators are an important subclass of supramolecular chemistry that is defined by ability to induce gel formation in organic solvents at low concentrations (typically > 5 wt %). While gelators have been known for over one hundred years, a renewed wave in study has recently begun in order to exploit these systems for unique material properties.⁷⁷ The definition of a gel has evolved since the discovery of gelators. The most comprehensive definition was offered by Flory in 1974 that tied gel formation to the presence of a continuous structure with macroscopic dimensions that is stable for a measureable timeframe and is soldlike in its rheological behavior.⁷⁸ Often, instead of studying the rheological behavior of a system to determine gel formation, a "vial inversion" test is applied. In this definition, if the solution becomes viscous enough to hold its shape when inverted, then it is considered a gel.

In a supramolecular system, gel formation occurs when small molecules assemble into a long fibrous assembly to create an entangled, three-dimensional network. Interconnects between one-dimensional assemblies are essential; otherwise there is no mechanism to trap solvent molecules and prevent flow.^{79, 80} Most often, gels are formed by simply heating the molecule in a solution to near the boiling point of the solvent, then allowing it to cool until the solution becomes immobile. The most efficient gelators induce gel formation at less than 1 wt%. Because the fibrous structures can be microns in length, they can efficiently intertwine and form and entangled network without the need for concentrated solutions (figure 1.2).

In general, for a molecule to form a gel it must possess the ability to form a long, onedimensional (1D) structure, a way to balance the solvent-fiber interactions to prevent solvation and crystallization, and a method of interacting with other fibers to form interconnects. Creation of one dimensional structures is typically achieved through the use peptides and



Figure 1.2. Demonstration of an organogelating aromatic-linker-steroid (**ALS**) molecule and the fibrous network formed. a) Optical micrograph of a 1.3 wt % in 1-octanol. b) Electron micrograph of a 2.2 wt % gel in n-dodecane. c,d) Electron micrographs of a 1.9 wt % gel in 1-octanol showing the entangled fibrous network. (Adapted from Weiss, R. G. et al, Acc. Chem. Res. **2006**, *39*,489-497.)

carbohydrates due to the directionality and strength of their hydrogen bonding.⁸¹ Outside of peptides and carbohydrates, bis-urea and cholesterol moieties have yielded many examples of gelating molecules as well. A careful balance must be achieved between solubility and crystallization, so the solubilizing portion is also an integral component of the overall design. Most systems rely on physical interconnects between fibers to form a three dimensional network, although chemical crosslinking⁸² and metal-ligand⁸³ interactions have been used as well.

1.2.3 Device fabrication in Organic Supramolecular Systems

Organic electronic devices have attracted much attention due to their ability to be fabricated on flexible substrates. Unlike their inorganic counterparts that need to be processed at temperatures well above the decomposition point of organic compounds, organic molecules can be deposited by solution phase or thermally at temperatures compatible with plastic backings.⁸⁴ In 1994, when Garnier and colleagues successfully fabricated an all organic thin film transistor based on polythiophene, plastic electronics were realized for the first time.⁸⁵ Since then, fieldeffect transistors,⁸⁵ light-emitting diodes,⁸⁶ and photovoltaic cells⁸⁷ have been produced using a wide range of materials on flexible substrates.

For high performance of plastic electronics, a high degree of molecular ordering in is necessary to create pathways for electron flow. Self-assembly is an attractive technique to impart the molecular ordering needed using a bottom-up deposition approach. Conduction in organic molecules occurs through overlapping π -orbitals.²⁵ If an unbroken pathway of π -orbital overlap exists between electrodes in a device, mobility values exceeding amorphous silicon can be obtained from organic molecules, but without a conduction pathway, the performance drops drastically.⁸⁸ If beneficial π -orbital overlap in a self-assembled structure can be promoted, then supramolecular chemistry could offer a facile route for performance improvement. Furthermore, since self-assembled structures can reach lengths of several microns, performance decrease associated with electron transport across grain boundaries can be avoided.²¹ If a fiber can stretch across an entire device, then a continuous path of π -orbital overlap should be present for optimal electron transport.

Techniques for imparting molecular ordering to organic systems are known, but are impractical for large area applications. Fabrication techniques such as Langumir-Blogett and layer-by-layer, and vacuum sublimation deposition give the ability to control nanoscopic and molecular ordering in films from solutions, but require special equipment and multiple steps.³² Bottom down approaches, like patterning, have problems reaching a size scale small enough for high performance applications. In order to use low cost fabrication techniques like spin coating or ink jet printing to their fullest potential, systems that are soluble, but still produce a high degree of ordering are needed.^{32, 33} Self-assembly is a promising route to achieve this goal due to its ability to create high order with little external processing.

1.3 Oligothiophene for Opto-Electronic Devices

Since the discovery of highly conducting polyacetylene in 1977, many conjugated π systems have been explored for electronic applications including pyrrole, phenylene,
phenylenevinylene, aniline, furan, and thiophene derivatives.⁸⁹ Polythiophene has become one of
the most studied conducting polymers due facile synthesis of many conducting derivatives.⁹⁰
Interestingly, substitution on the conjugated backbone does not affect the conductive properties

of the polymer, giving many derivatives high solubility. Originally, oligomers were studied as model systems for polymers, but it was quickly realized that oligomers could be used in novel material synthesis in their own right. In 1989, the first sexithiophene (6T) transistor was fabricated and it was found to have performances close to those of silicon based devices.⁹¹ Oligothiophene is now one of the most studied conjugated oligomers for electronic applications due to its low band gap, as seen in figure 1.3, and the ability to synthesis a wide array of derivatives.



Figure 1.3 Graphical plot of number of repeat units versus band gap energy for 1) OPV, 2) N-Boc protected oligopyrroles, 3) oligofuranes, 4) oligo(*p*-phenylene)s, 5) oligoenes, and 6) oligothiophenes. (Reproduced from Hernandez, V. et al, Phys. Rev. B. **1994**, *50*, 9815.)

High performance of small molecule devices is explained by the use of chemically pure and defined molecules. Polymers are prone to chemical defects formed during the polymerization process. In order for thiophene derivatives to be conductive, the molecule must possess all α -linkages (see figure 1.4).²⁵ π -Orbital conjugation cannot occur through β -linkages or sp³ defects.⁹⁰ Oligothiophene derivatives can avoid these defects all together because thiophene linkages are directly synthesized in a stereospecific fashion. The most common reaction used to install the thiophene linkages is a Stille coupling between an aryl bromide and a stannylated substrate.⁹² Because pure, discrete derivatives can be synthesized, oligothiophenes are able to crystallize into large single crystals giving a very high degree of structural order in the solid state.

Unlike polythiophenes, the conductive performance of oligothiophene is compromised by substitutions in the β -position. Conduction is known to occur through overlapping π -orbitals in face-to-face packed molecules.⁹³ This leads to a high anisotropic conduction properties with the best conduction pathway being perpendicular to the long axis of the molecule (Figure 1.5). A



Figure 1.4. Demonstrating the name convention with thiophene molecules. a) Molecular diagram showing an α -linkage. b) Molecular diagram showing a β -linkage. c) α -Linked thiophene group labeled with naming convention in the literature.



Figure 1.5. Representation of molecular orientation and hole mobility (μ_e) of a dihexyl substituted sexitiothphene derivative when molecule is a) perpendicular to the subsrate ($\mu_e =$) and b) parallel to the substrate($\mu_e =$). (Adapted from Garnier F et al, JACS, **1993**, *115*, 8716-8721.)

common problem of unsubstituted oligomers is their inherent lack of solubility. To increase solubility, substitutions must be made to the conjugated core of the molecule. Adding substituents to the β -position is known to reduce the planarity of the thiophene segment as well as prevent π - π stacking between adjacent molecules.⁹⁴ The net result is a several order of magnitude decrease in the electrical performance of a device. On the other hand, substitutions made to the α -position do not interrupt electrical performance because they do not disrupt the packing of the molecules, allowing a high degree of π -orbital.

1.4 Supramolecular Synthesis of Organic/Inorganic Hybrid Systems

1.4.1 Template Driven Mineralization

By first using self-assembly to create an organic scaffold and then introducing inorganic components to interact with the scaffold, researchers have been able to produce a wide array of inorganic structures. In this strategy, the inorganic phase directly copies the organic phase that is directing the mineralization process.^{35, 37} Usually, the inorganic phase is introduced to a preassembled organic structure in a solution, but the inorganic can also be introduced via the gas phase. While nature has employed a template driven mineralization in the formation of bone and teeth,⁹⁵ scientists have used this strategy in the formation a wide variety of inorganic structures including ribbons, spheres, and tubes.⁹⁶⁻⁹⁸ Using chiral templates, this technique has even been able to produce chiral ribbons and cylinders.⁹⁹ Metals, oxides, and semiconductors have all been successfully templated using this approach.^{37, 96, 100}

1.4.2 Co-assembly Mineralization

Instead of pre-forming an organic template, the co-assembly relies on the organic molecule to direct the inorganic phase growth during inorganic polymer growth. Pioneered by the Mobil Corporation, co-assembly gained popularity for the fabrication of mesoporous silica.¹⁰¹ Based on this technology, one the most popular co-assembly strategies to form ordered films on the nanoscale is known as evaporation induced self-assembly (EISA).^{102, 103} Here, an organic molecule is dissolved in a solvent, typically an alcohol, in a concentration lower than its critical micelle concentration. To the solution, an inorganic precursor is added along with a catalyst to promote an inorganic condensation reaction. Upon casting a film, the organic molecule assembles as the solvent evaporates, forming a template for an ordered hybrid material upon drying of the film. Besides sol-gel chemistry, the inorganic phase can also be synthesized by electrochemistry.¹⁰⁴ Instead of forming the inorganic phase by hydrolysis of a precursor in solution, the inorganic phase is formed upon the reduction of precursors in an electrochemical bath.

1.4 Summary of Work

Designing and synthesizing soluble, self-assembling conjugated oligomers remains an important scientific aim. Throughout this thesis, an effort has been made to synthesize novel oligothiophene molecules that are long enough to be electronically relevant and to understand what forces dictate their self assembly. Hydrogen bonding, solvatophobic, Coulombic, and π - π stacking interactions all can play an important role to the assembly of oligothiophene derivatives. In an attempt to harness secondary interactions to assemble oligothiophene derivatives, new
molecules containing structure-directing groups have been synthesized to probe their selfassembly properties. The lessons learned about self-assembly of conjugated systems should be useful in designing future generations of self assembling conjugated molecules.

In chapter 2, an amphiphilic oligothiophene derivatives are synthesized by conjugating poly(ethylene glycol) (PEG) to the thiophene segment and their assembly properties are explored. Quarter- and quinquethipophene (4T and 5T respectively) derivatives were synthesized. The 4T moieties were found to assemble into a highly ordered lamellar phase by Xray scattering, but not in the 5T derivatives. An interesting even-odd effect in the number of thiophene repeat units was discovered by optical spectroscopy. The length of PEG segment was also varied and found to play a role in chromophore packing. Chapter 3 explores the use of hydrogen-bonding for assembling thiophene derivatives. Gel formation was discovered for symmetric derivatives with hydrogen bonding segments flanking the thiophene core. It was also discovered that enhanced conductivity was achieved due to the presence of self-assembled structures. Chapter 4 looks at forming self-assembled structures in an aqueous environment. Peptide based quinquethiophene derivatives were synthesized and found to form gels at low concentrations. The affect the peptic segment has on self-assembly is explored. Finally, Chapter 5 describes the use of oligothiophene bolaamphiphiles as structure directing reagents for nanostructured hybrid materials. Surfactants were designed specifically for a silica sol-gel system and a zinc oxide electrochemical system. In each case, a facile, one-step synthesis of an ordered hybrid system was achieved. It was discovered that the composition of the surfactant directly correlates to the ordering within the hybrid material.

Chapter 2:

Asymmetric Amphiphilic Oligothiophene-poly(ethylene glycol)

Derivatives

Chapter 2. Asymmetric Amphiphilic Oligothiophene-poly(ethylene glycol) Derivatives 2.1 Introduction

The ability to control the molecular ordering of oligothiophene derivates into highly aligned π - π stacked aggregates is essential for high performance devices. Without a high degree of alignment of the π -orbitals, no pathway for electron flow can occur, thus limiting the conductivity and mobility of a device.^{25, 105, 106} Self-assembly is an ideal strategy order to form long range molecular order in a solution deposited system because no external processing is required.²¹ By relying on noncovalent interactions, the molecules can form highly aligned assemblies that can enhance electronic performance without the costly processing of other deposition methods.³² While self-assembling systems are known, the design principles behind self-assembling oligomers are still not well understood. In order to better design self-assembling conjugated oligomers, the effect noncovalent interactions have on the final structure must be investigated.

In order to create a solution processable and highly ordered system, a novel amphiphilic oligothiophene derivative consisting of a hydrophobic oligothiophene segment and a hydrophilic poly(ethylene glycol) (PEG) segment (see figure 2.1) was synthesized. With the addition of a sufficiently long PEG group to the thiophene core, the molecules are highly soluble in most common solvents including water. Due to the amphiphilic nature of these molecules, they are able to assemble into a highly ordered lamellar phase above a minimum concentration in an aqueous solution. In order to probe the role of each segment of the molecule on the final structure, the length of the PEG segment and the number of thiophene repeat units was varied. Both quaterthiophene (4T) and quinquethiophene (5T) molecules with PEG chain lengths of n =

24 and 45 have been synthesized. Previously, the Stupp group demonstrated that similar molecules with an oligo(p-phenylene vinylene) (OPV) were able to form both thermotropic and lyotropic liquid crystalline phases.¹⁰⁷ Since short OPV oligomers are known to be poor semiconductors, an oligothiophene core was substituted to investigate the potential use of this motif for electron transport.¹⁰⁸

After exploring the self-assembly properties of the derivatives, an attempt to use the assembly properties to order an inorganic phase is made for photovoltaic applications. Because hybrid photovoltaic devices operate under excitonic conditions, in order for a hybrid photovoltaic device to function, the p- and n-type phases must be within the exciton splitting distance.^{40, 109} If there is no donor/acceptor interface within the excitonic diffusion distance, then recombination will occur preventing a photovoltaic effect from occurring. The inorganic phase was chosen to be TiO₂ because of its well documented use as an n-type semiconductor in hybrid photovoltaic devices.⁴¹ Oligo- and polythiophene derivatives have been successfully integrated into photovoltaic devices with TiO₂, but most reports rely on a random mixing approach to create a bulk heterojunction.^{110, 111} Anatase TiO₂ nanorods were synthesized using a low temperature route developed by the Weller¹¹² group and were then mixed with the thiophene-PEG derivatives with the expectation that the hydrophilic PEG segments would interact with the inorganic phase to order the organic/inorganic interface while using self-assembly to order the hybrid material.

2.2 Synthesis of Non-ionic Thiophene Amphiphiles

2.2.1 Quaterthiophene Amphiphiles

The quaterthiophene derivatives where synthesized by synthesizing a hydrophilic thiophene/PEG segment and a hydrophobic thiophene/alkyl segment, followed by a Stille coupling¹¹³ to produce the final molecule as seen in Figure 2.1. In order to synthesize the hydrophilic segment, an ester forming reaction using carbodiimide chemistry between 2-bromo-5-thiophene carboxylic acid was employed. Conditions developed by Moore et al.¹¹⁴ using a carbodiimide as the acid activator and a 1:1 complex of p-toluenesulfonic acid and 4dimethylaminopyridine (DPTS) as the catalyst were used. The DPTS complex has been shown to suppress the formation of unreactive N-acylurea byproducts that can form during the course of the reaction. The N-acylurea is known be a significant byproduct when a weak nucleophile is used such as an aromatic carboxylic acid, thus limiting the yield of the desired product. Even with the use of the DPTS complex as catalysis the ester formation would take 1-2 days, but high yields were obtainable. 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) was used as the activator because it, along with its byproduct urea, can be removed via an aqueous work up. When diisopropylcarbodimide was initially used as the activator, the urea byproduct would co-elute with the PEGylated thiophene product during column chromatography making purification impossible.

The hydrophobic block of the molecule consists of an alkyl chain directly attached to a thiophene core. To form the hydrophobic segment, 2,2'-bithiophene was lithiated and reacted with 1-bromooctadecane to directly conjugate the alkyl tail to the thiophene ring via an bimolecular substitution reaction. Earlier attempts to use shorter alkyl tails were hampered because purification at this step was difficult due to similar retention factors (R_f) between the starting material and product for column chromatography. When the longer alkyl tail was used,

Synthesis of PEG Segment



Figure 2.1. Synthetic scheme for thiophene-PEG derivatives. a) DPTS/EDC, PEG mono methyl ether, DCM b) PEG mono methyl ether, TEA, Toluene c) n-butyl lithium, 1-bromododcane, THF d) NBS, DMF e) 2-tributyltin thiophene, Pd(PPh₃)₄, DMF f) n-butyl lithium, SnBu₃Cl, THF g) **1**, Pd(PPh₃)₄, DMF f) **2**, Pd(PPh₃)₄, DMF.

the product becomes crystalline allowing purification by recrystallization. Following the alkylation, the bithiophene derivative was brominated using *N*-bromosuccinimide (NBS) in dimethylformamide (DMF) which is known to selectively brominate the 2-position on thiophene moieties. A Stille coupling with the stannylated and 2-(tributyltin)thiophene is performed to produce an alkylated terthiophene derivative that is then subjected to another stannylation for the final coupling. A Stille coupling between the stannylated hydrophobic segment and the hydrophilic brominated thiophene-PEG portion was performed to yield the final product. This reaction sequence was successful for quaterthiophene derivatives with either 24 or 45 ethylene glycol repeats.

2.2.2 Quinquethiophene Amphiphiles

To further extend the π -conjugated segment of the molecule, 5T versions of the molecule were synthesized with PEG segments of n=25 and 45 length using a similar methodology of successive Stille coupling that was employed as discussed for the 4T derivative. Early attempts to synthesize the 5T molecules employed a coupling between a tributyltin substituted bithiophene and brominated bithiophene alkyl substrate as seen in Figure 2.2. The resulting 2octadecyl quaterthiophene was found to have very low solubility in all the solvents tried. Successful attempts were made to add a tributyltin group to the molecule by a nucleophilic procedure, but the limited solubility severely restricted the scale of the reaction. In order to avoid the solubility issue in this synthesis, the hydrophilic segment was redesigned. Instead of using a monothiophene carboxylic acid, 2-bromo-5'-bithiophene carboxylic acid was synthesized using a previously reported protocol.¹¹⁵ Because 2-bromo-5'-bithiophene carboxylic acid has low solubility in solvents compatible with DPTS/EDC esterification reactions, the thiophene-PEG ester was formed by first synthesizing the acid chloride of 2-bromo-5'-bithiophene carboxylic acid. The acid chloride derivative was found to have high solubility is common organic solvents, which allowed to esterification to proceed.



Figure 2.2 Synthetic scheme for 5T derivative a) n-butyl lithium, 1-bromododcane, THF b) NBS, DMF c) 2-tributyltin bithiophene, Pd(PPh₃)₄, DMF d) n-butyl lithium, SnBu₃Cl, THF e) **1**, Pd(PPh₃)₄, DMF.

Throughout this chapter, the molecules are named according to the length of the oligothiophene followed by the molecular weight of the PEG tail. For n=24 the number averaged molecular weight (M_n) is 1100 g/mol and for n=45, $M_n = 2000$ g/mol. As an example a

4T derivative with a PEG tail that has a molecular weight of 1100 g/mol would be known as 4T-1100.

2.3. Self-Assembly Properties

Very high concentration (> 10 wt %) solutions of all derivatives can be obtained in organic solvents and water without precipitation. At high concentrations in water (40 wt%) very dark self-supporting gels are formed for all derivatives. In order to form the gels, the molecules were dissolved at concentrations below the gel formation point followed by solvent evaporation until the desired concentration is obtained as seen in Figure 2.3. The aqueous gels do not melt even upon heating to the boiling point of water most likely due to strong a strong interaction between the solvent and PEG tails stabilizing the assembly. A self-supporting gel was also formed in acetonitrile (ACN) at 40 wt %. Because ACN has less ability to hydrogen bond, these gels melt before the boiling point of the solvent indicating the importance of hydrogen bonding in the final structure.



Figure 2.3. a) 40 wt% solutions of 4T-2000 in THF (right) and water (left). Inverted vial shows the self supporting nature of the gel. b) A 4T-2000 aqueous gel squeezed between glass slides to show the color of gel.

The thermal stability of the molecules was explored by thermogravimetric analysis (TGA) to make sure no degradation occurred during gel preparation. TGA traces of 4T-1100 and 4T-2000 are shown in Figure 2.4. Decomposition of both molecules did not begin until T > 200 °C which is well above the temperatures to which the molecules are subjected during gel formation. Interestingly, starting at T \approx 230 °C a slight decomposition was apparent before the onset of full thermal decomposition at T = 350 °C. In both 4T-1100 and 4T-2000 the initial mass lost is approximately 44 mass units. This is most likely the thermal cleavage of the ester and subsequent loss of carbon dioxide.

2.3.1 Lyotropic Liquid Crystalline Phase

In order to investigate the molecular order within the gel phase, the samples were submitted to Polarized Optical Microscopy (POM). In the case of all derivatives, a lyotropic liquid crystalline phase was discovered by the observation of highly birefringent domains that uniformly switch from light to dark upon a 45° rotation in respect to the cross-polarizers as seen in Figure 2.5. After applying sheer force to the gel, homogenous alignment was observed with the formation of large domains on the micron scale.

2.3.2 Structural determination of Liquid Crystalline Phase

Upon discovery of the of a lyotropic liquid crystalline phase Small Angle X-ray Scattering (SAXS) was used to determine the molecular structure in aqueous gel. In the 4T derivatives, X-ray scattering revealed the presence of lamellar ordering in the gel phase



Figure 2.4. a) Thermogravimetric analysis of 4T-2000 and 4T-1100 molecules showing degradation not occurring until T > 200 °C. b) Closer view of TGA curve showing loss of carbon dioxide at T = 225 °C.



Figure 2.5. POM images showing uniform switching from light to dark upon rotation of 45° with respect to the cross-polarizers.

as seen in Figure 2.6. With 4T-1100, the (001), (002), and (003) peaks were present at corresponding to d = 11.3, 5.7, and 3.0 nm respectively, while for 4T-2000 a strong (001) peak was present corresponding to d = 13.0 nm with a weak (002) peak at d = 6.1 nm. The disappearance of higher order peaks in the 4T-2000 derivative is indicative of less long-range ordering within the sample. Since the only structural difference between 4T-1100 and 4T-2000 is the PEG chain length, the disruption of the lamellar structure must come from the longer PEG tail. As PEG becomes longer, it has a greater propensity to crystallize. The crystallization is indicated macroscopically by the phase transition from a viscous liquid at low molecular weights to a solid at higher molecular weights with the transition occurring around 20 repeat units. In 4T-2000, the crystallization of the PEG segment is likely disrupting the ability to from regularly spaced lamellar layers. No diffraction peaks were found in the ACN gels so the analysis was focused on understanding the aqueous system.

Unlike the 4T derivatives, the 5T molecules did not show a lamellar phase in the aqueous gel by SAXS. While both the 5T-1100 and 5T-2000 derivatives form self-supporting gels, Bragg diffraction peaks were not observed by SAXS for either 5T derivative as seen in figure 2.6. This is surprising because the only structural difference between the 4T and 5T derivatives is the addition of one thiophene ring. OPV derivatives showed similar lamellar LC phases by SAXS as the 4T derivatives, indicating the propensity to form lamellar structures with similar molecules.¹⁰⁷ In oligothiophene crystal structures and vacuum-deposited films, it is known that odd-numbered thiophene oligomers are more prone to crystal defects and slips than their even-numbered analogues.¹¹⁶⁻¹¹⁸ Bragg diffraction peaks in the SAXS would not be expected if many defects were present in the conjugated planes of a lamellar structure due to the lack of long-range



Figure 2.6. Small angle X-ray plots of a) 4T-1100, b) 4T-2000, c) 5T-1100, and d) 5T-2000. 4T derivatives show lamellar ordering.

order. The change from a well-ordered system to a less ordered system with the addition of one thiophene ring further proves the importance of the conjugated moiety within the final supramolecular structure.

Due to the wide range of possible conformations in the reported molecules in solution, an accurate and realistic molecular length is difficult to determine. However, it is known that PEG polymers alone can form a 7/2, or seven monomer repeat units per two turns, helical conformation with a pitch of 1.93 nm.¹¹⁹ The hydrophilic segment is calculated to be 3.7 nm when fully extended, although it is to be partially collapsed in an aqueous environment. Considering the aforementioned conditions, a realistic length for 4T-2000 would be 12-15 nm and 4T-1100 would be 8-11 nm. The lamellar layer spacing found by SAXS would then be consistent with an interdigitated bilayer and a smectic LC phase as shown in figure 2.7. While it would be expected that the oligothiophene-PEG derivatives could form a hexagonal packing due to the bulkiness of the hydrophilic tail giving the molecule a conical shape, the presence of a lamellar shape is indicative of aggregation between the conjugated portions of the hydrophobic segment.^{120, 121} The π - π stacking between molecules is likely frustrating the hydrophobic collapse in the aqueous environment and effectively increasing the cross-sectional area of the segment.

In conjunction with SAXS, the nanostructure of the gels was investigated by atomic force microscopy (AFM). Films cast from dilute aqueous solutions on silicon wafers were allowed to completely dry before measurement. In 4T-1100 and 5T-1100 samples, sections of films with lamellar ordering were observed as seen in Figure 2.8. The average height of the lamellae for 4T-1100 was measured to be 12.9 ± 3.52 nm while the average height of 5T-1100 lamellae was found to be 10.1 ± 2.8 nm. There is no statistical difference in the lamellar height between the



Figure 2.7. a) Molecular structure of 4T-1100 color coded for model. b) Model of lamellar molecular packing found in aqueous gels.



0.0



1.7 μm

50 nm







Figure 2.8. Atomic Force Microscopy of a) 5T-1100 with b) height profile showing lamellar ordering. Atomic Force Microscopy of a) 4T-1100 with b) height profile showing lamellar ordering.

d)

molecules, which would be expected due to the similarity in molecular composition between the two derivatives. The theoretical difference in molecular length between the 4T and 5T derivatives would only be one thiophene ring with a molecular length of 2.7 Å, well within the error of the measurement. In the case of 4T-1100 the height of each lamellar layer by AFM coincides with the measured lamellar d spacing in SAXS, further confirming the presence of an ordered layered structure. Interestingly, a lamellar structure was observed in the 5T-1100 by AFM measurement even though no diffraction peaks were seen in X-ray. This is likely due to the lamellar structure being present but not ordered enough to be detected by X-ray.

2.3.3 Optical Properties of Nonionic Oligothiophene Surfactants

Understanding what molecular structural features affect the assembly of conjugated oligomers is important because the molecular orientation is the critical factor for electronic functions. Optical spectroscopy was used to investigate how the chromophores are ordered with respect to each other. Absorption and emission spectra of the derivatives were measured in water and THF. Water was chosen because it has been shown to induce assembly into ordered structures, unlike THF where gel formation was not observed even at high concentrations. In the case of the 4T molecules, large shifts of the absorbance and fluorescence maximum were observed between the two solvents as seen in Figure 2.9. When the absorbance is measured in THF the $\lambda_{max} = 418$ nm for both 4T-1100 and 4T-2000. On the other hand, in water the λ_{max} of absorption for 4T-2000 was found to be 379 nm and 370 nm for 4T-1100. For both 4T derivatives, the λ_{max} of emission was measured to be 508 nm in THF and 543 nm in water. With the 5T derivative the same trend was observed. In THF the absorbance $\lambda_{max} = 436$ nm for both



Figure 2.9. Optical pictures of a) 0.1 wt % solution of 4TG in water (left) and THF (right) and b) illuminated with 365 nm light showing emission contrast between solvents. c) UV-vis and d) fluorescence spectra of 4T-1100 and 4T-2000. e) UV-vis and f) fluorescence spectra of 5T-1100 and 5T-2000.

5T-1100 and 5T-2000, while in water the absorbance $\lambda_{max} = 395$ and 390 nm for 5T-2000 and 5T-1100 respectively. The data has been normalized to the peak maximums for ease of comparison between peaks.

The hypsochromic (blue) shift of the absorbance maximum coupled with the bathochromic (red) shift of the fluorescence maximum indicate face-to-face packing of the thiophene chromophores based upon exciton coupling theory.¹²² If two identical chromophores are in close proximity with each other, their transition dipole moments will begin to interact when excited by light. The interaction of the transition dipole moment causes the energy level of the excited state to split into a higher and lower energy state of which only one transition is allowed as seen in figure 2.10. Either a face-to-face (H-aggregation) or a head-to-tail (J-aggregation) orientation between the chromophores can occur. In the case of H-aggregation, the higher energy transition is allowed while in J-aggregation the lower energy state. Experimentally this results in a blue shifted absorption with a red shifted emission for the H-aggregate case and a red shift in both the absorbance and fluorescence in the J-aggregate case. Finally, amount of shift drastically decreases with increasing the distance between dipoles.¹²³

Based upon the optical spectroscopy results, it is concluded that the thiophene chromophores are packed in a face-to-face manner within the lamellar structures formed in aqueous conditions. Furthermore, the effect of the PEG tail on the chromophore packing is further illustrated by the absorbance spectra of each molecule. In the case of the 4T derivatives, the 4T-1100 derivative has a 48 nm hypsochromic shift while the 4T-2000 derivative only has a



Figure 2.10. Energy schematic of the absorbance of different aggregated chromophores orientations (left) and the transition dipole angular dependence on these excitations (right). (Reproduced from Whitten et al. *Acc. Chem. Res.* **1993**, *26*, 502-509.) ES and GS stand for excited state and ground state, respectively. Solid lines and dotted lines indicate allowed and disallowed transitions, respectively. The arrows in the circles represent the orientation of transition dipole moments for the allowed transitions of these orientations.

39 nm shift. In the 5T case, the 5T-2000 a 41 nm blue shift was observed while a 46 nm blue shift was observed for 5T-1100. As was previously discussed, the amount of shifting is highly dependent on the distance between chromophores.¹²³ Because there is a greater shift in both 4T-1100 and 5T-1100 than the PEG-2000 derivatives, the longer PEG tail seems to frustrate π - π stacking between chromophores more than the shorter PEG tail. This is likely due to the greater propensity of the longer chain PEG tail to crystallize and the crystallization is disrupting the packing of the chromophores.

To further understand the effect of concentration on the self-assembly of the system, the fluorescence emission of 4T-2000 was measured at various concentrations in water. At the



Figure 2.11. a) Photograph showing aqueous solutions of 4T-2000 from 10 wt% (left) to 0.001 wt % left. b) Normalized fluorescence emission of at various concentrations of 4T-2000. c) Plot of fluorescence emission intensity normalized by concentration versus solution concentration. Maximum indicates critical micelle concentration.



Figure 2.12. Differential Scanning Calorimetry trace of a) 4T-1100, b) 4T-2000, c) 5T-1100, and d) 5T-2000 (Exotherm up). All traces shown are the second cycle and all peaks are thermally reversible.

highest concentration measured (10 wt %) the $\lambda_{max} = 605$ nm indicating the presence of Haggregates in solution. Upon dilution, the emission maximum blue shifted, indicating the loss of aggregation at lower concentrations as seen in Figure 2.11. By plotting the emission intensity normalized to concentration, a sharp increase in intensity is observed upon dilution from 0.1 wt % to 0.01 wt % that upon further dilution causes an intensity decrease (figure 2.11c). The increase in intensity upon dilution is further indicative of loss of assembly because aggregation typically causes fluorescence quenching due to additional non-radiative decay pathways. The emission maximum blue shifting coupled with the sharp increase in intensity at 0.01 wt % indicates that 0.01 wt % is the concentration at which aggregation occurs.

2.3.4 Molecular Structure Influence on Packing in the Solid State

To further probe how molecular design affects molecular interactions, differential scanning calorimetry (DSC) was performed on each derivative as a solid. Two major phase transitions are observed for each derivative as seen in Figure 2.12. The transition at lower temperature corresponds to the melting of the PEG region of the molecule. For both derivatives the lower temperature transition occurs at the same temperature as the melting point of the PEG polymer alone. The higher temperature transition is then attributed to the melting of the hydrophobic portion of the molecule. Because the π - π stacking is the dominate force in the hydrophobic region, the transition temperature should related to the strength of this interaction.

Looking within the 4T or 5T pair of molecules, the effect of the length of PEG tail on molecular packing is demonstrated again. The higher temperature melting transition occurred at $T_m = 84$ °C for 4T-2000 and at $T_m = 90$ °C for 4T-1100. The same trend was observed in the 5T

system as well. For the 5T-1100 derivative the melting transition occurred from $T_m = 140$ °C and from $T_m = 133$ °C for the 5T-2000 derivative. Typically in PEG polymers, the melting temperature increases with increasing molecular weight, which is observed with the lower temperature transition. Because the transition temperature of the second transition occured at a higher temperature for the PEG-1100 derivatives than the PRG-2000 derivatives, it is our interpretation that the temperature increases are due to stronger π - π stacking in the PEG-1100 derivatives than the PEG-2000 derivatives.

By comparing the DSC traces of the 4T derivatives to the 5T derivatives, the effect of the conjugated segment can be elucidated. The first trend that is apparent is that the phase transition temperature is higher in the 5T derivatives than the 4T derivatives, signifying that more thermal energy is needed to disrupt the molecular ordering in 5T than 4T. Because the only molecular difference between the two derivatives is the addition of a thiophene ring, the added thermal stability of 5T is due to the increased π conjugation. The increased conjugation in the 5T derivatives gives rise to a greater amount of π - π stacking than the 4T derivatives. This observation is consistent with the fact that the strength of π - π interactions increases with an increase in π conjugation length. The other observed trend is the decrease in phase transition peak area of the 5T when compared with the 4T. In DSC, the area of the peak is known to correspond to the crystallinity of the system.¹²⁴ The decrease in peak area of the 5T derivatives further indicates a less crystalline molecular ordering of the 5T systems due to having an odd number of thiophene rings.

2.4 Electronic Properties of Non-Ionic Thiophene Surfactants

As stated above, both the length of PEG tail and number of thiophene rings has an effect on the packing of the conjugated segment. To probe the effect these substitutions have on the electronic properties of the system, the conductivity of all four derivatives was measured. To perform conductivity measurements, films were cast from 1 wt % solutions in water onto prepatterned gold electrodes as seen in Figure 2.13. After film deposition, the samples were dried overnight under vacuum to remove any solvent. Films were deposited onto lithographically patterned four point probe gold electrodes with a gap distance between the inner electrodes of 35 µm in order to minimize contact resistance.

All deposited films showed a high degree of birefringence as observed under POM indicating molecular ordering within the film (Figure 2.13b). The current-voltage (I-V) curve of each system is shown in Figure 2.14. From the I-V curves, the average conductivity of several devices is calculated based upon the conductance and the film thickness, measure by profilometery, assuming uniform resistivity across the electrode gap. In the 4T system, the average conductivity of 4T-2000 is 4.03×10^{-7} S/cm and 1.16×10^{-6} S/cm for 4T-1100. For the 5T system, the average conductivity of 5T-2000 was found to be 3.08×10^{-6} S/cm and 9.06×10^{-6} S/cm for the 5T-1100 system. For both 4T and 5T systems, the conductivity of the PEG-1100 molecules increases by almost and order of magnitude over the PEG-2000 molecules. Furthermore, the conductivity of the 4T derivatives is almost an order of magnitude lower than the analogous 5T derivative. The decrease in conductivity between the PEG-2000 and the PEG-1100 derivatives is attributed to the disruption in π - π stacking found with the longer PEG tail. In oligothiophene derivatives, the degree of π - π stacking often determines the efficiency of conduction in a film. It is also known that the longer the oligothiophene derivative, the higher the



Figure 2.13. a) Photograph of pre-fabricated electrodes for 4 point probe measurement of conductivity. b) POM image of film deposited on electrodes showing birefringence of the film. (device fabricated and measurement by Melanie Disabb)



Figure 2.14. I-V curves measured for a) 4T-1100, b) 4T-2000, c) 5T-1100, and d) 5T-2000 with the average conductivity reported.

conductivity of a film due to a decrease in the band gap energy.¹²⁵⁻¹²⁷ This trend is the cause of the increased conductivity of the 5T system.

2.5 Hybrid Materials with Titanium Dioxide Nanorods

2.5.1 Titanium Dioxide Nanorod Synthesis

In an attempt to exploit the supramolecular ordering found in the thiophene/PEG system for photovoltaic applications, titanium dioxide (TiO₂) nanorods where synthesized to be the acceptor in a bulk heterojunction cell. TiO₂ was chosen as the acceptor because it is one of the most commonly used acceptors in photovoltaic devices such as Graetzel cells.^{41, 87, 128, 129} In most synthetic procedures for making crystalline TiO₂ high temperatures (T > 400 °C) are required.¹³⁰ Because those temperatures are incompatible with organic molecules, a low temperature route developed by Weller in 2003 was used.¹¹² By mixing the preformed nanorods with the thiophene-PEG derivatives, the expectation was that the hydrophilic PEG tail will interact with the TiO₂ and then use the self-assembly properties of the organic phase to form an ordered hybrid material.

The TiO₂ nanorods were synthesized using sol-gel chemistry from the precursor titanium isopropoxide and oleic acid as the surfactant.¹¹² Oleic acid is first heated to 120 °C for 20 min to evaporate any residual water from the solution. Water was found to promote non-specific growth of nanoparticles so it is important to avoid at this step in the synthesis. Upon drying the oleic acid, the temperature is dropped to 90 °C and the precursor is added. After a short time, an aqueous solution of an amine base is added to the solution and allowed to age at 90 °C. The synthesized nanorods were found to be of the anatase crystal structure as seen in Figure 2.15.

The nanorods were also found to be 5-7 nm in width and 50-100 nm in length by TEM analysis. The oleic acid capping surfactant can be washed away by successive washes with ethanol.

2.5.2 Mixing Studies with Thiophene-PEG derivatives

Initially, transmission electron microscopy (TEM) was used to probe the interaction of the thiophene-PEG derivatives with the anatase nanorods. Nanorods with and without oleic acid were sonicated with 4T-1100 in solution and then cast onto a film. The TEM micrographs do not reveal the formation of a well-ordered hybrid structure as seen in Figure 2.16. The nanorods are more dispersed in the film when coated with oleic acid than the bare rods, possibly indicating that the 4T-1100 is not acting as a surfactant for the rods. Because TEM is not a good technique to probe the location of nanorods in 3D, Secondary Ion Mass Spectrometry (SIMS) was used to investigate the location of nanorods in the blend. The SIMS map again reveals clumps of TiO₂ interspersed in a bed of organic material further indicating a lack of interaction between the organic and inorganic phases (figure 2.17).

Without observing evidence of interaction between the organic and inorganic phase by microscopy, a fluorescence quenching experiment was used to investigate if the nanorods where close enough for electron transfer. If the thiophene moiety and the TiO₂ are close enough to split the exciton formed in the thiophene upon excitation, the electron will transfer to the TiO₂ thus preventing fluorescence from occurring.⁸⁷ Experimentally a quenching of fluorescence will be observed upon addition of the electron acceptor if electron transfer is occurring. Two additional molecules were synthesized to help understand what molecular features are important for TiO₂ binding. Two new terthiophene (3T) derivatives were synthesized as seen in figure 2.18. One



Figure 2.15. a) TEM image of TiO_2 nanorods formed in solution. b) X-ray diffraction pattern showing an anatase crystal phase.



Figure 2.16. TEM images of TiO_2 nanorods mixed with 4T-PEG1100. a) Nanorods coated with oleic acid. c) Bare nanorods with oleic acid removed. Images are unstained so all contrast comes from the nanorods.



Figure 2.17. From the depth profile of the 5T-PEG $1100:TiO_2$ hybrid, a 3-D reconstruction was created. The red is represents the CH₂ content in the film, and the white represents the TiO₂ nanorods. The overlay image is a combination of the two components.

derivative is simply a 3T conjugated to a hexyl tail (3T-hexyl). This was made to see if either the long PEG or alkyl tail was inhibiting electron transfer. The second derivative contains a phosphonic acid mono methyl ester (3T-PA) which is a known strong binder for inorganic nanocrystals.^{112, 131}

To test for fluorescence quenching, TiO_2 nanorods were titrated into a solution of organic chromophore. The fluorescence spectra obtained for the three molecules are seen in Figure 2.19.



Figure 2.18. Synthetic Schematic for 3T-PA. a) n-BuLi, 1,4 dibromobutane, THF b) P(OEt)₃ c) NBS, DMF d) 2-tributyltinthiophene, Pd(PPh₃)₄, DMF e) water, ethanol, KOH.



Figure 2.19. Synthetic procedure for 3T-hexyl a) NBS, DMF b) 2-tributyltinthiophene, Pd(PPh₃)₄, DMF.



Figure 2.20. Fluorescence spectra of TiO_2 mixed with a) 4T-PEG2000, b) 3T-PA, and c) 3T-hexyl in a chloroform solution.

In only the phosphonic acid derivative fluorescence quenching (92 %) was observed. In both the 4T-2000 and the 3T-hexyl derivatives, little to no decease in the fluorescence intensity was detected. The lack of quenching in the in the 4T-2000 and 3T-hexyl groups indicate that they are not able to interact with the inorganic phase. Either the molecules are not able to displace the oleic acid on the nanorods or there is not sufficient driving force for interaction in the molecules. Due to the efficient quenching on the 3T-PA, it is concluded that a TiO₂ binding group is essential for efficient electron transfer. The PEG group is unable to act as a TiO₂ binding group for the thiophene-PEG derivatives.

2.6 Summary and Outlook

This chapter discussed the synthesis and characterization of novel nonionic water soluble oligothiophene surfactants. The derivatives were found to assemble into lamellar LC phases due to the amphiphilicity and π - π stacking inherent to the molecules. The length of the PEG segment as well as the number of thiophene rings was shown to have a direct impact on the molecular ordering within the lamellar phase. Increasing the PEG tail was observed to disrupt the π - π stacking ability of the thiophene core. The disruption of π - π stacking directly affected the optical and electronic properties of the derivatives. The number of thiophene rings was discovered to dictate the molecular packing as well. An attempt was made to use the LC properties of the thiophene amphiphiles to obtain an ordered hybrid structure with TiO₂. The hydrophilicity of the PEG tail was insufficient to bind to the TiO₂ for efficient electron transfer. In order to obtain electron transfer, a TiO₂ binding group is essential. While the attempt to make an ordered hybrid
material was not successful using the materials described in this chapter, the influence of molecular design on the self-assembly properties of a molecule was clearly demonstrated.

2.7 Experimental

2.7.1 General

Unless otherwise mentioned, all starting materials were obtained from commercial sources (Sigma-Aldrich, TCI, Alfa Aesar) and used without further purification. ¹H NMR and ¹³C NMR spectra were recorded in a Varian Inova 500 (500 MHz for ¹H and 120 MHz for ¹³C NMR) spectrometer using the solvent proton signal as standard. DPTS¹⁰⁶ and 2-bromo-5'- bithiophene¹¹⁵ were synthesized according literature procedures. SIMS and conductivity analysis was performed by Melanie Disabb of the Stupp lab. TEM analysis was done by Melanie Disabb and Lorraine Hsu of the Stupp lab. TiO₂ nanorods were synthesized following a literature procedure.¹¹²

UV-Vis absorption spectra were collected on a Cary 500 spectrometer in double beam mode. All samples were prepared from a 0.1 wt % stock solution in water and then diluted into (15 μ L into 3 mL) of the desired solvent in a 1 cm pathlength cuvette. Fluorescence spectra were recorded on a PC1 Spectrofluorometer in right angle geometry using monochromators with a FWHM of 8 nm for both the excitation and emission. All spectra were collected by exciting at the absorption maxima.

All gels were formed by dissolving the derivative in a water beneath the gelation concentration (< 10 wt %) and then evaporating the solvent to the desired concentration. Solvent loss was measured by mass loss. Thermogravimetric analysis (TGA), preformed on these

molecules at 10 °C/min in air using a TA Instruments 2920 DSC/TGA, showed a decomposition onset by 200 °C for all amphiphiles. DSC was performed on the amphiphiles in the solid state with 5 mg of sample at heating and cooling rates of 5 °C/min. with two temperature cycles. Phase transitions were determined by using the second of the two cycles.

A Leitz Laborlux 12POL polarizing microscope was used with an attached Sony XC-ST-70 CCD camera was used for POM studies. POM images were taken by depositing a thin layer of gel (40 wt %) squished between two glass slides to make the sample thin enough to be transparent.

AFM measurements were taken on a Nanoscope Multimode ScanningProbe Microscope. Films were cast from a dilute aqueous solution (0.1 wt %) on to a freshly cleaned polished Silicon Wafer. The wafers were cleaned by soaking in a piranha bath followed by a water bath and then finally in an isopropanol bath for 15 min each. Transmission Electron Microscopy was performed on a Hitachi 8100 operating at 100 kV on holey carbon coated Cu TEM grids. All TEM samples are unstained so the inorganic phase can be clearly seen.

Conductivity measurements were performed in a bottom contact 4 point probe geometry. Films were deposited by spin casting onto pre-patterned electrodes at 1000 rpm and then allowed to fully dry. All samples were doped in iodine vapor for 30-60 min before measurement. Film thickness was measured using a Tencor P10 profilometer. I-V Curves were collected on a Micromanipulator Corp. model 1800 probe station connected to a Keithley 2000 Sourcemeter.

To probe the composition of the hybrid films as a function of depth, a Physical Electronics, PHI TRIFT III Time-of-flight secondary ion mass spectrometer (ToF-SIMS) was

used. Spectra from the neat components were collected and then tracked through the depthprofiling mode.

2.7.2 Organic Synthetic Procedures

2-bromo-5-thiophene PEG-1100 ester (1) In a round bottom flask, 2-bromo-5-thiophene carboxylic acid (1.00 g, 4.8 mmol) was dissolved in 150 mL of dichloromethane. To the solution, PEG-1100 mono methyl ether (5.28 g, 4.8 mmol), DPTS (1.69 g, 5.76 mmol), and EDC (1.66 g, 8.64 mmol) was added. The solution was stirred at room temperature for 16 h. The organic layer was then extracted with sat. NaHCO₃ three times. Following the extraction, the combined organic layer was dried with MgSO₄, and then concentrated. The crude product was purified by column chromatography (silica gel; methanol/chloroform, 5/95) to yield 6.26 g (66 %) for desired product as a waxy white solid. ¹H NMR (CDCl₃, ppm): δ 7.57 (d, 1H, J = 4 Hz), 7.09 (d, 1H, J = 4 Hz), 4.43 (t, 2H, J = 3 Hz), 3.81-3.55 (m, 95H, PEG), 3.39 (s, 3H)

2-bromo-5-thiophene PEG-2000 ester (1) Prepared in a similar mythology as previous molecule except using PEG-2000 mono methyl ester. ¹H NMR (CDCl₃, ppm): δ 7.58 (d, 1H, J = 4 Hz), 7.10 (d, 1H, J = 4 Hz), 4.47 (t, 2H, J = 3 Hz), 3.81-3.55 (m, 180H, PEG), 3.39 (s, 3H)

2-Bromo-5'-bithiophene PEG-1100 ester (2) In a 250 mL round bottom flask, 2-bromo-5'bithiophene carbonyl chloride (0.66 g, 2.16 mmol) was dissolved in toluene (100 mL). To the solution PEG-1100 mono methyl ether (2.37 g, 2.16 mmol) was added along with triethylamine (0.22 g, 2.16 mmol). The reaction was allowed to stir at room temperature for 16 hr. The toluene was removed *en vaccuo*. The solid was then dissolved in chloroform and extracted three times with 2M HCl. The combined organic layer was dried with MgSO₄ and then concentrated. The crude product was purified by column chromatography (silica gel; methanol/chloroform, 3/97) to yield 1.98 g (67 %) of the desired product as a waxy white solid.

2-octadecyl-5-(thiophen-2-yl)thiophene (3) In a flame-dried flask, 2,2'-bithiophene (3.0 g, 18 mmol) was dissolved in anhydrous THF (150 mL) and cooled to 0 °C. *n*-Butyllithium (7.2 mL, 2.5 M solution in cyclochexane) was added dropwise to the solution. The reaction was stirred for 30 min. Then 1-bromooctadecane (7.3 g, 22mmol) in 20 mL dry THF was added drop wise into the reaction mix. The reaction was warmed to room temperature and stirred for 16 h. The reaction was quenched with water and then extracted three times with sat. NaCl (aq). The organic layer was dried with Na₂SO₄ and concentrated. The crude product was purified by column chromatography (silica gel; chloroform/hexanes, 10/90) and recrystallized from CHCl₃/MeOH to yield 4.19 g (47%) the desired product as a yellow solid. ¹H NMR (CDCl₃, ppm): δ 7.18 (d, 1H, J = 5.0 Hz), 7.11 (d, 1H, J = 3.5 Hz), 7.01-6.99 (m, 2H), 6.68 (d, 1H, J = 4.0 Hz), 2.80 (t, 2H, J = 8), 1.69 (qn, 2H, J = 8 Hz), 1.39-1.23 (m, 30H), 0.90 (t, 3H, J = 6.5 Hz).

2-bromo-5-(5-octadecylthiophen-2-yl)thiophene (4) To a solution of **2** (3.0 g, 6.0 mmol) in DMF (250 mL) was added NBS (1.3 g, 6.6 mmol) was added over 4 h at 0 °C. The reaction stirred in the dark for 16 hr while warming to room temperature. To remove the solvent, the reaction was diluted in CHCl₃ and extracted six times with 5% citric acid (aq). The organic layer was dried with Na₂SO₄ and concentrated to yield 3.49 g (92 %) of the desired product. ¹H NMR

(CDCl₃, ppm): δ 6.95 (d, 1H, J = 4.0Hz), 6.92 (d, 1H, J = 3.0 Hz), 6.84 (d, 1H, J = 4.0 Hz), 6.67 (d, 1H, J = 3.5 Hz), 2.78 (t, 2H, J = 7.5 Hz), 1.68 (qn, 2H, J = 8.0 Hz). 1.23-1.38 (m, 30H), 0.90 (t, 3H, J= 7 Hz).

2-octadecyl terthiophene (5) A solution of **3** (2.0 g, 4.0 mmol) and 2-(tributylstannyl) thiophene (1.5 g, 4.0 mmol) in DMF (50 mL) was sparged with N₂ gas for 20 min.

Tetrakistriphenylphosphine palladium(0) (50 mg) was added to the solution. After stirring at 100 °C for 16 h, the reaction was cooled to room temperature. The reaction mix was diluted with chloroform and extracted three times with 5% citric acid (aq). The organic layer was dried over Na₂SO₄ and the solvent was removed in vacuo. The crude product was recrystallized from CHCl₃/MeOH to yield 1.32 g (66%) of the desired product as a yellow solid. ¹H NMR (CDCl₃, ppm): δ 7.22 (d, 1H, J = 5.0Hz), 7.17 (d, 1H, J = 3.5 Hz), 7.07 (d, 1H, J = 4.0 Hz), 7.03 (t, 1H, J = 4.5 Hz), 7.01 (d, 1H, J = 3.5 Hz), 7.00 (d, 1H, J = 4.0 Hz), 6.70 (d, 1H, J = 3.5 Hz), 2.80 (t, 2H, J = 7.5 Hz), 1.69 (t, 2H, J = 7.5 Hz), 1.23-1.39 (m, 30H), 0.90 (t, 3H, J = 7.0).

2-octadecyl-5'-tributylstannyl terthiophene (6) A solution of **4** (0.14 g, 0.28 mmol) in THF (40 mL) in a flame dried flask was cooled to -78 °C in a dry ice/acetone bath. To the solution *n*-butyllithium in a 2.5 M solution in cyclochexane (0.14 mL) was added drop wise to the solution. The reaction was stirred for 30 minutes, then tributyltin chloride (0.11g, 0.33 mmol) was added. After stirring for 16 h, the reaction was diluted with hexanes and extracted three times with sat. NaCl (aq), dried with Na₂SO₄, and concentrated to give the desired product. The product was used in the next step without purification.

4T-PEG1100 (7a) A solution of **6** (0.31 g, 0.40 mmol) and **1** (0.52 g, 0.40 mmol) in DMF (50 mL) was sparged with N₂ gas for 20 min in an air-free Schlenk flask. Tetrakistriphenylphosphine palladium(0) (4 mg, 1 % cat loading) was added to the solution. After stirring at 100 °C for 16 h, the reaction was cooled to room temperature. The reaction mix was diluted with chloroform and extracted three times with 5% citric acid (aq). The organic layer was dried over MgSO₄ and the solvent was removed in vacuo. The crude product was purified by column chromatography (CHCl₃/MeOH, 95/5 x2) to yield 0.65 g (67%) of the desired product as a red-orange solid. ¹H NMR (CDCl₃, ppm): δ 7.21 (d, 1H, J = 4 Hz), 7.18 (d, 1H, J = 4.5 Hz), 7.14 (d, 1H, J = 4.5 Hz), 7.07 (m, 2H), 7.03 (d, 1H, J = 3.5 Hz), 7.00 (d, 1H, J = 4 Hz), 6.69 (d, 1H, J = 3 Hz), 4.53 (t, 2H, J = 4.5 Hz), 3.87-3.57 (m, 94H, PEG), 3.41 (s, 3H), 2.51 (t, 2H, J = 7.5 Hz), 1.71 (q, 2H, J = 7.5 Hz), 1.35-1.20 (m, 30H), 0.84 (t, 3H, J = 8 Hz).

4T-PEG2000 (7b) A solution of **6** (0.95 g, 1.20 mmol) and **1** (2.65 g, 1.20mmol) in DMF (50 mL) was sparged with N₂ gas for 20 minutes in an air free Schlenk flask. Tetrakistriphenylphosphine palladium(0) (14 mg, 1 % cat loading) was added to the solution. After stirring at 100 °C for 16 h, the reaction was cooled to room temperature. The reaction mix was diluted with chloroform and extracted three times with 5% citric acid (aq). The organic layer was dried over MgSO₄ and the solvent was removed in vacuo. The crude product was purified by column chromatography (CHCl₃/MeOH, 96/4 x2) to yield 1.64 g (52%) of the desired product as a red-orange solid. ¹H NMR (CDCl₃, ppm): δ 7.14 (d, 1H, J = 4 Hz), 7.19 (d, 1H, J = 4 Hz), 7.13 (d, 1H, J = 4.5 Hz), 7.07 (m, 2H), 7.01 (d, 1H, J = 4 Hz), 7.00 (d, 1H, J = 4 Hz), 6.69 (d, 1H, J = 3 Hz), 4.45 (t, 2H, J = 4.5 Hz), 3.82-3.53 (m, 180H, PEG), 3.37 (s, 3H), 2.79 (t, 2H, J = 7.5 Hz), 1.68 (q, 2H, J = 7.5 Hz), 1.38-1.26 (m, 30H), 0.87 (t, 3H, J = 7.5 Hz).

5T-PEG1100 (8a) A solution of **6** (0.22 g, 0.28 mmol) and **2** (0.32 g, 0.23mmol) in DMF (50 mL) was sparged with N₂ gas for 20 min. Tetrakistriphenylphosphine palladium(0) (50 mg) was added to the solution. After stirring at 100 °C for 16 h, the reaction was cooled to room temperature. The reaction mix was diluted with chloroform and extracted three times with 5% citric acid (aq). The organic layer was dried over Na₂SO₄ and the solvent was removed in vacuo. The crude product was purified by column chromatography (gradient CHCl₃ to CHCl₃/5% MeOH to yield 0.40 g (80%) of the desired product as a red solid. ¹H NMR (CDCl₃, ppm): δ 7.73 (d, 1H, J = 4.0 Hz), 7.21 (d, 1H, J = 4.0 Hz), 7.15 (d, 1H, J = 4.0 Hz), 7.16 (ap, 2H, J = 4.0 Hz), 7.08 (J = 4.0 Hz), 7.02 (d, 1H, J = 3.5 Hz), 7.01 (d, 1H, J = 3.5 Hz), 6.70 (d, 1H, J = 3.5 Hz), 4.46 (t, 2H, J = 2 Hz), 3.83 (t, 2H, J = 5 Hz), 3.55-3.75 (m, 94H), 3.91 (s, 3H), 2.80 (t, 2H, J = 7.5), 1.69 (qt, 2H, J = 7.5 hz), 1.22-1.41 (m, 30H), 0.89 (t, 3H, J = 7 Hz).

5T-PEG2000 (8b) A solution of **10** (0.26 g, 0.30 mmol) and **1** (0.66 g, 0.30 mmol) in DMF (20 mL) was sparged with N₂ gas for 20 min in an air free Schlenk flask. Tetrakistriphenylphosphine palladium(0) (5 mg, 1 % cat loading) was added to the solution. After stirring at 100 °C for 16 hours, the reaction was cooled to room temperature. The reaction mix was diluted with chloroform and extracted three times with 5% citric acid (aq). The organic layer was dried over MgSO₄ and the solvent was removed in vacuo. The crude product was purified by column chromatography (gradient Chloroform to Chloroform/Methanol (90/10) x2) to yield 0.34 g (43%) of the desired product as a red-orange solid. ¹H NMR (CDCl₃, ppm): 7.73 (d, 1H, J = 3.5 Hz), 7.21 (d, 1H, J = 3 Hz), 7.15 (d, 1H, J = 3 Hz), 7.12 (d, 1H, J = 3.5 Hz), 7.10 (d, 1H, J = 4 Hz), 7.08 (d, 2H, J = 4 Hz), 7.01 (d, 1H, J = 3.5 Hz), 7.00 (d, 1H, J = 3 Hz), 6.70 (d, 1H, J = 3 Hz), 4.46 (t, 2H, J = 4.5 Hz), 3.83-3.51 (m, 180H, PEG), 3.38 (s, 3H), 1.69 (q, 2H, J = 3 Hz), 1.38-1.26 (m, 30H), 0.88 (t, 3H, J = 7 Hz)

2-octadecyl-quarterthiophene (9) A solution of **3** (0.45 g, 0.90 mmol) and 2-(Tributylstannyl) bithiophene (0.41 g, 0.90 mmol) in DMF (20 mL) was sparged with N₂ gas for 20 min inside a Schlenk flask. Tetrakistriphenylphosphine palladium(0) (10 mg, 1% cat loading) was added to the solution. After stirring at 100 °C for 16 h, the reaction was cooled to room temperature. The precipitate was filtered out, washed with dichloromethane and then dried. ¹H NMR was not possible to do poor solubility. MALDI-TOF: $[M]^+ = 582.10$ (calc 582.25).

2-octadecyl-5'-tributylstannyl quaterthiophene (10) A solution of **9** (0.14 g, 0.23 mmol) in THF (40 mL) in a flame dried flask was cooled to -78 °C in a dry ice/acetone bath. A suspension of **9** in THF was formed as the molecule is not soluble in the solvent. To the suspension *n*-butyllithium in a 2.5 M solution in cyclochexane (0.14 mL) was added drop wise to the solution. The reaction was stirred for 30 min and then tributyltin chloride (0.11g, 0.33 mmol) was added. After stirring for 16 hr, the reaction was diluted with hexanes and extracted times with sat. NaCl (aq), dried with Na₂SO₄, and concentrated to give the desired product. The product was used in the next step without purification.

2-(5'-bromobutyl)-bithiophene (11) In a flame dried Schlenk flask, bithiophene (5.00 g, 30.0 mmol) was dissolved in anhydrous THF (150 mL) and cooled to -78 °C. *n*-Butyllithium (1.6M in cyclohexane, 18.75 mL) was added slowly and allowed to react for 1 h. The 1,4-dibromobutane (6.49 g, 30.0 mmol) was added quickly to the reaction mixture. The reaction was allowed to warm to room temperature and stirred for 16 h. Water was then added to quench the reaction. The THF was removed by rotary evaporation and the remaining solid was dissolved in dichloromethane and extracted three times with sat. NaCl. The crude product was purified by column chromatography (hexanes) to yield 2.60 g (28%) of the desired product as a green oil. ¹H NMR (CDCl₃, ppm): δ 7.20 (d, 1H, J = 5 Hz), 7.12 (d, 1H, J = 3.5 Hz), 7.01 (m, 2H), 6.71 (d, 1H, J = 3.5 Hz), 3.45 (t, 2H, J = 6 Hz), 2.85 (t, 2H, J = 7.5 Hz), 1.96 (qn, 2H, J = 7 Hz), 1.86 (qn, 2H, J = 7 Hz).

diethyl 5-(bithiophene)butylphosphonate (12) In a round bottom flask, 11 (1.79 g, 6.0 mmol) was heated in triethyl phosphite (1.19 gm 7.2 mmol) at 130 °C for 4 h. The reaction mixture was allowed to cool to room temperature. The crude product was purified by column chromatography (EtOAc) to yield 2.15 g (quant.) of the desired product as oil. ¹H NMR (CDCl₃, ppm): δ 7.18 (d, 1H, J = 5 Hz), 7.10 (d, 1H, J = 3.5 Hz), 7.00 (m, 2H), 6.69 (d, 1H, J = 5.0 Hz), 4.11 (sx, 4H, J = 3 Hz), 2.82 (t, 2H, J = 2.5 Hz), 1.81-1.71 (m, 6H), 1.33 (t, 6H, J = 2 Hz).

diethyl 5-(2-bromobithiophene)butylphosphonate (13) In a round bottom flask, **12** (0.40 g, 1.12 mmol) was dissolved in DMF (100 mL), cooled to 0 °C and covered in tinfoil to prevent light in the reaction. NBS (0.25 g, 1.34 mmol) was added in portions over 4 hours to the reaction

mixture. The reaction was then allowed to warm to room temperature and stirred for 16 h. After completion of the reaction, the reaction mixture is diluted with dichloromethane and extracted with 5% citric acid (aq) until all the DMF is out of the organic layer. The organic layer is then dried with MgSO₄ and concentrated to yield 0.48 g (quant) of the desired product as an oil. ¹H NMR (CDCl₃, ppm): δ 6.95 (d, 1H, J = 4 Hz), 6.92 (d, 1H, J = 3Hz), 6.83 (d, 1H, J = 4 Hz), 6.68 (d, 1H, J = 3.5 Hz), 4.11 (sx, 4H, J = 3 Hz), 2.82 (t, 2H, J = 2.5 Hz), 1.81-1.71 (m, 6H), 1.33 (t, 6H, J = 2 Hz).

diethyl 5-(bithiophene)butylphosphonate (14) A solution of 13 (0.57 g, 1.3 mmol) and 2-(Tributylstannyl) thiophene (0.48 g, 1.3 mmol) in DMF (50 mL) was sparged with N₂ gas for 20 minutes in a Schlenk flask. Tetrakistriphenylphosphine palladium(0) (10 mg) was added to the solution. After stirring at 100 °C for 16 h, the reaction was cooled to room temperature. The reaction mix was diluted with chloroform and extracted three times with 5% citric acid (aq). The organic layer was dried over MgSO₄ and the solvent was removed in vacuo. The crude product was purified by column chromatography (EtOAc) to yield 0.46 g (80 %) of the desired product as a yellow oil. ¹H NMR (CDCl₃, ppm): δ 7.22 (d, 1H, J = 4.5 Hz), 7.17 (d, 1H, J = 3.5 Hz), 7.07 (d, 1H, J = 4 Hz), 7.03 (dd, 1H, J = 3.5 Hz), 7.01 (d, 1H, J = 3.5 Hz), 6.00 (d, 1H, J = 3 Hz), 6.70 (d, 1H, J = 3.5 Hz), 4.11 (sx, 4H, J = 3 Hz), 2.82 (t, 2H, J = 2.5 Hz), 1.81-1.71 (m, 6H), 1.33 (t, 6H, J = 2 Hz).

3T-Phosphonic acid (3T-PA) (15) In a round bottom flask, **14** (0.46 g, 1 mmol) was added to a mixture of water (30 mL) and ethanol (50 mL) containing KOH (1 g). The reaction mixture was

refluxed for 2 days. The reaction was then cooled to room temperature and diluted with water (100 mL). The ethanol was then removed by evaporation leaving the crude potassium salt dissolved in the aqueous phase. The aqueous layer was then acidified with concentrated HCl until a ppt is formed. The ppt is then dissolved with dichloromethane, washed with water, then dried with MgSO₄. Upon removal of the solvent, the product was afforded in quantitative yield as a brown oil. ¹H NMR (CDCl₃, ppm): δ 11.43 (br s, 1H) 7.22 (d, 1H, J = 4.5 Hz), 7.17 (d, 1H, J = 3.5 Hz), 7.07 (d, 1H, J = 4 Hz), 7.03 (dd, 1H, J = 3.5 Hz), 7.01 (d, 1H, J = 3.5 Hz), 6.70 (d, 1H, J = 3.5 Hz), 4.11 (qn, 2H, J = 7.5 Hz), 2.82 (t, 2H, J = 3 Hz), 1.83-1.73 (m, 6H), 1.35 (t, 3H, J = 7 Hz). ¹³C NMR (CDCl₃, ppm): δ 144.60, 137.50, 136.87, 135.87, 135.00, 128.10, 125.36, 124.56, 124.51, 123.88, 123.78, 123.66, 61.33 (d), 32.41, 29.92, 26.42, 25.27, 22.04.

2-bromo-5'-hexyl bithiophene (16) In a round bottom flask, 2-hexyl-bithiophene (1.00, 4.0 mmol) was dissolved in DMF (100 mL) and cooled to 0 °C. The reaction was kept dark and NBS (0.85 g, 4.8 mmol) was added over 4 h. The reaction was allowed to warm to room temperature and stirred overnight. The reaction was then diluted with ether and washed with 5% citric acid until the DMF was no longer in the organic layer. The organic layer was the dried with MgSO₄ and evaporated. The product was then recrystallized from water yielding 1.30 g (99%) of the desired product as a white solid. ¹H NMR (CDCl₃, ppm): δ 6.96 (d, 1H, J = 4 Hz), 6.93 (d, 1H, J = 3.5 Hz), 6.85 (d, 1H, J = 3.5 Hz), 6.68 (d, 1H, J = 4 Hz), 2.80 (t, 2H, J = 8 Hz), 1.69 (qn, 2H, J = 7.5 Hz), 1.41-1.31 (m, 6H), 0.92 (t, 3H, J = 7 Hz). ¹³C NMR (CDCl₃, ppm): δ 146.19, 139.73, 133.97, 130.72, 125.03, 123.93, 123.25, 110.37, 31.82, 30.41, 29.01, 22.84, 14.35.

2-hexyl bithiophene (17) A solution of **16** (0.50 g, 1.52 mmol) and 2-(Tributylstannyl) thiophene (0.56 g, 1.52 mmol) in DMF (50 mL) was sparged with N₂ gas for 20 minutes in a Schlenk flask. Tetrakistriphenylphosphine palladium(0) (20 mg) was added to the solution. After stirring at 100 °C for 16 hours, the reaction was cooled to room temperature. The reaction mix was diluted with chloroform and extracted three times with 5% citric acid (aq). The organic layer was dried over MgSO₄ and the solvent was removed in vacuo. The crude product was recrystallized from methanol to yield 0.42 g (85 %) of the desired product as a yellow solid. ¹H NMR (CDCl₃, ppm): δ 7.22 (d, 1H, J = 5.5 Hz), 7.17 (d, 1H, J = 3.5 Hz), 7.07 (d, 1H, J = 4 Hz), 7.03 (dd, 1H, J = 3.5 Hz), 7.01 (d, 1H, J = 3 Hz), 7.00 (d, 1H, J = 3 Hz), 6.70 (d, 1H, J = 3 Hz), 2.81 (t, 2H, J = 3 Hz), 1.70 (qn, 2H, J = 7 Hz), 1.41-1.32 (m, 6H), 0.91 (t, 3H, J = 7 Hz).

Chapter 3:

Self-Assembly and Conductivity of Hydrogen Bonded

Oligothiophene Gelators

Chapter 3. Self-Assembly and Conductivity of Hydrogen Bonded Oligothiophene Gelators 3.1 Introduction

Control over supramolecular structure is essential to achieve high-performance optoelectrical devices based on electronically conjugated organic molecules. One of the most popular classes of small molecules studied for organic electronic applications are oligothiophene derivatives due to their low band gaps that facilitate efficient charge mobility ^{94, 106, 132-135} In oligo- and polythiophene derivatives, charge conduction is known to occur by an interchain hopping mechanism through overlapping π -orbitals in adjacent molecules.^{93, 136, 137} High conductivity and mobility values can be achieved if a continuous pathway of overlapping π - π orbitals exists; however, this structural feature is largely lost in amorphous films.^{25, 105} Langumir-Blodgett, layer-by-layer, and vacuum sublimation deposition methods have been used to impart molecular ordering in films, but they are not ideal for large area depositions.¹³⁸⁻¹⁴⁰ For large area electronics, such as photovoltaic cells, field effect transistors, or light emitting diodes, a simple, one-step fabrication from spin-casting or dip-coating is desired.³² In this context, spontaneous self-assembly of molecules into ordered systems that promote orbital overlap is a promising strategy to create large area devices with conducting soft matter.^{31, 62, 107, 141-145}

There have been several reports of self-assembling oligothiophenes, but few have studied molecules with four to six repeat units that are typically required for significant electronic conductivity .^{106, 133, 146-148} A challenge in materials processing with the extended thiophene oligomers is their inherently low solubility.¹⁴⁹ In order to solubilize oligothiophene derivates for solution deposition, chemical substitutions on thiophene moiety.¹³² The specific atomic position of solubilizing groups on thiophene units can affect significantly electronic properties of the

molecule.^{150, 151} Substitutions at the β -position of the thiophene core are known to reduce electronic conductivity drastically due to interruption of π - π stacking. However, substitutions at the α position do not degrade electrical performance.²⁵ Most substituted oligothiophene derivatives unfortunately form amorphous films when solution deposited on substrates as a result of nonspecific aggregation.

To create a well-ordered film using solution deposition techniques, a secondary interaction in addition to π - π stacking should be included in the molecular design to help create conductive assemblies. In this chapter, hydrogen bonding and π - π stacking are used in an attempt to form a well ordered and solution processable oligothiophene derivatives. We report here the synthesis, self-assembly, and conductivity properties of self-assembling quater- and quinquethiophene derivatives that form self-supporting gels at low concentrations (less than 1 wt %) consisting of bundled, 1D nanostructures in various organic solvents. The role of hydrogen bonding and π - π stacking on the supramolecular structure was also explored. The formation of long ranged π - π stacked within nanofibers was then used to form conductive pathways without additional processing with conductivity values comparable to a commercial polymer (P3HT) deposited by the same method.

3.2 Self-Assembly Properties

3.2.1 Molecular Design and Synthesis

The molecular design of the molecules reported here includes an oligothiophene core attached to a hydrogen-bonding region that is flanked by alkyl tails. The thiophene core serves as a source of π - π stacking for self-assembly purposes. The hydrogen-bonding segment contains an

ethylenediamine moiety because amides formed with these units are known to promote self assembly.¹⁵²⁻¹⁵⁵ Finally, in order to avoid interrupting π - π stacking, all solubilizing alkyl tails were attached to the end of the molecule to avoid β -substitutions on the thiophene core. Since single alkyl tails flanking a thiophene core rarely impart high solubility, a gallic acid scaffold was used to attach alkyl tails to. Using gallic acid, three alkyl tails per gallic acid can be attached in a single moiety giving six solubilizing groups per molecule. Similar molecules without a hydrogen-bonding region have been found to form liquid crystal phases, but gel formation and 1D structures have not been observed.¹⁵⁶

Oligothiophene derivatives were synthesized using well-known reactions as shown in Figure 3.1. First, the phenolic groups on the gallic acid methyl ester were alkylated with 1bromododecane using a phase transfer catalyst to form the outer segment of the molecules. The methyl ester was then quantitatively deprotected under basic conditions to afford the free acid. The alkylated gallic acid was then reacted with mono-Boc-protected ethylenediamine to obtain amide **3** using carbodiimide chemistry. After acidic deprotection of the Boc-protected amine, amide **5** was formed by a reaction with 5-bromothiophene-2-carboxylic acid. The final molecules were formed by a double Stille coupling reaction between **4** with a distannylated bithiophene or terthiophene to afford the symmetric quaterthiophene (**4TG**) or quinquethiophene (**5TG**) derivative, respectively. All steps were purified by column chromatography or recrystallization. The structure of each derivative is shown in figure 3.2.



Figure 3.1. Synthesis of oligiothiophene gelator. a) $C_{12}H_{25}Br$, K_2CO_3 , acetone, 18-crown-6, reflux; b) NaOH, water/THF/MeOH; c) N-Boc-ethylenedianime, EDC, DCM; d) 4M HCl/dioxane; e) 5-bromo-2-thiophene-carboxylic acid, EDC, DPTS, DCM; e) 2,2'-di(tributylstannyl)bithiophene, Pd(PPh₃)₄, DMF, 100°C for **6a**, 2,2'-di(tributylstannyl)terthiophene, Pd(PPh₃)₄, DMF, 100°C for **6b**.

3.2.2 Gel Formation

Upon synthesis of the derivatives, their solubility was explored in various solvents. Both **4TG** and **5TG** were found to have low solubility in most solvents tried. In low concentrations (1-5 wt %), both derivatives were soluble in solvents such as THF, dichloromethane, and chloroform. In solvents such as DMF, DMSO, hexanes, pentane and simple alcohols both derivatives were found to be insoluble. High solubility was only achieved in solvent mixtures of dichloromethane with methanol. The high solubility in solvent mixtures with methanol is indicative of hydrogen bonding within the amide region being the cause for the low solubility in most single solvents.

In aromatic and some chlorinated solvents, both derivatives were found to form selfsupporting gels. To induce gel formation, solutions of either **4TG** or **5TG** were heated close to the solvent's boiling point and allowed to cool to room temperature. In this chapter, gel formation is defined as the loss of solvent flow that is stable to inversion of a vial. Gel formation was found to occur at the lowest concentrations (< 1.0 wt %) in toluene, styrene, and chlorocyclohexane, while at higher concentrations (> 1.0 wt %) gel formation is observed in 1,2-dichloroethane and chlorobenzene as seen in figure 3.3. The **4TG** was found to form a gel in thiophene at higher concentrations, although the **5TG** remained soluble until the saturation point of the solution. A summary of gel formation conditions can be seen in Table 3.1. Attempts to polymerize the thiophene monomer to trap nanostructures formed in the gel were unsuccessful. Adding oxidants to the solution (such as FeCl₃) to polymerize the thiophene monomer caused the gel to dissolve. The loss of gel formation is most likely due to the more charged nature of oxidized oligothiophene causing charge repulsion between the oligothiophenes, preventing hydrogen bonding and π - π stacking from occurring.

3.2.3 Determination of Nanostructure within Gel

Atomic force microscopy (AFM) and transmission electron microscopy (TEM) were used to characterize the structure of thin films deposited from dilute solutions of gel-inducing solvents. In thin films deposited from a dilute solution in a solvent that induces gel formation and thus self-assembly, one observed bundled networks consisting of 1D nanostructures



Figure 3.2. Molecular structures of molecules synthesized for this chapter.



Figure 3.3. Photographs of gels of a) 4TG and b) 5TG. Inverted vials demonstrate the lack of solvent flow in the gel state.

Solvent	4TG	5TG
Acetonitrile	Insoluble	Insoluble
Chlorobenzene	Gel (3 mg/mL)	Gel (3 mg/mL)
Chlorocyclohexane	Gel (<1 mg/mL)	Gel (<1 mg/mL)
Chloroform	Soluble	Soluble
1,2-Dichloroethane	Gel (2 mg/mL)	Gel (3 mg/mL)
Dichloromethane	Soluble	Soluble
DMF	Precipitate	Precipitate
DMSO	Precipitate	Precipitate
Ethanol	Insoluble	Insoluble
Hexanes	Precipitate	Precipitate
Pentane	Precipitate	Precipitate
Styrene	Gel (<1 mg/mL)	Gel (<1 mg/mL)
Tetrahydrofuran	Soluble	Gel (5 mg/mL)
Thiophene	Gel (5 mg/mL)	Soluble
Toluene	Gel (<1 mg/mL)	Gel (<1 mg/mL)

Table 3.1. Table of gel formation conditions for 5TG and 4TG. Concentrations in parenthesis is the minimum concentration for gel formation.

extending to several microns in length as seen in Figure 3.4 for **4TG** and Figure 3.5 for **5TG**. Since the nanostructures appear to have a large propensity to bundle upon solvent evaporation, it is difficult to find isolated, individual nanofibers. The bundling of nanostructres is most likely due to the attractive London interactions among alkyl chains on the periphery of fibers. Hydrocarbon chains are known to aggregate into well-ordered, interdigitated structures in some organic solvents, so it is likely that the alkyl tails on the exterior of the fiber are interacting to cause the high degree of bundling seen in the microscopy.^{157, 158} The large bundles of fibers are found to be typically 40-300 nm in diameter for both the **4TG** and **5TG** derivatives in TEM and AFM. Often, smaller bundles can be seen branching off of the larger branches is both derivatives, indicating that the larger structures are made up of bundles of smaller fibers structures.

Since no functional groups are present on the derivatives for selective TEM staining, it was not possible to detect ordering within the bundles by microscopy. In an attempt to detect regular ordering that could be indicative of the subunit that makes up the bundled structures observed by microscopy in the films, the **4TG** and **5TG** derivatives were studied by SAXS. Diffraction peaks were evident in both samples. In **5TG** a single diffraction peak was observed where d = 4.9 nm. In **4TG**, two peaks were observed where d = 5.3 and 4.5 nm respectively as seen in Figure 3.6. In a fully extended conformation, **5TG** was calculated to be 7.2 nm in length while the **4TG** was calculated to be 7.0 nm in length. The length of rigid portion of the molecule (the thiophene core with hydrogen bonding segment) is calculated to be 4.4 nm or 4.2 nm in length for **5TG** and **4TG** respectively. A fully extended conformation of the entire molecule would not be expected upon drying, although the rigid core should remain mostly extended.



Figure 3.4. a) AFM images of **4TG** showing the highly bundled aggregates of nanofibers. b) TEM image of **4TG** films cast from cyclohexylchloride. c) Higher magnification TEM image of **4TG**.



Figure 3.5. a) AFM images of **5TG** showing the highly bundled aggregates of nanofibers. b) TEM image of **5TG** films cast from cyclohexylchloride. c) Higher magnification TEM image of **5TG**.

Because the repeat spacing found by SAXS matches the calculated length of an individual molecule, it is likely that the base nanostructure within the bundles observed by microscopy is a fiber with the width of a single molecule.

3.3 Optical Properties of Oligothiophene Gelators

3.3.1 Solvent Dependence of Optical Properties

Because microscopy cannot determine molecular orientation within the nanofiber, optical spectroscopy was used to probe the orientation of the thiophene chromophore. Both 4TG and **5TG** showed a colorimetric change upon gel formation indicating that the optical properties of the chromophore must be different between an aggregated and a solvated state. Both UV-vis absorption and fluorescence spectroscopy were performed on the molecules in either a gelinducing solvent (chlorocyclohexane (CCH)) or a solvent that prevented gel formation (THF) (see Figure 3.7). In the case of **5TG**, we observed a hypsochromic shift of 45 nm in the absorption maximum when measured in an assembling solvent (CCH) as compared to a solvating solvent (THF). The fluorescence spectra revealed significant quenching coupled with a 51 nm bathochromic shift in the emission maxima upon assembly. In the self-assembled state, vibrational fine structure was evident on the shoulder of the main absorption peak as seen in Figure 3.7a,c. The appearance of vibrational fine structure peaks in the absorbance spectra is indicative of increased conformational ordering of the π -conjugated core as a result of the selfassembly. The 4TG derivative shows similar behavior to 5TG with a 42 nm hypsochromic shift in absorption maxima, as well as quenching and a 51 nm bathochromic shift in fluorescence maxima. These results are consistent with the existence of H-aggregation. Using the exciton



Figure 3.6: SAXS of a dried gel of a) **5TG** and b) **4TG**, showing diffraction peaks that correspond to d = 4.9 nm for **5TG** and d = 5.3 and 4.5 nm for **4TG**.



Figure 3.7. Optical Spectroscopy of **4TG** and **5TG** in assembling (CCH) and nonassembling solvents (THF). Spectra of a) absorption and b) fluorescence for **4TG**. Spectra of c) absorption and d) fluorescence for **5TG**. All spectra measured at 3×10^{-6} M.

coupling model,¹²² the optical spectroscopy data indicates face-to-face ordering of the thiophene cores within the nanofibers. This orientation is needed for conduction of electron to occur in oligothiophene derivatives.

3.3.2 Effect of Hydrogen Bonding on Self-Assembly

Because both π - π stacking and hydrogen bonding can occur among the molecules studied here, it is difficult to ascertain which intermolecular forces are most responsible for the formation of 1D nanofibers. FTIR spectra obtained from a dried CCH gel revealed the NH stretching band (3300 cm⁻¹), as well as the amide I (1630 cm⁻¹) and amide II (1540 cm⁻¹) stretching bands at longer wavelengths than typically found, suggesting the amide bonds are involved in hydrogen bonding (Figure 3.8). To further investigate the role of hydrogen bonding, the change in absorbance and emission spectra was probed upon the addition of methanol to a solution in CCH where self-assembly has already been shown to occur. Because methanol is a hydrogen bond donor, it can prevent hydrogen bond formation among the amides in the **4TG** and **5TG** derivatives by blocking all the available hydrogen bonding is necessary for the formation of H-aggregates, addition of enough methanol to the solution should shift the absorbance and emission spectra relative to the spectra recorded in THF where the molecules are molecularly dissolved.

When methanol was titrated into a solution of **5TG** in CCH, both the absorption and fluorescence spectra shifted to a signal consistent with molecularly dissolved molecules. As indicated by Figure 3.9, a recovery of fluorescence intensity and shifting of the peak maximum



Figure 3.8. FTIR spectra of a **5TG** dried gel from CCH showing the amide bands occurring at lower energy due to hydrogen bond formation.

Band	Observed Wavelength
Amide I	$1630 (\text{cm}^{-1})$
Amide II	$1540 (\text{cm}^{-1})$
Amide A	$3300 (cm^{-1})$

Table 3.2. Table of the wavenumber where the peaks associated with the amide bond in FTIR are located. The measurement was taken of a film of **5TG** cast from CCH.



Figure 3.9. Absorbance a) and fluorescence b) spectra of **5TG** from 0 to 10 vol % methanol. All spectra measured at 3×10^{-6} M in CCH.

from an assembled state to an unassembled state was also observed. When 10 vol % of methanol was added to the CCH solution, the absorption and fluorescence spectra are consistent with the fully solvated molecular state. The shift from an aggregated state to an unassembled state upon addition of methanol indicates that hydrogen bonding is necessary to form self-assembled aggregates of these molecules.

3.3.3 Variable Temperature Spectroscopy

On the macroscopic scale, gel formation was found to be thermally reversible in all gel forming solvents. To further investigate this observation, the absorbance spectra of both **4TG** and **5TG** were measured as a function of temperature. Variable temperature UV-vis absorption spectra showed the self-assembled structures of **4TG** and **5TG** formed in CCH disassembled upon heating as seen in Figure 3.10. Upon cooing, the absorbance peak returns to the original position, indicating that the formation of self-assembled structures is fully reversible with heat. Interestingly, as seen in Figure 3.10a,b, the temperature at which the supramolecular structures dissolved was not the same for both derivatives.

In order to further probe the melting behavior of the **4TG** and **5TG** derivatives, the absorbance each derivative was measure at the maximum of the solvated peak as a function of temperature. The melting point (the inflection point on the melting curve) of **5TG** assembly was found to be $T_m = 68$ °C, while the melting of **4TG** was found to be $T_m = 52$ °C as seen in Figure 3.10c. Because the melting point of **5TG** was found to be higher than that of **4TG** ($\Delta T_m = 16$ °C), the attractive intermolecular forces in **5TG** must be stronger than those in **4TG**. Since the only molecular difference between the **4TG** and **5TG** is the length of the thiophene core,



Figure 3.10. Variable temperature absorption spectra of a) 4TG and b) 5TG. c) Melting curve measure at the absorption maxima of the respective molecule.

hydrogen bonding strength should be similar in both molecules, the increased nanostructure thermal stability found for **5TG** is then attributed to an increase in the π - π stacking strength due to the longer conjugated thiophene. This finding shows that π - π stacking is an important interaction in the aggregation of these molecules along with hydrogen bonding.

3.4 Electronic Characterization of Self-Assembled Films

The presence of micrometer long fibers of π - π stacked aggregates could be beneficial for the fabrication of conductive films using a simple, one-step, drop-casting deposition procedure. Using these novel 1D nanofibers, multiple thin-films were prepared using a simple drop-cast technique in order to investigate the electrical properties of the materials obtained. Solutions of 4TG and 5TG molecules were prepared in chlorobenzene below gel forming concentrations (0.1 wt %), sonicated, heated to 100 °C for 15 minutes, and cooled to room temperature. From these solutions, films were drop cast onto the glass surface by four sequential depositions. To measure conductivity, devices were fabricated employing the common top-contact geometry depicted in Figure 3.11. Source-drain spacings of several microns were fabricated using a TEM grid as a shadow mask, followed by gold metal (~200 nm) deposited directly onto the film, and removal of the shadow mask. Several metals were investigated for use as electrodes with gold and nickel giving the best conductivities. Gold was untimely chosen as the electrode material due to ease of deposition and better stability than the nickel electrodes. This methodology resulted consistently in channel widths of 5 to 8 micrometer wide deposited on top of thin films consisting of bundles f nanofibers that do not contain any metal contamination from the electrode deposition procedure (Figure 3.12).



Figure 3.11. a) Schematic representation of fabricated device. b) Optical micrograph of a two probe device. c) SEM image of a typical device channel where light areas are metal and dark region is the organic channel.



Figure 3.12. a) SEM image showing a **5TG** device. b) Energy Dispersive X-Ray SEM (EDX) showing elemental composition on a gold pad and within an organic channel. In the organic channel there is no gold signal present.

From the I-V measurements, conductivity values were obtained using device conductance and thickness as well as the channel length and width as seen in Figure 3.13. Due to the low-bias charge injection barrier, conductance values were determined based on the slope of the high-bias end of the curve. The average conductivity, based on ~30 devices, of **5TG** films was found to be $8.8 \pm 1.1 \times 10^{-6}$ S/cm measured at 50 V, while **4TG** films did not reveal any detectible conductivity above the noise of the measurement apparatus ($\sigma > 1 \times 10^{-12}$). Even though both **4TG** and **5TG** show extensive π - π overlap in spectroscopic measurements mentioned earlier, conductivity is only observed in the **5TG** derivative. This finding is in agreement with previous literature reports that show electrical performance increases with extension of π -orbital conjugation.¹⁵⁹ When the **5TG** device was illuminated with UV light, a 10 % increase in conductivity is observed indicating the conductivity measured originates in semiconducting oligothiophene derivative. Upon photoexcitation, still no detectible conductivity was measured in **4TG**.

To determine if self-assembly is important to the observed conductivity, the conductivity of films deposited from a self assembling or a solvating solvent were compared. As previously discussed, films cast from chlorobenzene form films of large bundles of nanofibers. In contrast, when films are cast from chloroform (gel formation is not observed in chloroform), amorphous films are produced (Figure 3.14). Complete loss of conductivity was observed in devices fabricated form films cast from chloroform (Figure 3.14c). Our interpretation of this result is that the extended pathways for electron conductivity generated by self-assembly are no longer present in these amorphous films. Furthermore, the conductivity of our self-assembled materials containing the 1D supramolecular nanostructures is of the same order of magnitude as thin films

of poly(3-hexylthiophene) (P3HT) prepared with the same deposition technique (Figure 3.15). The comparable conductivity with a P3HT shows the potential of self-assembly to create wellordered films using small molecules from solution based-deposition techniques.



Figure 3.13. Current-Voltage curves for 5TG, 4TG, and 5TG irradiated with light (365 nm).



Figure 3.14. a) AFM and b) SEM micrographs of amorphous films cast from chloroform. c) IV curve of films of **5TG** cast from chlorobenzene and chloroform.


Figure 3.15: I-V curve of P3HT from a device prepared in the same fashion as the **5TG** devices. Conductivity was calculated to be $\sigma = 7.45 \pm 1.05 \times 10^{-6} \text{ S/cm}^2$.

3.5 Summary and Outlook

This chapter has reported the synthesis of self-assembling molecules containing electronically-active conjugated segments of quater- and quinquethiophene and segments capable of forming hydrogen bonds. Both π - π stacking and hydrogen bonding contribute to the self-assembly of these molecules into well-defined 1D nanostructures. The formation of 1D nanostructures by self-assembly in quinquethiophene derivatives is directly responsible for the high electronic conductivity of films of these molecules that bridge electrodes by simple

evaporation of solvent. When amorphous films are cast from the quinquethiophene derivative, no conductivity was measured, demonstrating the importance of the nanostructure to the electrical performance of the material. The conductivity values measured for these materials are comparable to those of thiophene-based polymers deposited in a similar method. Thus, these systems offer a promising reproducible solution deposition technique for organic electronics relative to amorphous materials.

3.6 Experimental

3.6.1 General

Unless otherwise noted, all starting materials were obtained from commercial suppliers and used without further purification. DPTS¹⁰⁶, mono-Boc-protected ethylenediamine¹⁶⁰ and the distannyl thiophene derivatives¹³⁵ were synthesized according to published procedures. ¹H NMR and ¹³C NMR spectra were recorded in a Varian Inova 500 (500 MHz for ¹H and 120 MHz for ¹³C NMR) spectrometer using the solvent proton signal as standard. All device fabrication and analysis was completed by Alok Tayi of the Stupp Lab. TEM microscopy was performed by Josh Goldberger of the Stupp lab. X-ray analysis was performed by Maria Sofos of the Stupp Lab. AFM was performed by Liam Palmer and Lorraine Hsu.

UV-Vis absorption spectra were collected on a Cary 500 spectrometer and fluorescence was measured on an ISS PC1 spectrofluorometer. All optical spectroscopy was collected at 3.0×10^{-6} M. Solutions were made my diluting a stock solution in CCH to the desired concentration.

Transmission Electron Microscopy (TEM) was performed on a JEOL 1230 microscope. Films were prepared by drop casting dilute solutions onto copper grids. All samples were stained with uranyl acetate for 3 min. Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) analysis was performed on a Hitachi S4800 microscope on films prepared as described in the device fabrication section. AFM measurements were taken on a Nanoscope Multimode ScanningProbe Microscope. Films were cast from a dilute aqueous solution (0.1 wt %) on to a freshly cleaned polished silicon wafer. The wafers were cleaned by soaking in a piranha bath followed by a water bath and then finally in an isopropanol bath for 15 min each.

3.6.2 Device Fabrication and Measurement

All two-probe conductivity devices, using 4TG, 5TG, and P3HT materials, were fabricated in the same manner. First, a 0.1% solution (by weight), in chlorobenzene, was prepared for each conductive molecule. Thin film depositions were performed on cleaned glass substrates. On glass, 4 μ L of the solution was deposited in 1 μ L increments. After each deposition, the film was allowed to air dry and then placed under vacuum for approximately 15 minutes to remove and residual solvent.

When sufficiently dry, a copper evaporation mask was adhered to the polymer film. We employed transmission electron microscopy grids (SPI Quad) as the shadow mask. Using this mask, 200 nanometers of gold were evaporated on the surface of the nanofiber film. Though most groups employ bottom contact geometry, the alkylated exterior may hinder charge injection. Thus, top-contact geometry provided pervasive electronic contact to much of the nanofiber thin-film. Two-probe conductivity measurements were performed using a Keithley 2400 SMU. Based on the resistance, thickness, and device length & width, a conductivity value was calculated for each measurement. To ensure that conduction was due to the nanofibers, not metal, we performed numerous photoconductivity experiments to verify. Furthermore, scanning electron microscopy and energy dispersive x-ray spectroscopy proved that little metal existed in the semiconducting channel.

3.6.3 Organic Synthesis

methyl 3,4,5-tris(dodecyloxy)benzoate (1): In a 500 mL round bottom flask, 1 (3.00 g, 16.3 mmol), K₂CO₃ (13.51 g, 99.7 mmol), 18-crown-6 (1.29 g, 4.88 mmol, and 1-bromododecane (16.25 g, 65.2 mmol) were added to 250 mL of acetone. The reaction mixture was refluxed overnight and cooled to room temperature. The solution was filtered and the acetone was evaporated. The resulting residue was dissolved in ether and extracted three times with sat. NaCO₃ (aq). The organic layer was then dried with Na₂SO₄ and concentrated. The crude product was purified by column chromatography (silica gel; dichloromethane/hexanes, 30:70) to yield 10.87 g (96%) of the compound as a waxy while solid. ¹H NMR (500 MHz, CDCl₃, δ): 7.27 (s, 2H, Ar H), 4.04-4.01 (m, 6H, OCH₂), 3.90 (s, 3H, COOCH₃), 1.84-1.73 (m, 6H, CH₂), 1.48 (qn, J = 8 Hz, 6H; CH₂), 1.38-1.27 (m, 48H, CH₂), 0.89 (t, J = 7.5 Hz, 9H; CH₃); ¹³C NMR (120 MHz, CDCl₃, δ): 167.1, 153.0, 142.5, 124.8, 108.1, 73.7, 69.3, 52.3, 32.1, 30.5, 29.9, 29.8, 29.8, 29.7, 29.6, 29.5, 29.5, 26.2, 22.9, 14.3.

3,4,5-tris(dodecyloxy)benzoic acid (2): In a 250 mL round bottom flask, **2** (5.00g, 7.30 mmol) was dissolved in 100 mL of THF. NaOH (3.00 g, 73.0 mmol) dissolved in 100 mL of water was then added to the solution along with a few drops of methanol. The reaction mixture was refluxed for 16 h, allowed to cool to room temperature and then acidified with 2M HCl. The organic layer was then evaporated leaving a white precipitate in the aqueous layer. The precipitate was dissolved with dichloromethane and separated from the aqueous layer. The aqueous layer was extracted three times with dichloromethane. The combined organic layer was then extracted three times with dichloromethane. The combined organic layer was then extracted three times with 2M HCl (aq). The organic layer was then dried with Na₂SO₄ and concentrated. The desired product was afforded after purification by column chromatography (silica gel; ethyl acetate/ hexanes, 40:60) as 4.88 g (99%) of a waxy white solid. ¹H NMR (500 MHz, CDCl₃, δ): 7.31 (br s, 1H, COOH), 7.27 (s, 2H, Ar H), 4.04-4.01 (m, 6H, OCH₂), 1.84-1.73 (m, 6H, CH₂), 1.48-1.46 (m, 6H; CH₂), 1.38-1.27 (m, 48H, CH₂), 0.89 (t, J = 7.5 Hz, 9H; CH₃); ¹³C NMR (120 MHz, CDCl₃, δ): 153.0, 143.3, 123.8, 108.7, 73.7, 69.3, 32.1, 30.5, 29.9, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 26.3, 26.2, 22.9, 14.3.

tert-butyl 2-(3,4,5-tris(dodecyloxy)benzamido)ethylcarbamate (3): To a solution of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) (1.06 g, 5.55 mmol), 4-Dimethylaminopyridine/*p*-toluenesulfonic acid (DPTS) (1.50, 4.81 mmol), and **3** (2.50 g, 3.70 mmol) in 300 mL of dichloromethane was added N-Boc-ethylenediamine (0.77 g, 4.81 mmol). The reaction was stirred at RT overnight. The reaction mixture was extracted three times with 2M HCl (aq) and the organic layer was dried with Na₂SO₄. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel; dichloromethane/methanol, 95:5) to yield 2.90 g (96%) of the compound as a waxy while solid. ¹H NMR (500 MHz, CDCl₃, δ): 7.37 (br s, 1H, NH), 7.07 (s, 2H, Ar H), 5.09 (br s, 1H, NH), 4.02 (t, J = 6 Hz, 4H; OCH₂), 3.99 (t, J = 6 Hz, 2H; OCH₂), 3.53 (app q, J = 5 Hz, 2H; CH₂), 3.39 (app q, J = 5 Hz, 2H; CH₂), 1.80 (qn, J = 7.5 Hz, 4H; CH₂), 1.74 (qn, J = 8 Hz, 2H; CH₂), 1.49-1.44 (m, 6, CH₂), 1.43 (s, 9H, CH₃), 1.39-1.23 (m, 48H, CH₂), 0.89 (t, J = 7.5 Hz, 9H; CH₃); ¹³C NMR (120 MHz, CDCl₃, δ): 167.7, 157.9, 153.2, 141.1, 129.1, 105.7, 80.1, 73.6, 69.4, 42.6, 40.4, 32.2, 32.1, 32.1, 30.5, 30.0, 29.9, 29.9, 29.8, 29.8, 29.6, 29.6, 29.6, 28.5, 26.3, 22.9, 14.3.

N-(2-aminoethyl)-3,4,5-tris(dodecyloxy)benzamide (4): In a 100 mL round bottom flask, 4 (1.50, 1.80 mmol) was dissolved in 3M HCl in ethyl acetate (50 mL). The reaction was monitored by TLC. When the reaction had completed, typically 2 h, the reaction was evaporated *in vacuo* to remove the solvent and acid. The product was dried under high vacuum and used without further purification.

N-(2-(3,4,5-tris(dodecyloxy)benzamido)ethyl)-5-bromothiophene-2-carboxamide (5): To a solution of 5-bromothiophene-2-carboxylic acid (0.19 g, 0.96 mmol), DPTS (0.32 g, 1.04 mmol), and EDC (0.23 g, 1.20 mmol) in dichloromethane (100 mL) was added **5** (0.61 g, 0.80 mmol). The reaction mixture was stirred overnight at RT. The reaction is then extracted 3 times with sat. NaHCO₃ (aq), then the organic layer is dried with Na₂SO₄. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel; dichloromethane/methanol, 95:5) to yield 0.63 g (86%) of the compound as a waxy while solid. ¹H NMR (500 MHz, CDCl₃, δ): 7.73 (br s, 1H, NH), 7.50 (br s, 1H, NH), 7.37 (d, J = 4 Hz, 1H; Ar H), 7.03 (s, 2H, Ar H),

6.99 (d, J = 4 Hz, 2H; Ar H), 4.06-3.97 (m, 6H, OCH₂), 3.60 (app s, 4H, CH₂), 1.80 (qn, J = 8 Hz, 4H; CH₂), 1.74 (qn, J = 8 Hz, 2H; CH₂), 1.49-1.43 (m, 6H, CH₂), 1.39-1.24 (m, 48H, CH₂), 0.89 (t, J = 7 Hz, 9H; CH₃); ¹³C NMR (120 MHz, CDCl₃, δ): 169.2, 162.7, 153.3, 141.3, 140.5, 131.0, 128.8, 128.7, 118.6, 105.7, 73.8, 69.4, 41.3, 40.8, 32.2, 30.6, 29.9, 29.6, 26.4, 22.9, 14.2.

4TG (**6a**): A 100 mL flask was flame dried and cooled under nitrogen. In 50 mL of DMF, 2-(5-(tributylstannyl)bithiophene (0.15g 0.21 mmol) and **6** (0.41g, 0.46 mmol) were dissolved. The solution was then degassed by the freeze-pump-thaw method three times.

Tetrakistriphenylphosphine palladium(0) (0.012 g, 5% cat loading) was added to the solution and allowed to react overnight at 100 °C. The reaction was allowed to cool to room temperature and then filtered through a silica plug. The collected solution was evaporated to yield a yellow solid. The crude solid was recrystallized three times with chloroform/methanol to give 0.25g of the desired product as a yellow solid (30.6% yield). ¹H NMR (500 MHz, CDCl₃/CD₃OD (9:1), δ): 7.45 (d, J = 4 Hz, 2H; Ar H), 7.11 (d, J = 4 Hz, 2H; Ar H), 7.07 (d, J = 4.5 Hz, 2H; Ar H), 7.06 (d, J = 3.5 Hz, 2H; Ar H), 6.99 (s, 4H, Ar H), 3.97 (t, J = 6 Hz, 8H; OCH₂), 3.93 (t, J = 6.5 Hz, 4H; OCH₂), 3.54 (br s, 8H, CH₂), 1.76 (qn, J = 7.5 Hz, 8H; CH₂), 1.68 (qn, J = 7.5, 4H; CH₂), 1.44-1.38 (m, 12H, CH₂), 1.32-1.16 (m, 96H, CH₂), 0.83-0.80 (m, 18H, CH₃); ¹³C NMR (100 MHz, CDCl₃, δ): 169.2, 163.6, 153.1, 141.9, 140.9, 137.1, 137.0, 135.7, 129.3, 128.8, 125.8, 124.9, 124.1, 105.7, 73.7, 69.2, 40.6, 39.9, 32.0, 30.4, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 26.3, 26.2, 22.8, 14.2.

5TG (**6b**) Prepared and purified following an analogous procedure to that used for compound 7, but using 2-(5-(bitributylstannyl)terthiophene. Product collected as an orange solid in 64% yield. ¹H NMR (500 MHz, CDCl₃/CD₃OD (9:1), δ): 7.90 (br s, 2H, NH), 7.78 (br s, 2H, NH), 7.40 (d, J = 4 Hz, 2H; Ar H), 7.07 (d, J = 4 Hz, 2H; Ar H), 7.03-7.00 (m, 10H, Ar H), 3.98 (t, J = 6.5 Hz, 8H; OCH₂), 3.95 (t, J = 6.5 Hz, 4H; OCH₂), 1.78 (qn, J = 8 Hz, 8H; CH₂), 1.70 (qn, J = 8 Hz, 4H; CH₂), 1.47-1.40 (m, 12H, CH₂), 1.38-1.19 (m, 96H, CH₂), 0.86-0.83 (m, 18H, CH₃); ¹³C NMR (100 MHz, CDCl₃, δ): 169.1, 163.4, 153.2, 141.9, 141.4, 137.3, 137.0, 136.2, 135.5, 129.3, 128.9, 125.7, 124.9, 124.7, 124.0, 106.1, 73.7, 69.5, 40.6, 40.1, 32.0, 20.4, 28.8, 29.7, 29.6, 20.5, 29.4, 26.2, 26.1, 22.7, 14.0.

Chapter 4

Oligopeptide Quinquethiophene Hydrogels

Chapter 4: Oligopeptide Quinquethiophene Hydrogels

4.1. Introduction

Self-assembly of π -conjugated oligomers has attracted much attention for use in organic electronic devices such as photovoltaic cells and field effect transistors.^{31, 87} Molecular assembly into highly ordered 1D nanostructures has been shown to enhance the electronic function of oligomeric derivatives because the self-assembled structures enforce a high degree of π -orbital overlap that is needed for electronic performance.^{144, 161} Electronic substrates have become of interest in the study of biological systems due the prevalence of electrical signals in the function of heart muscle cells and neurons.¹⁶²⁻¹⁶⁴ Electrical stimulation in biological systems has been shown to be important to stem cell differentiation, as well as cell growth and organization.¹⁶⁵⁻¹⁶⁷ Most electrically active surfaces used as substrates in the lab to study the effect of electrical signals on biological systems are based conductive polymers and not tailored specifically for cell adhesion.¹⁶⁸ As an example, neurite growth increased upon electrical stimulation of neurons cultured directly on a polypyrole surface.¹⁶⁹ A conductive surface specifically tailored for interaction with cells would be ideal for the study of electrically active biological systems.

For a self-assembled material to be biologically relevant, the π -conjugated derivatives must assemble in aqueous conditions. The vast majority of self-assembling π -conjugated molecules assemble in organic solvents and are not soluble in water.^{3, 21, 24, 72, 106} Recently, water soluble conjugated oligomers prepared by attaching poly(ethylene glycol) to a conjugated core.^{107, 117, 141} While these derivatives are assemble in water, poly(ethylene glycol) has no inherent biological functionality for cellular adhesion or signaling.¹⁷⁰ Self-assembly of

conjugated moieties facilitated by peptidic segments is a promising, and still largely unexplored, route to introduce biologically relevant surfaces on a conducting substrate.

To date, derivatives of polydiacetylene,¹⁷¹⁻¹⁷⁴ OPV,¹⁷⁵ and oligothiophene¹⁷⁶⁻¹⁷⁸ have been incorporated into peptide based self-assembled structures. While polydiacetylene is a well-know conducting polymer, its conductivity is very low when undoped.¹⁷⁹ Oligomers of OPV also have low conductivity due to their high bandgap.¹⁰⁸ Oligothiophene derivatives with four or more repeat units are known to be semiconducting without the need for external doping.^{161, 180} A quaterthiophene derivative conjugated to a silk inspired peptide sequence was found to assemble in the solid state into ordered structures, but no assembly in solution was reported.¹⁷⁸ A bithiophene derivative was found to self-assembly into 1D nanostructures in aqueous conditions using a peptide sequence based on amyloid fibers, but bithiophene is not conductive without doping.¹⁷⁶ This chapter discusses the design, synthesis, and self-assembly of peptidic quinquethiophene (5T) bolaamphiphiles that form 1D nanostructures in aqueous conditions for potential use in the study of electrically active biological systems. To the best of the author's knowledge, this is longest reported peptide based oligothiophene derivative found to self assemble in aqueous conditions.

4.2 Design and Synthesis

The general synthetic design of the 5T-peptide derivative consists of a symmetric bolaamphiphile that has three segments as demonstrated in Figure 4.1. The molecular segments consist of an outer region of polar amino acids for solubility, followed by a β -sheet forming region for directional hydrogen bonding, and then the thiophene core for conductivity. The



Figure 4.1. a) Schematic of the molecular design showing where the hydrophilic, β -sheet, and thiophene segments are located. b) Molecular structures of the peptidic thiophene amphiphiles with color coded segments that match the schematic.

derivatives synthesized are listed in Figure 4.1b. Either two or three lysine residues per side of the molecule were used giving the molecule a net positive charge to impart solubility. Valine, alanine, and leucine were chosen to be used in the β -sheet forming region. To explore the role of the amino acids in the β -sheet region, amino acids of different β -sheet forming propensity were used in this region. Valine is known to have a higher β -sheet propensity than leucine, and alanine is known to prefer an α -helical structure over a β -sheet conformation.¹⁸¹ For one derivative, an alkyl spacer was added between the amino acid segment and the thiophene core for added molecular flexibility. Quinquethiophene was chosen as the conductive core because oligothiophenes of this length are known to have semiconducting properties when undoped unlike oligomers with fewer repeat units.¹⁶¹

All peptide derivatives were synthesized using solution-phase peptide couplings. The peptidic and thiophene segments where synthesized separately, and then coupled together to form the final amphiphile. Synthesis of the peptide segment consisted of sequential peptide couplings followed by selective deprotection of the N-terminus amine. As an example, the synthesis of H-L-L-K(Boc)-K(Boc)-*t*Bu is shown in Figure 4.2. Purification of the intermediate protected peptidic segments was accomplished by column chromatography on silica gel.

In order to synthesize the 5T-methyl dicarboxylic acid derivative (**5T-mDCA**) used as the conjugated moiety, a strategy of successive Stille couplings completed by a global deprotection was used to afford the 5T-mDCA product as seen in Figure 4.3. The methyl substitution was introduced to the molecule starting with the commercially available 2,5dibromo-3-methylthiophene derivative used the starting material for the synthesis. A double Stille coupling was performed on the 2,5-dibromo-3-methylthiophene with 2-tributyltin









Figure 4.2. Synthetic schematic of H-L-L-K(Boc)-K(Boc)-tBu demonstrating the general strategy of the peptide synthesis. a) Cbz protected amino acid, EDC, HOBT, TEA, CH₂Cl₂. b) Pd/C, H₂, CH₂Cl₂, MeOH.



Figure 4.3. Synthetic scheme for **5T-mDCA**. a) tributyl(2-thiophene)stannane, Pd(PPh₃)₄, DMF, b) n-BuLi, tributyltin chloride, THF, c) tert-butyl 5-bromothiophene-2-carboxylate, EDC, DPTS, DCM, d) DCM, TFA.



Figure 4.4. Synthetic schematic demonstrating the final global deprotection reaction on **5TLLKK**. a) HBr, acetic acid, 10 min.

thiophene to yield a methyl-terthiophene derivative **9**. The methylated terthiophene derivative was then doubly substituted with tributyltin at the 2-position by lithiation followed by quenching with tributyltin chloride to form **10**. A *t*-butyl protected 2-bromo-5-thiophene carboxylic acid molecule was synthesized by carbodiimide chemistry to be coupled to the terthiophene core. The double substituted 5T *t*-butyl protected carboxylic acid **11** was synthesized by a Stille coupling. High solubility was observed for the protected 5T derivative in common organic solvents such as THF, dichloromethane, and chloroform. The final diacid **12** was afforded by acidic deprotection of the acids without the need for further purification. The final products were obtained upon an acidic global deprotection using HBr/acetic acid as demonstrated in Figure 4.4 for **5TLLKK**. Each final product was purified by preparative RP-HPLC.

4.3 Self-Assembly of Peptidic Quinquethiophene Amphiphiles

4.3.1 Gel Formation and Microscopy of Peptidic Thiophene Derivatives

The formation of a self-supporting gel is often indicative of the formation of an entangled network of 1D nanostructures.⁷⁷ The formation of a 3D network of nanostructures is desirable because it closely mimics the extracellular matrix that is important to cellular adhesion.¹⁸² Gel formation was investigated as an indication of the presence self-assembled 1D nanostructures. Both the **5TLLKK** and **5TAHXLLKK** derivatives were found to form self-supporting gels in aqueous solutions at 1 wt% as seen in Figure 4.5. In contrast, **5TALKKK** remained soluble in up to 5 wt % in water. Adding base to neutralize the charge on the lysine and avoid charge repulsion did not induce gel formation either. The time for gel formation, as defined by the solution

remaining stable to vial inversion, of both **5TAHxLLKK** and **5TLLKK** depended on the concentration of the initial solution. At 1 wt%, the formation of a self-supporting gel occurs over five days, while at 3 wt% gel formation occurs within 3-5 hours. All attempts to solubilize **5TVVKK** were unsuccessful presumably because the valine residues created too strong of an aggregative force.



Figure 4.5. a) Photograph of **5TAHxLLKK** as a 1 wt% gel in water (left) and a 1 wt% solution in methanol (right). b) Photograph of **5TAHxLLKK** as a 1 wt% gel in water (left) and a 1 wt% solution in methanol (right) illuminated at 365 nm. A strong emission is observed in the methanol solution, but emission is quenched in the aqueous gel.

For the gel-forming compounds, microscopy was utilized to determine the nanostructure within the gel. TEM revealed the presence of intertwined network of uniform 1D nanostructures with a width of 6.30 ± 0.85 nm in the case of **5TAHxLLKK** as seen in Figure 4.6. The molecular length of **5TAHxLLKK** fully extended was calculated to be 6.47 nm. Since the modeled length of the molecule matches the width of the nanostructure observed by TEM, it is likely that the nanofiber consists of fully extended oligothiophene derivatives aligned along the length of the fiber. Since the peptide segments are significantly more hydrophilic than the oligothiophene, the peptidic portion of the molecule is expected to be on the periphery of the

nanostructure with the oligothiophene moiety in the center. AFM measurements revealed a similar bundled 1D nanostructure to that observed by TEM. The heights of the nanostructures range from 5 to10 nm, which is also approximately the length of one molecule. Since the height and width are similar, the 1D nanostructure formed are likely a nanocylinder, but we cannot exlude the possibility of a tightly twisted nanoribbon.

AFM microscopy of **5TLLKK** prepared under identical conditions as presented earlier revealed a different morphology in the solid state. With this derivative, mats of very short 1D structures were observed covering the mica surface as shown in Figure 4.7. It is possible that this derivative forms of longer 1D nanofibers in the gel, but upon drying the nanostrucutres break into the shorter structures observed by AFM. The breaking of nanostructures upon drying of only **5TLLKK** may indicate a less robust 1D nanostructure being formed upon self assembly compared to **5TAHXLLKK**.

4.3.2 Optical Spectroscopy of Peptidic Quinquethiophene Amphiphiles

Optical spectroscopy was utilized to probe the conformation of the conjugated moiety within the nanostructure. Because quinquethiophene is a conjugated π -structure that absorbs in the visible region, it gives a convenient handle for absorbance, fluorescence, and circular dichroism (CD) spectroscopy. The absorbance and fluorescence spectra of **5TAHxLLKK** in both water and methanol are shown in Figure 4.8a. Gel formation was not observed in methanol solutions for any of the derivatives, so ordered aggregation is not expected in the methanol solutions. The lack of gel formation in methanol is likely because methanol is a hydrogen bonding donor, thus blocking intercmolecular hydrogen bonding ability of the amino acids.



Figure 4.6. a) Molecular structure of **5TAHxLLKK** with the calculated molecular length shown beneath. b) and c) TEM micrographs of **5TAHxLLKK** showing 1D nanostructures with a width of 6.30 ± 0.85 nm. d) and e) AFM micrographs of **5TAHxLLKK** on mica showing highly bundled 1D nanostructures with heights ranging from 5-10 nm.



Figure 4.7. a) Molecular structure of **5TLLKK** with the calculated molecular length shown beneath. b) and c) AFM micrographs of **5TAHxLLKK** on mica showing a mat of short 1D nanostructures with heights ranging from 4-6 nm on mica cast from aqueous solutions.

In methanol, the absorbance maximum was found at 425 nm and the fluorescence maximum at 514 nm. These values are consistent with molecularly dissolved quinquethiophene derivatives.¹⁸³ In water, the absorbance maximum did not shift from 425 nm, but a broadening of the peak indicated by a lower energy shoulder does occur. This broadening and shoulder formation are typical spectroscopic behavior of the formation of aggregates. The fluorescence emission maximum in water shifted 77 nm to lower energy compared to methanol. In addition to the large shift, the emission in water was quenched by 93 %. Fluorescence quenching and the red shift of the fluorescence emission maxima may be indicative of the formation of h-aggregates of the thiophene chromophore.¹²² In classical h-aggregates, a blue shift in absorbance, along with a red shift in fluorescence is red shifted. Because β -sheets are known to form twisted structures in nature, it is likely that the aggregates formed in the reported system are also twisted.¹⁸⁴ If the chromophores are in a twisted h-aggregate geometry, the absorbance shift may be less pronounced than a non-twisted system.¹⁸⁵

CD spectroscopy was used to further investigate if the thiophene chromophore was in a twisted geometry. In water, the CD spectra of **5TAHxLLKK** showed strong absorbance in the thiophene region. A bisignated Cotton effect was observed with a positive sign at low wavelength and a positive sign at high wavelengths shown in Figure 4.8b. The zero point of the bisignated Cotton effect is equal to the absorbance maximum in UV-Vis spectroscopy indicating that the thiophene chromophore excitons are coupled in a chiral environment. When the CD spectra were measured in methanol, no absorption in the thiophene region is observed. The lack absorption indicates the chromophores are no longer in a chiral environment; further indicating



Figure 4.8. a) UV-vis absorbance and fluorescence spectra of **5TAHxLLKK** in water and methanol. b) CD spectroscopy plot of **5TAHxLLKK** in water and methanol at room temperature. Inset is an expanded view of the low wavelength region of the plot. All spectra measured at a concentration of $200 \mu M$.

5TAHxLLKK is molecularly dissolved in methanol. Since the CD absorption observed in water is lost in methanol, the hydrogen bonding of the peptide region must be responsible for the aggregation of the thiophene chromophore.

CD spectroscopy was also used to investigate the conformation of the peptide segment of the **5TAHxLLKK**. Initially, in both water and methanol absorption in the amide region of the CD spectra does not occur until about 205 nm (Figure 4.8b). Typically in peptidic systems, absorption around 200 nm is indicative of a random coil geometry which lacks ordered secondary structure.^{186, 187} Upon heating, a negative peak at 219 nm is observed at high temperatures as seen in Figure 4.9. Since the absorbance spectrum does not significantly change upon heating, the change in CD signal is a result of a change the supramolecular ordering of the peptide region. The appearance of a peak at 219 nm is indicative of β-sheet ordering of the peptidic segment region being induced by heating. Upon cooling, the β -sheet signal remains in the CD spectra, although slightly diminished in intensity. The β -sheet signal remains stable at room temperature for a minimum of four days (Figure 4.9d). In the thiophene region of the CD plot, the intensity of the bisignate Cotton effect decreases upon heating and then increases upon cooling. When cooled, the peak does not quite return to the initial state before heating. Since the absorbance spectrum does not change significantly upon heating, the changes observed by CD must be due to changes in the chiral supramolecular ordering.

The changes in the CD spectrum could be indicative of the competition between hydrogen bonding and π - π stacking forces in the assembly of the molecule. Since both noncovalent forces are present in **5TAHxLLKK**, both are expected to play a role in the overall self-assembly. It is likely that initially π - π stacking dominates the formation of aggregates in



Figure 4.9. a) Variable-temperature CD spectra of **5TAHxLLKK** upon heating in water. Inset is an expanded view of the low wavelength region of the plot showing a peak increasing at 219 nm. b) Variable-temperature CD spectra of **5TAHxLLKK** upon cooling. Inset is an expanded view of the low wavelength region of the plot. c) Variable temperature UV-Vis absorbance spectrum of **5TAHxLLKK**. d) CD spectrum of **5TAHxLLKK** as a function of time after cooling at room temperature. All spectra measured at 200 µM



Figure 4.10. Variable temperature CD spectra of 5TLLKK with heating and b) subsequent cooling. All spectra were acquired at 200 μ M in water.

solution as evidenced by the lack of an ordered peptidic region in CD spectroscopy. Upon heating, the π - π stacking weakens as suggested by the weaker CD intensity at 375 and 425 nm allowing the peptidic region to reorganize into its preferred β -sheet geometry. As the sample is cooled back to room temperature, some π - π stacking returns to the aggregate, but it is not strong enough to break the β -sheet formed upon heating. Since the amino acids are in a β -sheet conformation, the thiophene region cannot achieve as tight of packing as the initial sample, so the CD signal does not fully recover to its initial intensity.

For **5TLLKK**, the CD spectrum showed a strong bisignated CD signal in the thiophene region that was coincident with the UV-Vis absorption maximum indicating a chiral geometry of coupled exactions in the excited state similar to the 5TAHxLLKK derivative shown in Figure 4.10. A weak absorption below 250 nm is observed but does not match the absorption profile of any peptidic secondary structure. It is not possible to determine if the absorption observed at lower wavelengths is attributed to the amide bonds or higher energy absorption of the thiophene core. Since the CD absorbance peak does not match any known peptide secondary structure, it is unlikely that the amides of the peptide segment are in a well ordered geometry. Upon heating, no change is observed in the short wave length region of the spectra, but an increase in CD signal intensity increase in the thiophene absorption region (Figure 4.10b). Cooling the sample leads to a further strengthening of the thiophene CD absorption signal with no significant change in the lower wavelength region of the spectrum. The increase of intensity in the thiophene region upon heating and then cooling likely indicates an increase in π - π stacking of the thiophene core. Annealing the solution would allow the supramolecular aggregate to reach a thermodynamic minimum upon cooling that may not be accessible upon initial gel formation. Because no



Figure 4.11. a) UV-Vis absorbance and fluorescence emission spectra of **5TALKKK** in water. b) Variable temperature CD spectroscopy of **5TALKKK** in water showing a lack of absorption where the thiophene moiety absorbs. All spectra were measured at 200 μ M.

absorption in the CD spectrum that can be attributed to the amides in the peptidic region is observed, it is likely that π - π stacking is the dominant force of aggregation in the **5TLLKK** derivative at all of the temperatures studied. In contrast, when there is a flexible spacer between the peptidic and thiophene segments as in the case of **5TAHxLLKK**, the hydrogen bonding and π - π stacking forces are able to be accommodated in the supramolecular structure.

In the non-gel forming derivative **5TALKKK**, the absorbance and emission spectra revealed symmetric peaks that correspond to typical spectra of non-aggregated quinquethiophene derivatives as seen in Figure 4.11. CD spectroscopy does not reveal any significant absorption in the thiophene region indicating the thiophene chromophores are not exciton coupled. A weak absorption at shorter wavelengths could correspond to a random-coil conformation of the peptidic segment, further indicating the lack of a well ordered self-assembled aggregate in solution. Upon heating, no absorption signal in the thiophene region is observed (Figure 4.11b). Cooling back to room temperature does not produce any detectable absorbance in the thiophene region either. A negative signal increases around 230 nm upon heating that is cannot be attributed to a signal for a typical peptidic secondary structure. It is also possible that this peak arises from higher energy absorption of the thiophene chromophore. The addition of lysine residues along with decreasing the β -sheet propensity of the amino acids in the peptidic segment leads to a soluble derivative instead of a self-assembled structure in water. The solubility of this derivative indicates the importance of the composition within the peptidic segment of the derivatives. A balance between hydrogen bonding, π - π stacking and Columbic repulsion must be achieved in order to form an ordered self-assembled nanostructure.



Figure 4.12. a) UV-Vis absorbance spectrum comparing **5TLLKK**, **5TAHxLLKK**, and **5TALKKK**. b) Fluorescence emission spectra comparing **5TLLKK**, **5TAHxLLKK**, and **5TALKKK**. All spectra are normalized to their respective emission maximum for ease of comparison of shape and emission maximum. c) CD spectra of **5TLLKK**, **5TAHxLLKK**, and **5TALKKK** in water. All spectra are measured at 200 μM in water after heating to 80 °C and cooling to room temperature.

Comparing the absorbance, fluorescence, and CD spectra of the three derivatives demonstrates the role of the peptidic segment on the overall assembly. Since the same thiophene segment is used for each derivative, the changes is spectroscopic behavior should be due to the affect of the peptidic segment. In the absorbance spectrum, all three derivatives have a similar intensity at the absorption maximum, but the maximum is shifted for each derivative as seen in Figure 4.12a. Since all spectra were collected in the same solvent and the same concentration, the shift is likely due to packing differences among the derivatives. The fully soluble **5TALKKK**

5TAHXLLKK. Following the theory of exciton coupling, if h-aggregation occurs then a blue shift if absorption will be observed. Furthermore, the closer the chromophores are packed, the larger the blue shift is expected. In this case, the aggregates of **5TAHXLLKK** would be in a face-to-face geometry to a greater extent than the derivative without the alkyl spacer.

Fluorescence spectroscopy reveals the same trend as the absorbance plots. The absorbance maximum of **5TAHxLLKK** is more red shifted than **5TLLKK** indicating a greater formation of h-aggregates in **5TAHxLLKK**.CD spectroscopy reveals a stronger absorbance of the thiophene region for the **5TLLKK** derivative. On the other hand with **5TAHxLLKK**, a β -sheet signal is observed upon annealing indicating the formation of highly ordered hydrogen bonding among the peptidic region. Since the only difference between **5TLLKK** and **5TAHxLLKK** is an alkyl spacer between the thiophene and peptide segment, it is likely that the added flexibility from the alkyl spacer allows more conformational freedom between the peptide and conjugated region. Typically π - π stacking occurs at shorter distances then hydrogen bonding in β -sheets, creating a spatial mismatch between the two segments.^{75, 188} Without a

conformationally flexible linker between the two segments, a balance between the two forces is not achieved and β -sheet formation is prevented in the **5TLLKK** derivative. With the spacer, the spatial difference can be accommodated and both π - π stacking and β -sheet formation is observed spectroscopically.

4.4 Summary and Outlook

This chapter described the design and self assembly of novel peptidic quinquethiophene bolaamphiphiles that self-assemble to form self-supporting hydrogels at low concentrations. Microscopy revealed 1D nanostructures were formed upon gel formation. The composition of the peptidic segment was found to directly affect the self-assembly properties of the thiophene derivative. If the β -sheet propensity was too weak, no self-assembly is observed. If the β -sheet propensity of the amino acids was too great, then all solubility was lost. Among the derivatives that were found to self-assemble, the addition of an alkyl spacer was necessary to allow both π - π stacking and β -sheet formation so coexist. Without the alkyl spacer, π stacking was found to dominate the aggregation and suppress β -sheet formation. Further spectroscopic evidence indicated face-to-face among the thiophene moiety. This type of packing is essential to the formation of conductive pathways in oligothiophene derivatives. The derivatives discussed here show the formation of self-assembled 1D nanofibers consisting of a π - π stacked thiophene core with amino acids on the periphery. Although no biologically relevant epitope was used in this chapter, one could easily be synthetically added to the fiber. Then a potential electroactive substrate with coated with peptidic epitopes for a specific cellular function would be realized.

4.5 Experimental

4.5.1 General

Unless otherwise noted, all starting materials were obtained from commercial sources (Sigma-Aldrich, TCI, Alfa Aesar) and used without further purification. ¹H NMR and ¹³C NMR spectra were recorded in a Varian Inova 500 (500 MHz for ¹H and 120 MHz for ¹³C NMR) spectrometer using the solvent proton signal as standard. ESI mass spectrometry was performed on a LCQ Advantage. Preparative HPLC was performed on a Varian System using a Phenomenex Jupiter preparative column (10 μ m size particle, 250 x 30.0 mm). Compound purity was analyzed by an analytical reverse-phase high-performance liquid chromatography (RP–HPLC) on an Agilent HP 1050 system equipped with a Phenomenex Jupiter analytical column (10 μ m particle size, 150 × 4.6 mm). Conformation of mass and purity includes mass spectrometry and RP-HPLC. TEM images taken by Lorraine Hsu of the Stupp lab.

UV-Vis absorption spectra were collected on a Cary 500 spectrometer in double beam mode. All samples were prepared measured at 200 μ M in a 0.1 cm pathlength quartz cuvette. Fluorescence spectra were recorded on a PC1 Spectrofluorometer in right angle geometry using monochromators with a FWHM of 8 nm for both the excitation and emission. All spectra were collected by exciting at the absorption maxima. CD spectroscopy was performed on a model J-714 Jasco Circular Dichroism Spectrometer at the same concentration as UV-Vis spectroscopy. For temperature dependent measurements, the samples were allowed to equilibrate for 5 min at the specified temperature before measurement.

All gels were formed by dissolving the derivative at the desired concentration. The samples were then heated to 80 °C and allowed to cool to room temperature. Gel formation was considered to occur when the solution was stable to vial inversion.

AFM measurements were taken on a Nanoscope Multimode ScanningProbe Microscope. Films were cast from a dilute aqueous solution (0.05 wt %) on to a freshly cleaved mica surface. Transmission electron microscopy was performed on a Hitachi 8100 operating at 100 kV on holey carbon coated Cu TEM grids. All TEM samples were stained with uranyl acetate for 15 minutes.

4.5.2 Molecular Synthesis of Peptidic Segments

All amino acid coupling in this chapter occurred under the same general conditions as follows. In a round bottom flask the free amine (1 equiv), free acid (1.2 equiv), HOBT (1.2 equiv), TEA (1.2 equiv) and EDC (1.2 equiv) were dissolved in dichloromethane. The reaction was stirred for 16 hours at room temperature. The reaction mixture was extracted three times with sat. NaHCO₃ (aq), followed by three times with 2M HCl. The organic layer was then dried with Na₂SO₄ and then removed by rotary evaporation. The crude product was purified by column chromatography (silica gel, CH₂Cl₂/MeOH (95/5)) to yield the desired product.

All benzyl deprotection reactions followed the same procedure as follows. In a round bottom flask the carbobenzyloxy (Cbz) protected amine was dissolved in dichlormethane with 1 mL of methanol. To the solution, palladium on carbon (10 wt % Pd) was added (10 wt % cat loading). The reaction was allowed to stir for 16 hours under hydrogen. The reaction mixture was filtered through Celite to remove the catalyst, dried with Na₂SO₄ and then the solvent was removed by rotary evaporation. The crude product wass purified by column chromatography (silica gel, CH₂Cl₂/MeOH (95/5)) to yield the desired product.

Conformation of product was based on ESI mass spectrometry. Sever line broadening made ¹H NMR analysis difficult.

Cbz-K(Boc)-K(Boc)-*t***Bu**: Prepared by the general method described above using Cbz-K-(Boc)-OH (1.00 g, 3.0 mmol), H-K(Boc)-*t*Bu (0.95 g, 2.5 mmol), HOBT (0.40 g, 3.0 mmol), EDC (0.57 g, 3.0 mmol) and TEA (0.30 g, 3.0 mmol). Colum chromatography yielded 1.95 g (98 % yield) as a white solid. ESI-MS m/z calculated for C₃₄H₅₆N₄O₉, 664.83; found, 687.93 (M+Na).

H-K(Boc)-K(Boc)-*t***Bu**: Prepared by the general method above for Cbz cleavage on Cbz-K(Boc)-*t*Bu (1.95 g, 3 mmol). Colum chromatography yielded 1.56 g (quant.) as a white solid. ESI-MS m/z calculated for C₂₆H₅₀N₄O₇, 530.37; found, 531.80 (M+H).

Cbz-L-K(Boc)-K(Boc)-*t***Bu**: Prepared by the general method described above using H-K-(Boc)-K(Boc)-*t*Bu (1.35 g, 2.5 mmol), Cbz-L-OH (0.79 g, 3.0 mmol), HOBT (0.38 g, 2.5 mmol), EDC (0.48 g, 2.5 mmol) and TEA (0.30 g, 3.0 mmol). Colum chromatography yielded 1.88 g (95 % yield) as a white solid. ESI-MS m/z calculated for C₄₀H₆₇N₅O₁₀, 777.49; found, 800.83 (M+Na).

H-L-K(Boc)-K(Boc)-*t*Bu: Prepared by the general method described above for Cbz deprotection on Cbz-L-K(Boc)-*t*Bu (1.88 g, 2.5 mmol). Colum chromatography yielded 1.56 g

(quant.) as a white solid. ESI-MS m/z calculated for C₃₂H₆₁N₅O₈, 643.45; found, 645.03 (M+2H).

Cbz-L-L-K(Boc)-K(Boc)-*t***Bu**: Prepared by the general method described above using H-L-K-(Boc)-*t***Bu** (0.56 g, 0.87 mmol), Cbz-L-OH (0.36 g, 1.0 mmol), HOBT (0.11 g, 0.87 mmol), EDC (0.17 g, 0.87 mmol) and TEA (0.08 g, 0.87 mmol). Colum chromatography yielded 0.77 g (99 % yield) as a white solid. ESI-MS *m/z* calculated for C₄₆H₇₈N₆O₁₁, 890.57; found, 914.17 (M+Na).

H-L-L-K(Boc)-K(Boc)-tBu: Prepared by the general method described above for Cbz deprotection on Cbz-L-L-K(Boc)-K(Boc)-*t*Bu (0.40 g, 0.45 mmol). Colum chromatography yielded 0.34 g (quant.) as a white solid. ESI-MS m/z calculated for C₃₈H₇₂N₆O₉, 756.54; found, 758.28 (M+2H).

Cbz-AHx-L-L-K(Boc)-K(Boc)-*t***Bu**: Prepared by the general method described above using H-L-L-K-(Boc)-K(Boc)-*t*Bu (0.37 g, 0.45 mmol), Cbz-AHx-OH (0.16 g, 0.06 mmol), HOBT (0.06 g, 0.45 mmol), EDC (0.08 g, 0.45 mmol) and TEA (0.04 g, 0.45 mmol). Colum chromatography yielded 0.45 g (99 % yield) as a white solid. ESI-MS *m*/*z* calculated for $C_{52}H_{89}N_4O_{12}$, 1003.66; found, 1027.56 (M+Na+H).

H-AHx-L-L-K(Boc)-K(Boc)-*t*Bu: Prepared by the general method described above for Cbz deprotection on Cbz-AHx-L-L-K(Boc)-K(Boc)-*t*Bu (0.45 g, 0.45 mmol). Colum chromatography

yielded 0.39 g (quant.) as a white solid. ESI-MS m/z calculated for C₄₄H₈₃N₇O₁₀, 869.62; found, 871.55 (M+2H).

Cbz-K(Boc)-K(Boc)-tBu: Prepared by the general method described above using H-K-(Boc)-tBu (0.55 g, 1.0 mmol), Cbz-K(Boc)-OH (0.53 g, 1.4 mmol), HOBT (0.17 g, 1.3 mmol), EDC (0.25 g, 1.3 mmol) and TEA (0.13 g, 1.3 mmol). Colum chromatography yielded 0.83 g (95 % yield) as a white solid. ESI-MS m/z calculated for C₄₄H₇₄N₆O₁₂, 878.54; found, 917.63 (M+K).

H-K(Boc)-K(Boc)-K(Boc)-*t***Bu**: Prepared by the general method described above for Cbz deprotection on Cbz-K(Boc)-*K*(Boc)-*t*(Boc)-*t*Bu (0.83 g, 0.95 mmol). Colum chromatography yielded 0.65 g (92 % yield) as a white solid. ESI-MS *m/z* calculated for $C_{37}H_{70}N_6O_{10}$, 758.52; found, 760.06 (M+2H).

Cbz-L-K(Boc)-K(Boc)-K(Boc)-*t***Bu**: Prepared by the general method described above using H-K(Boc)-K-(Boc)-K(Boc)-*t*Bu (0.65 g, 0.85 mmol), Cbz-L-OH (0.27 g, 1.0 mmol), HOBT (0.13 g, 1.0 mmol), EDC (0.19 g, 1.0 mmol) and TEA (0.10 g, 1.0 mmol). Colum chromatography yielded 0.79 g (93 % yield) as a white solid. ESI-MS *m/z* calculated for $C_{51}H_{87}N_7O_{13}$, 1005.64; found, 1028.68 (M+Na).

H-L-K(Boc)-K(Boc)-*t*Bu: Prepared by the general method described above for Cbz deprotection on Cbz-K(Boc)-K(Boc)-K(Boc)-*t*Bu (0.79 g, 0.78 mmol). Colum chromatography
yielded 0.49 g (72 % yield) as a white solid. ESI-MS m/z calculated for C₄₃H₈₁N₇O₁₁, 871.60; found, 873.32 (M+2H).

Cbz-A-L-K(Boc)-K(Boc)-K(Boc)-tBu: Prepared by the general method described above using H-L-K(Boc)-K-(Boc)-K(Boc)-tBu (0.49 g, 0.50 mmol), Cbz-L-OH (0.15 g, 0.70 mmol), HOBT (0.09 g, 0.7 mmol), EDC (0.13 g, 0.70 mmol) and TEA (0.10 g, 1.0 mmol). Colum chromatography yielded 0.35 g (66 % yield) as a white solid. ESI-MS m/z calculated for C₅₄H₉₂N₈O₁₄, 1076.67; found, 1099.95 (M+Na).

H-A-L-K(Boc)-K(Boc)-K(Boc)-*t***Bu**: Prepared by the general method described above for Cbz deprotection on Cbz-A-K(Boc)-K(Boc)-K(Boc)-*t*Bu (0.35 g, 0.35 mmol). Colum chromatography yielded 0.32 g (quant) as a white solid. ESI-MS m/z calculated for C₄₆H₈₆N₈O₁₂, 942.64; found, 944.66 (M+2H).

4.5.3 Molecular Synthesis of 5T-methyl Dicarboxylic Acid

3-methyl-2,5-di(thiophen-2-yl)thiophene 9: In a dry and degassed flask, a solution of 2,5dibromo-3-methylthiophene (1.0g, 4.0 mmol) in DMF (40 mL) was added 2-(tributylstannyl)thiophene (3.6 g, 9.6 mmol). The solution was sparged with N₂ gas for 20 minutes. Tetrakistriphenylphosphine palladium(0) (52 mg) was then added to the solution. After stirring at 100 °C for 16 h, the reaction was cooled to room temperature. The reaction mix was diluted with chloroform and extracted three times with 5% citric acid (aq). The organic layer was dried over Na₂SO₄ and the solvent was removed in vacuo. The crude product was purified by column chromatography (silica gel; chloroform/hexanes, 10:90) to yield 0.86 g (88%) of the compound as a yellow oil. ¹H NMR (CDCl₃, ppm): δ 7.32 (d, 1H, J = 5 Hz), 7.23 (d, 1H, J = 5 Hz), 7.19-7.18 (m, 2H), 7.10 (at, 1H, J = 4 Hz), 7.04 (at, 1H, J = 4), 7.00 (s, 1H), 2.40 (s, 3H). ¹³C NMR (CDCl₃, ppm): δ 137.39, 136.59, 134.90, 134.79, 130.29, 128.15, 128.14, 127.76, 125.65, 125.38, 124.63, 123. 84, 15.79. ESI-MS (m/z): [M]⁺ calcd for C₁₃H₁₀S₃, 262.41; found, 262.63.

2,5-bis(5-(tributylstannyl)thiophen-2-yl)-3-methylthiophene 10: A solution of **1** (0.30 g, 1.1 mmol) in anhydrous THF (30 mL) was cooled to -78 °C. *n*-Butyllithium in a 2.5M solution of cyclohexane (1.2 mL) was added and the reaction was stirred for 1 h while warming to room temperature. Tributyltin chloride (0.94 g, 2.9 mmol) was added and the reaction stirred for 16 h at room temperature. The reaction was diluted with hexanes and extracted three times with sat. NaHCO₃ (aq), dried with Na₂SO₄, concentrated and used without purification in the next step.

tert-butyl 5-bromothiophene-2-carboxylate: To a solution of 4-(*N*,*N*-dimethylamino)pyridine (0.86 g, 7.0 mmol), 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) (1.34, 7.0 mmol), tert-butyl alcohol (10 mL, 105 mmol) in dichloromethane (30 mL) was added 5-bromo-2-thiophenecarboxylic acid (1.0 g, 4.8 mmol). After stirring for 16 h at room temperature, the solvent was removed. The mixture was then dissolved in dichloromethane and extracted 3 times with 2M HCl (aq) followed by three times with sat. NaHCO₃. The organic layer was dried with Na₂SO₄ and concentrated to yield 1.16 g (92 %) of the desired product as a clear oil. ¹H NMR

(CDCl₃, ppm): δ 7.47 (d, 1H, J = 4 Hz), 7.05 (d, 1H, J = 4 Hz), 1.57 (s, 9H). ¹³C NMR (CDCl₃, ppm): δ 160.62, 137.12, 133.12, 130.92, 119.56, 82.55, 28. 41.

ditertbutyl ester 3-methyl-quinquethiophene 11: In a Nitrogen atmosphere, tert-butyl 5bromothiophene-2-carboxylate (0.69 g, 2.6 mmol) was added to a solution of **2** (0.84 g, 1.1mmol) in DMF (40 mL). The solution was sparged with nitrogen gas for 20 min and tetrakistriphenylphosphine palladium(0) (57mg) was added. The reaction stirred at 100 °C for 16 h. The reaction mixture was cooled to room temperature, diluted with chloroform, and extracted 3x with 5% citric acid (aq) to remove the DMF. After drying the organic layer over Na₂SO₄, the product was purified by column chromatography (silica gel; chloroform/hexanes, 65:35) to yield 0.62 g (90 %) of the desired product as a red-orange powder. ¹H NMR (CDCl₃, ppm): δ 7.64 (d, 1H, J = 4 Hz), 7.63 (d, 1H, J = 4 Hz), 7.24 (d, 1H, J = 4 Hz), 7.18 (d, 1H, J = 3.5 Hz), 7.18 (d, 1H, J = 3.5 Hz), 7.14 (d, 1H, J = 3.5 Hz), 7.12 (d, 1H, J = 4 Hz), 7.09 (ad, 2H, J = 4 Hz), 7.01 (s, 1H), 2.43 (s, 3H), 1.61 (s, 18H). ¹³C NMR (CDCl₃, ppm): δ 161.56, 161.54, 143.22, 143.20, 137.41, 136.87, 136.31, 135.64, 135.56, 134.91, 134.00, 133.82, 133.80, 130.42, 128.68, 126.36, 125.98, 125.63, 124.74, 123.94, 123.88, 82.21, 82. 20, 25.50, 16.05. MALDI-TOF (m/z); [M]⁺ calcd for C₃₁H₃₀O₄S₅, 626.89; found, 627.18.

dicarboxylic acid 3-methyl-quinquethiophene (5TmDCA) 12: In a solution 25 mL solution of Dichloromethane and TFA (5:1) 3 (50 mg, 0.79mmol) was stirred at room temperature for 2 h. The solvent was removed and the product was triturated three times with methanol and dried to yield 37 mg (92%) the desired product as a red solid. ¹H NMR (DMSO-d₆, ppm): δ 7.68 (d, 1H,

J = 1.5), 7.67 (d, 1H, J = 1.5), 7.52 (d, 1H, J = 3.5), 7.48 (d, 1H, J = 4), 7.41 (d, 1H, J = 4), 7.39 (d, 1H, J = 4), 7.35 (d, 1H, J = 3.5), 7.31 (s, 1H), 7.28 (d, 1H, J = 4), 2.39 (s, 3H). ¹³C NMR (100 MHz, DMSO-d₆, ppm): 163.26, 146.78, 136.94, 136.54, 136.43, 135.69, 135.11, 135.03, 134.00, 133.47, 130.03, 129.91, 127.78, 127.61, 127.55, 127.45, 126.23, 125.56, 125.52, 16.18. ESI-MS (m/z): $[M]^+$ calcd for C₂₃H₁₄O₄S₅, 514.68; found, 515.53.

4.5.3 Molecular Synthesis of Peptidic Quinquethiophene Amphiphiles



5TLLKK Protected: In a 100 mL round bottom flask 5TmDCA (0.11 g, 0.22 mmol), H-L-L-K(Boc)-*t*Bu (0.40 g, 0.53 mmol), EDC (0.10 g, 0.53 mmol), HOBT (0.07 g, 0.53 mmol) and TEA (0.05, 0.53 mmol) were dissolved in DMF (50 mL). The reaction stirred for 16 hours at room temperature. The DMF was removed by rotary evaporation and further dried under high vacuum. The crude product was purified by column chromatography (silica gel; chloroform/methanol, 95:05) to yield 0.31 g (73% yield) as a red-orange solid. The desired compound was not observed by ESI or MALDI-TOF, so the molecule was carried forward for deprotection.



5TLLKK: The fully protected 5TLLKK derivative (0.10 g) was reacted with HBr (48% in water) in acetic acid in a 4:1 (25 mL) ratio for 10 min. The solution was then diluted with methanol (5 mL) and the product was precipitated with ether. The product was precipitated three times from methanol with either and collected by centrifugation. The product was purified by RP–HPLC. ESI-MS *m/z* calculated for $C_{71}H_{106}N_{12}O_{12}S_5$, 1478.67; found, 1479.33 [M]⁺.



5TAHXLLKK Protected: In a 100 mL round bottom flask 5TmDCA (0.10 g, 0.19 mmol), H-AHx-L-L-K(Boc)-K(Boc)-*t*Bu (0.39 g, 0.45 mmol), EDC (0.09 g, 0.45 mmol), HOBT (0.06 g, 0.45 mmol) and TEA (0.05, 0.45 mmol) were dissolved in DMF (50 mL). The reaction was stirred for 16 h at room temperature. The DMF was removed by rotary evaporation and further dried under high vacuum. The crude product was purified by column chromatography (silica gel; chloroform/methanol, 95:05) to yield 0.28 g (67% yield) as a red-orange solid. The desired compound was not observed by ESI or MALDI-TOF, so the molecule was carried forward for deprotection.



5TAHXLLKK: The fully protected 5TAHXLLKK (0.10 g) derivative was reacted with HBr (48% in water) in acetic acid in a 4:1 (25 mL) ratio for 10 min. The solution was then diluted with methanol (5 mL) and the product precipitated with ether. The product was precipitated three times from methanol with either and collected by centrifugation. The product was purified by RP–HPLC. ESI-MS *m/z* calculated for $C_{83}H_{140}N_{14}O_{14}S_5$, 1706.86; found, 1706.30 [M]⁺.



5TALLKKK Protected: In a 100 mL round bottom flask 5TmDCA (0.08 g, 0.14 mmol), H-A-L-K-(Boc)-K(Boc)-K(Boc)-*t*Bu (0.32 g, 0.35 mmol), EDC (0.07 g, 0.35 mmol), HOBT (0.05 g, 0.35 mmol) and TEA (0.04, 0.35 mmol) were dissolved in DMF (50 mL). The reaction stirred for 16 hours at room temperature. The DMF was removed by rotary evaporation and further dried under high vacuum. The crude product was purified by column chromatography (silica gel; chloroform/methanol, 95:05) to yield 0.34 g (90% yield) as a red-orange solid. The desired compound was not observed by ESI or MALDI-TOF, so the molecule was carried forward for deprotection.



5TALKKK: The fully protected 5TALKK (0.10 g) derivative was reacted with HBr (48% in water) in acetic acid in a 4:1 (25 mL) ratio for 10 min. The solution was then diluted with methanol (5 mL) and the product precipitated with ether. The product was precipitated three times from methanol with either and collected by centrifugation. The product was purified by RP–HPLC. ESI-MS m/z calculated for C₇₇H₁₂₂N₁₆O₁₄S₅, 1654.79; found, 1653.00 [M]⁺.

Chapter 5

Ordered Hybrid Nanostructures with Conjugated Surfactants

Chapter 5: Ordered Hybrid Nanostructures with Conjugated Surfactants

5.1 Introduction

Hybrid materials consisting of an organic and inorganic phase offer a strategy for improved mechanical and electronic properties that are unobtainable in materials made from purely organic or inorganic phases. Initial interest in hybrid materials focused on novel mechanical properties, but recently the optoelectronic properties hybrid materials have been explored in transistor, light emitting, and photovoltaic devices.^{36, 40, 109, 111} For these devices, the interfacial and macroscopic ordering of the organic and inorganic phases is crucial to the overall performance of the device.^{109, 189, 190} Preliminary work on electronic hybrid devices relied on simple mixing of the two phases to form the contact between the inorganic and organic phase, but control over interface and hybrid structure was not easily obtained in this methodology.^{191, 192}

In order to better control hybrid structures, several mineralization techniques have been developed. During the process of mineralization, the inorganic phase is typically formed from precursor molecules in the solution or gas phase. Self-assembly offers a facile approach to achieve nanoscale ordering of hybrid phases using a bottom up methodology.^{96, 193} The most common approaches to self-assembled hybrid materials used a templated mineralization approach or a co-assembly approach. In a templated mineralization, first an organic molecule forms a self-assembled structure on a surface.^{67, 100} An inorganic precursor is then introduced to the preformed organic nanostructure. If the organic molecule is designed correctly, the inorganic precursor will interact with the organic template and the inorganic phase will copy the organic nanostructure.¹⁹⁴ Many structures of hybrid materials have been formed this way, but the

nanostructure formation relies on the ability of the organic material to self-assemble to form highly ordered structures.

Co-assembling techniques rely on synergistic self-assembly of solvated organic molecules and inorganic precursors to form a highly ordered hybrid materials upon deposition onto a surface. One of the most popular co-assembly methodologies is called Evaporation Induced Self-Assembly (EISA).^{103, 195, 196} EISA offers the ability to create mesoporous and nanostructured silicate films from inorganic precursors and organic surfactants using only dipcoating or spin-casting deposition techniques.¹⁹⁷ During evaporation, the hydrophilic groups of the amphiphilic surfactants interact with hydrophilic inorganic precursors resulting in bilayers, micelles, or cylindrical micelles and directing the condensation of the inorganic framework.^{198,} ¹⁹⁹ Typically, the organic surfactant's only role is to control the structure so the surfactants are often charged end goups with alkyl tails such as cetyltrimethylammonium bromide (CTAB) or sodium dodecylsulfate (SDS).^{102, 199} The surfactants can then be thermally removed from the inorganic phase once the nanoscale ordering is achieved.¹⁰² Therefore, introducing an electronically active organic phase is an attractive method to forming highly ordered hybrid devices.

Recently, electroactive molecules have been introduced into inorganic nanostructures formed by EISA in attempts to add electronic functionality to the system, but a high loading of organic material is not possible.²⁰⁰⁻²⁰² In order to achieve a high density of electroactive organic molecules within the inorganic frame, our lab has synthesized a dicationic OPV molecule to directly template mesoporous silicon dioxide.²⁰³ When rhodamine-functionalized silica precursors are included in the deposition solution, enhanced energy transfer is observed over an amorphous film of OPV and rhodamine. In this report, two diffraction peaks by X-ray analysis where observed indicating nanoscale ordering, but the structure was only probed by 1D X-ray techniques.

As an alternative to EISA, electrodeposition has become an attractive method to impart nanoscale ordering of hybrid materials. Instead of relying on sol-gel chemistry to form the inorganic phase, mineralization occurs by electrolytically reducing salt precursors to form the desired inorganic phase.²⁰⁴⁻²⁰⁹ Recently, electrodeposition of zinc oxide (ZnO) into lamellar structures has been observed using simple alkyl surfactants such as SDS and CTAB.^{205, 210, 211} By tailoring the synthesis to conjugated surfactants, a one step synthesis of an electronically functional hybrid material could be realized. Since ZnO, a well know n-type semiconductor, is the inorganic phase in this methodology. The use of a p-type semiconducting surfactant would also lead to a promising route for the fabrication of a photovoltaic device.^{109, 212}

The first part of this chapter studies the nanostructure formed within the hybrid film synthesized by EISA with the use of Grazing Incidence X-Ray Scattering (GIXS) performed at the Advanced Photon Source (APS) at Argonne National Lab using a 2D CCD detector to observe out-of-plane peaks. GIXS offers the ability to sample a large area film to evaluate long-range ordering without damaging the sample.²¹³ Furthermore, to probe the generality of EISA to ordered hybrid materials with conjugated surfactants, both OPV and oligothiophene moieties were used to synthesize films for analysis by GIXS. The role of the organic molecule and the ratio of surfactant to inorganic precursor in the deposition condition were also explored to elucidate their affect on the overall structure. The second part of the chapter details the development on an anionic oligothiophene surfactant to be compatible with the electrodeposition

of layered ZnO hybrid films. The hybrid structure was investigated by X-Ray diffraction, SEM, and TEM. This methodology was used to create a deice with a measurable photoconductivity.

5.2 Evaporation Induced Self-Assembly with Conjugated Surfactants

5.2.1 Molecular Design and Synthesis

The most common surfactant utilized in EISA is CTAB. The hydrophilic quaternary ammonium end group interacts with the inorganic precursor giving rise to the temptation of the hybrid material.^{103, 199} Because conjugated moieties often have low solubility, especially in the polar solvents needed for EISA (eg. methanol/water mixtures are used), dicationic bolaamphiphilic molecules were synthesized to increase the charge per molecule. Solubility was greatly improved by the increased charge per molecule over asymmetric single-charged derivatives of a similar structure. Trimethylammonium head groups were chosen to closely mimic the head group responsible for interacting with the inorganic precursors in the traditional CTAB system. Additional substitutions along the conjugated segment of each derivative were avoided to maximize packing of the conjugated segments.

The OPV dicationic amphiphile was synthesized following the procedure previously published detailing the energy transfer properties of a hybrid film by Dr. Keisuke Tajima in the Stupp lab.²⁰³ The synthesis of the bolaamphiphile consisted of a convergent strategy based on Horner-Wadsworth-Emmons (HWE) chemistry to form the alkene bonds as seen in Figure 5.1.²¹⁴ The HWE reaction was chosen over the similar Wittig reaction because the HWE reaction produces almost exclusively E-isomers when aromatic aldehydes are used unlike the Wittig reaction that tends to yield the Z-isomer.²¹⁵ Furthermore, the dialkylphosphate salt byproduct of

the HWE reaction can be more easily removed than the triphenylphosphine oxide byproduct of the Wittig reaction. The amine containing segment was introduced by alkylating 4-hydroxybenzaldehyde with 2-(dimethylamino)ethyl methanesulfonate using potassium carbonate in acetone with 18-crown-6 as a phase transfer catalyst to yield **2**. The center ring of



Figure 5.1. Synthesis scheme for dicationc OPV derivative **4**. a) P(OEt)₃, 100 °C, b) 2- (dimethylamino)ethyl methanesulfonate, 18-crown-6, K₂CO₃, acetone, c) KOtBu, THF, d) MeBr, THF, 3 days.

the OPV system was prepared by a Michaelis-Arbuzov reaction with 1,4bis(bromomethyl)benzene in neat triethyl phosphite to yield the symmetric benzyl diethylphosphonate **1**. A double HWE reaction was then used between **1** and **2** to yield thesymmetric uncharged OPV derivative **3**. The uncharged tertiary amine has low solubility in most solvents, but is soluble in a dichloromethane/methanol (80:20) mixture. The final dicationic OPV derivative was synthesized by a Menshutkin reaction between the uncharged precursor and methyl bromide. Typically, the reaction proceeds over 3-4 days and the desired product precipitates from the reaction mixture. The dicationic OPV was in polar solvents such as methanol, DMF, DMSO, and even water. Addition of hydrochloric acid (HCl) to the aforementioned solvents increases the solubility due to the protonation of the amines.

The synthesis quaterthiophene bolaamphiphile followed a similar convergent synthesis strategy. To make this derivative, the thiophene core was constructed using a carbon-carbon bond forming reaction as seen in Figure 5.2. The Stille coupling was used as the carbon-carbon bond forming reaction because it has been found to afford higher yields for couplings between thiophene couplings than other organometallic catalyzed approaches.¹¹³ To form amine **6**, 2-(dimethylamino)ethyl methanesulfonate was linked to the thiophene moiety through an ether



Figure 5.2. Synthesis scheme for cationc 4T derivative **8**. a) LAH, THF, b) 2- (dimethylamino)ethyl methanesulfonate, NaH, THF. c) 2,5'-di(tributyltin)bithiophene, Pd(PPh₃)₄. d) MeBr, THF, 3 days.

linkage. In order to synthesize the alcohol need for an ether forming reaction, 5-bromothiophene-2-carbaldehyde was quantitatively reduced to 5-bromo-2-thiophenemethanol **5** by lithium aluminum hydride (LAH). Attempts to use milder reducing reagents, such as sodium borohydride, were unsuccessful. Alcohol **5** was deprotonated with odium hydride (NaH) and reacted with 2-(dimethylamino)ethyl methanesulfonate to give substrate **6** for use in the Stille coupling. The other substrate for the Stille coupling was synthesized by forming a dianion of bithiophene and subsequent quenching with tributyltin chloride.¹¹⁷ The uncharged oligothiophene derivative **7** was more soluble than the OPV derivative. When the OPV derivative formed a suspension in THF, the oligothiophene derivative was found to be soluble. The added solubility is most likely a result of the ether linkage on the periphery of the thiophene structure. Finally, the dicationic thiophene derivative **8** was synthesized by a Menshutkin reaction between the uncharged precursor and methyl bromide over 3-4 days. The thiophene derivative was in polar solvents such as methanol, DMF, DMSO, and water. Addition of hydrochloric acid (HCl) to the aforementioned solvents increases the solubility as well.

5.2.2 Structural Determination of OPV Hybrid Films by GIXS

To create hybrid films with electronically relevant molecules, the cationic OPV amphiphile was used to template films using EISA. In methanol, the OPV derivative, tetraethyl orthosilicate (TEOS), and an acid catalyst (HCl) were dissolved and films were deposited by spin casting onto a glass substrate. TEOS in the presence of an acid catalyst is known undergo an oligomerization to form short chains of silicon dioxide with charged terminal groups.¹⁹⁹ Due to the charged nature of the silica oligomers, they are expected to interact with the charged region

of the conjugated surfactants. As the film dries after deposition, the silica oligomers polymerize further yielding long silicon dioxide polymers that have been templated by the organic surfactant.

During the initial structural analysis of the OPV/silica hybrid, X-ray diffraction scans revealed Bragg diffraction peaks with d-spacings of 2.76 and 1.37 nm, indicating the presence of order in the hybrid film.²⁰³ In that initial report, it was proposed that these two peaks could be assigned to a lamellar structure. However, a hexagonal structure could instead be present in these systems resulting from the packing of cylindrical micelles aligned parallel to the substrate, giving rise to only the (01) and (02) reflections being observed and the (11) reflection being unobserved. To help elucidate the nanoscale structure parallel and perpendicular to the substrate within the hybrid film, GIXS measurements were performed at APS with a 2D CCD detector. The GIXS data was acquired by the author in close collaboration with Marina Sofos who was also in the author's research group. The data analysis was also performed by Marina Sofos.

GIXS was chosen as the analysis method for its ability to determine long-range ordering over a large area of film without damaging the sample. To protect the film from oxidative damage due to oxone formed by irradiation of air with the X-ray beam, the sample was purged with nitrogen during the measurements. The sample chamber was made out of Kapton foil because Kapton is known to not suffer from radiation damage and has a high transmittance to Xrays. The GIXS patter for an oligomer/silica hybrid films shown in Figure 5.3 with momentum transfer reciprocal space coordinates q_x - q_z where q_z in the out-of-plane direction, and q_x is the inplane and perpendicular to the incident beam. The powder ring observed partially eclipsing the (04) peak is attributed to the Kapton foil on the sample chamber. The oversaturation along the q_z axis is due to the strong intensity of the beam in the specular direction.

The GIXS pattern was measured for a film with a molar ratio of OPV to TEOS of 1:6.67 (Figure 5.3b), the same ratio used in the energy transfer work. This film revealed the presence of a slightly distorted 2D hexagonal phase with the perpendicular-to-plane spacing slightly shorter than the parallel-to-plane spacing. The pattern shows a slightly distorted 2D hexagonal phase with the q_z vector than the q_x vector. Accounting for the vertical depression, a rectangular facecentered unit cell with parameters arec and crec was used to index the diffraction spots and represent a vertically constrained hexagonal lattice. When the observed diffraction spots are indexed, arec is found to be equal to 3.4 nm and crec is equal to 5.1 nm using the following equations: $a_{rec} = 2 * d_{20}$ and $c_{rec} = 2 * d_{02}$. This characterized the nanostructure as distorted cylinders with diameters of 3.4 nm parallel to the substrate and 3.1 nm out-of-plane to the substrate as shown in Figure 5.4. The fully extended length of the dicationic OPV amphiphile was calculated to be 2.5 nm. Therefore, the observed overall cylinder diameters, 3.4 nm wide by 3.1 nm high, are consistent with molecules fully extended with a 0.5 to 1.0 nm shell of silica. The charged end groups of the OPV amphiphile are expected to interact with the TEOS, thus directing the formation of the observed cylinders.

For an undistorted 2D hexagonal phase, the ratio of the rectangular face-centered spacings would be $c_{rec}/a_{rec} = \sqrt{3}$. The vertical shrinkage of the cylinders observed in the GIXS plot creates an elliptical, rather than circular, shape to the cylindrical cores. This effect has been previously attributed to vertical compressive strain caused by drying effects a siloxane condensation occurring after the hexagonal mesophase forms.¹⁰³ The hexagonally packed



Figure 5.3. a) Schematic of sample measurement by grazing incident X-ray (GIXS) scattering showing coordinate geometry of the detector. b) GIXS pattern obtained showing a vertically strained hexagonal ordering. Labels on diffraction spots correspond to the hl indices for a face centered unit cell.



Figure 5.4. Schematic of the Evaporation Induced Self-Assembly process and final structure. Vertically strained hexagonal packed cylinders are formed that lie parallel to the surface. The 2D hexagonal (hex) unit cell axes are shown as red-dashed line vectors. The 2D rectangular face-centered (rec) unit cell axes are indicated by black arrows.

cylindrical micelles formed in the hybrid films are oriented parallel to the substrate surface. The observed diffraction spots do not change their positions when the samples are rotated about their surface normal. This indicates the presence of individual domains consisting of aligned hexagonally packed cylinders. The cylindrical axis of each domain is aligned parallel to the surface, but there is no in-plane orientation of these domains. While most of the domains lie flat on the substrate, the faint powder rings produced around the diffraction spots indicated that a small fraction of the domains are randomly oriented.

To study the effect of the molar ratio of silica precursor to OPV molecule in the initial solution to the final structure, hybrid film samples were prepared from solutions with varying TEOS to OPV ratios. The initial concentration of OPV in solution remains constant at 6 mg/mL, while the molar concentration of the silica precursor and the acid catalyst were adjusted. In these cases, the same pseudo-hexagonal packing or rectangular face-centered unit cell is generated. In fact, the resulting d spacings and cylinder dimensions remain constant for the unit cell in all three cases with starting molar ratios of TEOS to OPV of (a) 10, (b) 6.67, and (c) 3.33 equivalents as seen in Figure 5.5. Because the cylinder dimensions do not change with the amount of TEOS, the results suggest that there is a maximum molar ratio of TEOS that will interact with the fixed number of charged end groups of OPV amphiphilic molecules to generate the hexagonally packed nanoscale structure. When more TEOS was added, a fixed number of charged end groups on the OPV amphiphile prevent further silica from being incorporated around the cylindrical aggregates. Additional XRR studies suggest that the additional silica formed is not incorporated within the cylindrical hybrid nanostructure.¹³⁵ As we previously reported, a uniform distribution of the amphiphiles is implied by the linear relationship between the optical density and film

thickness of the hybrids.²⁰³ In the absence of TEOS and the acid catalyst, a film cast from a solution of the cationic OPV in methanol at a concentration near its solubility limit of 9.0 mM did not lead to the hexagonal structure (see Figure 5.5d). This implies that the ordering observed is a direct result of the mineralization process.

5.2.3 Structural Determination of Quaterthiophene Hybrid Films by GIXS

To test the generality of this self-assembling hybrid system with a different amphiphile, we used a more conductive conjugated segment. A dicationic quaterthiophene derivative was synthesized for use in hybrid films formed by EISA. Interestingly, upon mineralization with silica we obtained the same distorted hexagonally packed cylindrical micelle nanostructured films. Figure 5.6 shows the CCD image obtained for one quadrant of the q_x - q_z plane for a film prepared from a 1-mL solution in MeOH of 6 mg of **8** and 14 µL of TEOS with a molar ratio of TEOS to **8** of 7.23, close to the ratio of the original OPV hybrid of 1:6.67 (**4**/TEOS). In the case of **8**, the slightly longer extended molecular length of 2.8 nm compared to **4** (2.5 nm) is also reflected in a slight increase of the unit cell dimensions with $a_{rec} = 3.6$ nm and $c_{rec} = 5.8$ nm leading to cylinder dimensions of 3.6 nm parallel to the substrate and 3.4 nm out-of-plane. This result using GIXS on a second compound supports our hypothesis that the conjugated molecules are oriented perpendicular to the long axis of a one-dimensional cylindrical aggregate and surrounded by silica. Furthermore, the diameter of the cylinder can be readily controlled with the choice of organic molecule.



d(Å) 28.00 25.42 17.20 14.93 14.08

h	Ι	d(Å)
1	1	27.72
0	2	25.57
2	0	16.68
1	3	14.89
2	2	14.20

Figure 5.5. GIXS plots of OPV/silica hybrid films cast at varying ratios of surfactant to silica precursor showing a vertically strained hexagonal phase is produced in all hybrid films. The starting molar ratio of OPV/TEOS of: (a) 1:10, (b) 1:6.67, (c) 1:3.33, (d) 1:0. Insets showed magnified portions of weaker intensity peaks. Tables to right show positions for indexed spots.

 $q_x(A^{-1})$



Figure 5.6. a) GIXS plots of 4T/silica hybrid films cast from methanol showing a vertically strained hexagonal phase is produced in all hybrid films. Inset showed magnified portions of weaker intensity peaks. Tables to right show positions for indexed spots. b) Schematic of the Evaporation Induced Self-Assembly process and final structure. Vertically strained hexagonal packed cylinders are formed that lie parallel to the surface. The 2D hexagonal (hex) unit cell axes are shown as red-dashed line vectors. The 2D rectangular face-centered (rec) unit cell

5.2.4 Role of Charge on the Molecular Packing

The uncharged precursor to the OPV amphiphile (3) shown below contains dimethylamine groups on both termini and was used to investigate the role of charge on molecular packing. Attempts to cast a film of **3** from solution were unsuccessful due to its insolubility in organic solvents at sufficient concentrations. Consequently, measurements were made on the neat powder of the molecule and compared to the neat form of the cationic version used in mineralization to generate hybrid material. The X-ray powder diffraction pattern (Figure 5.7) of **3** indicates formation of a layered structure with d spacings of 2.71, 1.36, and 0.91 nm corresponding to (001), (002), and (003) reflections, respectively. The first-order peak is slightly larger than the fully extended length of the molecule between the two nitrogen atoms (2.5 nm), suggesting a layered packing of the molecule. Upon formation of the charged end groups, the cationic OPV 4 only generated an extremely faint peak, almost two orders of magnitude weaker in intensity than the first-order peak of the uncharged analog at 2.1 nm. This peak corresponds roughly to the distance of the rigid conjugated segment of the molecule. This observation strongly suggests that repulsion between like charges disrupts long-range ordering of the molecules. The width of the peaks observed for 3 indicate that domains of uncharged molecules are larger than those of the cationic amphiphile. The results suggest that the single broad peak for the cationic amphiphile is due to weak ordering from small domains. We believe that this weak ordering is due to the small fraction of rigid cores that are able to π -stack in the presence of the charged groups at the termini of molecules. We conclude that the highly charged nature of the conjugated amphiphiles is detrimental for long range ordering in the neat amphiphile, but essential for the formation of highly ordered hybrid materials



Figure 5.7. a) SAXS plot of an uncharged OPV showing lamellar packing and a charged OPV derivative in the solid state. Inset is a blow up of SAXS plot of the cationic derivative with a weak diffraction peak. b) Structure of the uncharged OPV derivative with the full molecular length and length of the conjugated segment shown.



Figure 5.8. Model of proposed mechanism of self-assembly in the EISA process with silica omitted from images. a) Cationic derivative is fully soluble is solution. b) As silicon dioxide oligomers form and coordinate to the charged end groups, the organic surfactant aggregates into a lamellar-like structure. c) As the silicon dioxide polymer grows, the end group becomes more sterically hindered causing the molecule to rotate into a cylinder like structure.

In the absence of mineralization, charges on these molecules clearly disrupt packing, but binding of TEOS by the end groups and the subsequent mineralization screens charges in the cationic amphiphiles. This screening, in turn, allows the possibility of forming the long range order observed in the hexagonal phase of the hybrid. On the basis of the work demonstrating a similar behavior of CTAB that has been previously reported, we conclude that aggregates of the conjugated molecules are sterically forced into the curved hexagonal structure as the film is formed and solvent is evaporated. This results in the transformation from a lamellar to a hexagonal nanostructure as seen in Figure 5.8. The presence of two binding sites for TEOS per molecule and the ability to π - π stack may also contribute to the transformation and the longrange order observed in these hybrid structures.

5.3 Electrodeposition of ZnO/Oligothiophene Hybrid Films

5.3.1 Molecular Design and Synthesis

While highly ordered hybrid films of conjugated oligomers with silica could be synthesized, silicon dioxide is not an electronically relevant material so it is not ideal for use in electronic devices. Once organic molecules are encased in silica, electrons can no longer flow to electrodes, so fabrication of highly conductive devices is not possible. Electrodeposition of ZnO (a well-known semiconductor) with surfactants has been demonstrated to yield nano-ordered hybrid materials at low temperatures in a one step synthesis. We aim to couple the technique of electrodeposition with the principles of self-assembly in order to synthesize ordered hybrid films by designing strongly interacting amphiphilic molecules containing electronic functionality.

These films are typically grown on the surface of the substrate electrode, enabling their direct integration into functional devices.

The quaterthiophene derivative discussed in the previous section is not a good candidate for this technique due to the amine terminus. Previous work shows that amine surfactants do not template electrodeposited ZnO as well as other functional groups such as carboxylic acids and sulfates.²⁰⁵ Furthermore, the onset of absorption of quaterthiophene derivatives occurs around the bandgap of ZnO (3.37 eV). Shifting to a quinquethiophene derivative pushes the absorption onset to lower energy, thus below the onset of ZnO absorption. Since the electrodeposition typically occurs in water or water/DMSO mixtures, the molecules must be soluble in polar solvents. A bolaamphiphile was designed to increase the solubility over a singularly substituted 5T core. Finally, a methyl substituent was added to the center thiophene ring so further increase solubility with minimal disruption to the the π - π stacking necessary for electronic function.

In order to synthesize the 5T-methyl dicarboxylic acid derivative (5T-mDCA **12**) for electrodeposition with ZnO, we developed a strategy of successive Stille couplings followed by a deprotection to afford the final product as seen in Figure 5.9. The methyl substitution was introduced to the molecule by the commercially available 2,5-dibromo-3-methylthiophene derivative used the starting material for the synthesis. A double Stille coupling was performed on the 2,5-dibromo-3-methylthiophene with 2-tributyltin thiophene to yield a methyl-terthiophene derivative **9**. The methylated terthiophene derivative was then doubly substituted with tributyltin at the 2-position by lithiation followed by quenching with tributyltin chloride to give **10**. A *t*-butyl protected 2-bromo-5-thiophene carboxylic acid molecule was synthesized by carbodiimide



Figure 5.9. Synthetic scheme for 5T-mDCA **12**. a) tributyl(2-thiophene)stannane, Pd(PPh₃)₄, DMF, b) n-BuLi, tributyltin chloride, THF, c) *t*-butyl 5-bromothiophene-2-carboxylate, EDC, DPTS, DCM, d) TFA, DCM.

chemistry to be coupled to the terthiophene core. The double substituted 5T *t*-butyl protected carboxylic acid **11** was synthesized by a Stille coupling. High solubility was observed for the protected 5T derivative in common organic solvents such as THF, dichloromethane, and chloroform. The pure final product **12** was afforded by acidic deprotection of the carboxylic acids without further purification.

5.3.2 Electrodeposition of hybrid 5T-mDCA/ZnO Films

Hybrid films of organic material and ZnO were deposited by cathodic deposition from an aqueous bath of $Zn(NO_3)_2$. A schematic of the three-electrode electrodeposition set-up, where

ITO-coated glass was the cathode where nucleation and growth of the inorganic phase occurs is shown in Figure 5.10. The electrochemical equations of the deposition process are shown in Figure 5.10b. At the cathode, a two-step reactions occurs. First, in the presence of water, the nitrate ion is reduced to the nitrite ion and two hydroxide ions are liberated. This reduction is followed by the formation of $Zn(OH)_2$ which is further converted to ZnO. At the reference electrode, zinc is oxidized to Zn^{2+} in order to complete the cell. A typical deposition occurs from a solution consisting of 0.02 M $Zn(NO)_3$ •6H₂O, 0.05 wt% surfactant, and a 1:1 (v/v) ratio of H₂O/DMSO. While the presence of water is required for deposition, DMSO was added to aid in the solubility of the organic surfactants.

Using a commercially available conjugated surfactant, pyrenebutyric acid (PyBA), it was found that platelet structures were deposited on the electrode surface. For a typical 2 h long synthesis, these sheets are on average 10-50 nm in thickness and 1-5 µm in length and width as seen in Figure 5.11. This morphology is homogeneously deposited across the entire substrate. As observed in the cross-sectional SEM (Fig. 5.11b), the nanostructures are randomly oriented growing off of the surface and the largest structures are oriented in a nearly vertical direction. Transmission electron microscopy (TEM) of these sheets (Fig. 5.11b) reveals that these structures have a lamellar morphology where the normal of each lamella is the same as that of the macroscopic platelet. The structure has a periodicity of 3.2 nm and is comprised of alternating inorganic layers (dark), 0.7-1.0 nm in width, and organic layers (bright), 2.4 nm in width, corresponding roughly to a bilayer of organic surfactant PyBA molecules (Fig. 5.11d). Furthermore, through X-ray absorption studies it was determined that insulating Zn(OH)₂ was deposited initially, but upon annealing to 150 °C, the inorganic phase converted to the semiconducting ZnO with retention of the lamellar ordering.

Because PyBA neither absorbs in the visible region nor is an organic semiconductor, it is not expected to contribute to the electronic function of the material. For the material to be useful in a photovoltaic device, the organic material needs to absorb in the visible range and be a p-type semiconductor. For these reasons, 5T-mDCA was used as the surfactant using the same conditions worked out for the PyBA surfactant. Electrodeposition using this surfactant resulted in fiber-like (Figure 5.12) rather than the flake-like morphologies previously observed. Scanning TEM (STEM) (Figure 5.12b) showed that these fibers also had well-defined lamellar ordering with a periodicity of 2.5 nm that is retained upon annealing above 150 °C. Based on a calculated 2.4 nm molecular length of 5TmDCA, surfactant molecules likely pack in a tilted structure as is well-documented for other thiophene oligomers in lamellar packing motifs.²¹⁶ The single molecule spacing of the hybrid structure is attributed to the fact that the each surfactant molecule has two carboxylic acid binding sites. Zinc ions can bind to either side of the surfactant and form a lamellar structure, unlike the PyBA with only one binding site. Upon annealing at 150 °C, the lamellar structure of the hybrid film is maintained as observed by SAXS (Figure 5.13) for 5TmDCA. When an alkyl surfactant is used, a lamellar structure is observed in the deposited material. When the hybrid material with an alkyl surfactant is annealed at 150 °C, the lamellar structure is not retained upon conversion to ZnO. The rigidity of the conjugated surfactant likely stabilizes the lamellar structure through the inorganic phase transition.

The presence of sulfur in the organic chain allowed us to determine the relative surfactant/Zn stoichiometry via Energy Dispersive X-ray Spectroscopy (EDS) analysis. EDS



b) • Cathode (ITO substrate) : $NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^ E_{red} = 0.01 V$ $2(OH^-) + Zn^{2+} \rightarrow Zn(OH)_2$ $Zn(OH)_2 \rightarrow H_2O + ZnO$ • Anode (Zn wire) : $Zn \rightarrow Zn^{2+} + 2e^ E_{red} = -0.764 V$ $Zn + NO_3^- \rightarrow NO_2^- + ZnO$

Figure 5.10. Schematic of electrodeposition cell with an ITO substrate as the working electrode, Zn wire as the counter electrode, and a Ag/AgCl reference electrode. b) electrochemical equations describing the deposition of ZnO.

analysis of the average of ten lamellar sheets yielded a S/Zn atomic ratio that corresponds to an average of 1.04 ± 0.05 organic molecules per atom of Zn. There was no statistically significant change in the observed 5T:Zn ($1.013 \pm .019$) ratio after annealing at 150 °C for 12 hours indicating the organic molecule does not decompose due to the annealing process. This dye loading ratio for a hybrid material is very high, which is important for a potential application in a photovoltaic cell.

The photoconductive properties of the lamellar ZnO/5TmDCA hybrid were studied by incorporating films grown on pre-patterned ITO into functional two-terminal devices. The average resistivity value from four devices is $6 \pm 3 \times 10^3 \Omega$ cm. Remarkably, a significant increase in the spectral responsivity (Figure 5.14) is observed at wavelengths ranging from 450 nm to 560 nm coincident with the absorption spectrum of the quinquethiophene. The absorption spectrum of the resulting ZnO/5TmDCA hybrid shows a strong absorption band onset at 580 nm. This data indicates that selective photoexcitation of the quinquethiophene moiety leads to an increase in photocurrent, likely via electron transfer directly from the organic layer into the ZnO layer. As is observed for unfunctionalized ZnO thin films,²¹⁷ a more pronounced photocurrent response is observed upon excitation at wavelengths below 450 nm, with a peak response below380 nm. Together, both the ZnO and the organic surfactant actively contribute to the overall device performance.



Figure 5.11. a) SEM of electrodeposited PyBA/ZnO film showing a typical surface coverage. b) Cross sectional SEM of deposited film showing the orientation of the sheets. c) TEM of a single sheet formed by electrodeposition showing the presence of lamellar layers with in a sheet. The dark regions are layers of ZnO and the light regions are the organic molecules. d) Schematic of molecular packing within the lamellar sheets.







Figure 5.13. a) SAXS plot of an electrodeposited film using decanoic acid as the surfactant at RT and after annealing at 150 °C. Upon annealing, Bragg diffraction peaks are lost. b) SAXS plot an electrodeposited film with **5T-mDCA** as the surfactant. Lamellar diffraction peaks are maintained upon annealing.



Figure 5.14. a) IV curve of a device fabricated from electrodeposited **5T-mDCA**/ZnO film showing an increase is current upon photoirradiation. Top inset is a photograph of a typical device. Bottom inset shows the increase in current as a function of illumination time. b) UV-Vis absorption (blue) and spectral responsivity (red) measured at 1 V of a photoconducting device fabricated using this hybrid film. Inset is an energy level diagram of the system.
5.4 Summary and Outlook

The growth of highly ordered organic/inorganic hybrid materials is an attractive route to achieving high performance electronic devices. In order to achieve the ordering needed for electronic performance, techniques such as EISA and electrodeposition have been explored. Most of the previously developed systems use simple single-tail alkyl surfactants. Here we have shown that semiconducting moieties can be directly introduced into the system during the formation of the inorganic framework. This chapter has focused on the development of novel, electroactive conjugated surfactants to directly template highly ordered hybrid materials. Cationic OPV and oligothiophene amphiphiles were synthesized to be incorporated into silica hybrid films by EISA. Using GIXS, it was found that hybrid films composed of hexagonally packed cylindrical micelle structures oriented parallel to the surface. Without the inorganic phase, no long-range ordering of the surfactant was observed by X-ray scattering, showing the importance of the interaction between the organic and inorganic phase in the formation of order within the material. Because silicon dioxide is an insulator and therefore is not a practical material for electronic devices, electrodeposition of ZnO was explored to create a fully electronically active hybrid material. For use in electrodeposition, a dicarboxylic quinquethiophene derivative was synthesized. A lamellar hybrid structure was observed upon deposition of a film. The conjugated surfactant was found to stabilize the lamellar structure upon a thermal transition from insulating $Zn(OH)_2$ to semiconducting ZnO. Photoconductivity measurements showed that the thiophene surfactant directly contribute to the electrical performance of the material. By directly using conjugated surfactants in the formation of hybrid

materials, a much higher dye loading can be achieved which could be important for photovoltaic devices.

5.5 Experimental

5.5.1 General

Unless otherwise mentioned, all starting materials were obtained from commercial sources (Sigma-Aldrich, TCI, Alfa Aesar) and used without further purification. ¹H NMR and ¹³C NMR spectra were recorded in a Varian Inova 500 (500 MHz for ¹H and 120 MHz for ¹³C NMR) spectrometer using the solvent proton signal as standard. GIXS measurements were taken in collaboration with Marina Sofos and the Bedzyk group. Analysis of the GIXS data was performed by Marina Sofos. The electrodeposition of films and analysis was performed by Marina Sofos and Josh Goldberger in the author's group. The synthesis of the cationic OPV derivative followed the literature procedure.²⁰³ The synthesis of 5T-mDCA was described in Chapter 4 of this thesis.

UV-Vis absorption spectra were collected on a Cary 500 spectrometer in double beam mode. Fluorescence spectra were recorded on a PC1 Spectrofluorometer in right angle geometry using monochromators with a FWHM of 8 nm for both the excitation and emission. All spectra were collected by exciting at the absorption maxima.

GIXS measurements were carried out at the 5ID-C beam line of the Advanced Photon Source (APS) at Argonne National Laboratory at an energy of 12.4 keV (1.00 Å wave-length). The incident angle was set at or near the critical angle for the glass substrate ($q_c = 0.032 \text{ Å}^{-1}$) to enhance scattering from the film with a MAR CCD 2D area detector located 340 mm away from the sample for the OPV studies. The detector was located 388 mm away from the sample for measurements on the thiophene derivative. The sample was kept under flowing nitrogen so as to prevent ozone formation and minimize radiation damage. Frames were collected for 30-100 s.

SEM was performed on a Hitachi S-4800-II cFEG, a LEO Gemini 1525 sFEG, and a FEI Quanta sFEG operating at 5-25 kV. Images were captured by a CCD camera. TEM samples were prepared on lacey formvar/carbon 300 mesh Cu grids (Ted Pella, Inc.) by gently contacting the grid with the carbon-coated side face down over the deposited film for transfer. Grid coverage was inspected with an optical microscope. Samples were imaged at 200 kV on a JEOL JEM-2100F TEM. Images and electron diffraction patterns were recorded using a Gatan CCD camera. Electron diffraction patterns were calibrated against a gold standard, and measured digitally in Adobe Photoshop. EDS line and map scans were performed using the Inca Software.

5.5.1 EISA Film Preparation

Precursor solutions of the amphiphile/silica hybrid films were prepared by first dissolving 6.0 mg of the amphiphile in 1.0 mL of MeOH. Solutions were ultrasonicated to fully dissolve the amphiphile, and then 15 μ L of 35 wt % aqueous HCl and 14 μ L of tetraethylorthosilicate (TEOS) were added for a molar ratio of 1:6.67 (OPV/TEOS) or 1:7.23 (4T/TEOS). For concentration-dependent studies, the ratio of amphiphile to TEOS was varied by adjusting the amount of TEOS and acid added to the amphiphile solution. Hydrolysis and condensation of TEOS to form silica and the subsequent interaction with the charged end groups of the amphiphile occurred during solution stirring for 30 min at room temperature. Solutions of the pure OPV amphiphile films were prepared by dissolving 6.0 mg of the amphiphile in 1.0 mL of MeOH and further sonicating

for full dissolution. All solutions were membrane filtered (pore size: 0.45 μ m) and deposited on 2.5 cm × 2.5 cm float glass substrates by spin-casting at 1000 rpm for 30 s. Substrates were treated prior to deposition in piranha solution (7:3 (v/v) H₂SO₄/H₂O₂ (30% aq)) for 10 min at 100 °C to remove organic contaminants from the surface followed by rinsing with DI water, soaking in (4:1 (*v*/*v*) NH₄OH/H₂O₂ (30% aq)) for 5 min, rinsing with ultrapure 18 MΩ cm water and finally drying under a stream of dry nitrogen. *Caution: piranha solution is an extremely dangerous oxidizing agent and should be handled with care.* The films were left overnight at ambient atmosphere and subsequently dried under high vacuum for 3 h for full solvent evaporation.

5.5.3 Electrochemical Synthesis

The electrochemical syntheses were run on a computer controlled EG&G Princeton Applied Research potentiostat model 263A using a conventional three-electrode set-up in an undivided cell. For device measurements, the working electrodes used were 2.0 cm² glass substrates with pre-patterned indium-doped tin oxide (ITO) (140 nm thick, ~50 Ω sheet resistance, Kintek). Substrates were cleaned prior to use by gently scrubbing with a 2% Alkinox soap solution using a cotton swab, rinsing with water (Millipore Milli-Q-purified, 18.3 M Ω cm) three times, and UV-ozone treating for 20 min. For all other characterization, the working electrodes used were 2.5 cm x 2 cm ITO-glass (120 nm thick, ~100 Ω sheet resistance, Applied Thin Films) or FTO-glass (TEC#8/3, ~9 Ω sheet resistance, Hartford Glass). Substrates were cleaned prior to use by sequential ultrasonication (10 min each) in acetone, isopropanol, and 2% alkinox soap solution. Rinsing in water (Millipore Milli-Q-purified, 18.3 M Ω cm) was followed by a 15 s dip in 5M HCl and subsequent rinsing in water. Substrates were then dried under a stream of dry N_2 .

Solutions were prepared by dissolving 1.5-3.0 mg of surfactant in 6 mL of 0.02 M zinc nitrate hexahydrate (Zn(NO)3•6H2O) (98% purity, Aldrich) in a glass cell vial (BAS Inc. model MF-1082). Solutions, therefore, consisted of 0.025-0.05 wt% surfactant. To remove all trace metal and organic impurities, the cell vials were cleaned in an aqua regia solution ((3:1 (v/v) HCl/HNO₃) for 15 min, rinsed three times with water (Millipore Milli-Q-purified, 18.3 M Ω cm), dried under a stream of dry N2, and stored in an oven at 110 °C to remove residual water. Unless otherwise noted, the zinc nitrate solution was a 1:1 (v/v) mixture of DMSO/H2O. The water used was purified by a Millipore filtration system to a resistivity of 18.3 M Ω cm. Solutions were ultrasonicated to insure full mixing of the surfactant into the electrolyte solution. Prior to electrodeposition, solutions were purged for 20 min with Ar under constant magnetic stirring at 80 °C.

Unless otherwise noted, the following electrodeposition procedure was used. Working electrode substrates were placed upright in the glass cell vial not touching but within 2.5 cm (vial diameter) from the counter electrode (1.0 mm diameter-Zn wire (99.9997% purity, Alfa Aesar)) and the reference electrode (Ag/AgCl in a 3 M NaCl solution (BAS Inc. model RE-5B)). To prevent solvent evaporation during deposition, all three electrodes were inserted into the cell vial through the three openings of a teflon cell top (BAS Inc. model MR-3750). Deposition was achieved potentiostatically at -0.9 V for 30 min-24 h, depending on the growth time. The cell vial was kept under constant magnetic stirring at 80 °C throughout the deposition. All deposited films were rinsed by water and ethanol and then dried under a stream of dry N₂. For temperature-

dependent studies, unless otherwise noted, deposited films were subsequently annealed under N_2 for 12 h. at the designated temperature. TGA (Mettler Toledo TGA/SDTA851) was measured by heating from room temperature to 600 °C at 1 °C/min under N_2 flow.

5.4.4 Cationic 4T Synthesis

5-Bromo-2-thiophene methanol (5). 5-bromo-2-thiophene carboxaldehyde (7.23 g, 39 mmol) was dissolved in dry THF (100 mL). The solution was cooled to 0°C. Lithium aluminum hydride in a 1 M solution of THF (12 mL, 12 mmol) was slowly dripped into the solution. The reaction was stirred at 0°C for 10 min. Water (7 mL), aqueous 2M NaOH (7 mL), and then water (21 mL) was added and allowed to stir for 20 min. during which time a gray precipitate was observed to form. The precipitate was filtered off, and the resulting filtrate was evaporated, dissolved in dichloromethane, and dried with MgSO₄. The solution was evaporated to give 6.63 g (34 mmol, 88% yield) of **5** as a black oil. ¹H NMR (CDCl3, ppm): δ 6.90 (d, 1H, *J* = 3.5 Hz), 6.72 (d, 1H, *J* = 4.0 Hz), 4.68 (s, 2H), 2.58 (s, 1H). ¹³C NMR (120 MHz, CDCl3): δ 145.8, 129.8, 125. 9, 112.4, 60.2.

(5-bromothiophen-2-yl)methyl methanesulfonate. A mixture of compound 5 (3.0 g, 15.5 mmol), triethylamine (2.26g, 23.3 mmol), and methanesulfonyl chloride (2.13 g, 18.6 mmol) in 150 mL of dichloromethane was stirred overnight at room temperature was extracted twice with HCl (2 M) and once with saturated NaCl. The organic layer was dried with MgSO4, filtered, and concentrated in vacuo to give the product as a brown oil (3.60 g, 85% yield). ¹H NMR (CDCl3, ppm): δ 6.92 (d, 1H, *J* = 4 Hz), 6.85 (d, 1H, *J* = 4.5 Hz), 4.72 (s, 2H), 3.69 (s, 3H).

2-((5-bromothiophen-2-yl)methoxy)-N,N-dimethylethanamine (6). In a dry flask, NaH (0.76 g, 31.8 mmol) was added to 100 mL of dry THF. The solution was cooled to 0°C. 2-(Dimethylamino)ethanol (2.83 g, 31.8 mmol) was added and the mixture was stirred for 30 min. 5-bromothiophen-2-yl)methyl methanesulfonate (3.60 g, 13.3 mmol) dissolved in 20 mL dry THF was dripped into the solution and let stir at room temperature overnight. The reaction mixture was diluted with dichloromethane and washed three times with 2M HCl. 4M NaOH was added to the aqueous layer until a white precipitate was obtained. The aqueous layer was then extracted three times with dichloromethane. The combined organic layer was dried with MgSO4, evaporated, and the crude product was purified by column chromatography (silica gel; CH2Cl2/MeOH, 85:15) to give **6** (1.00 g, 28% yield) as a black oil. ¹H NMR (CDCl3, ppm): δ 6.90 (d, 1H, *J* = 3.5 Hz), 6.73 (d, 1H, *J* = 3.5 Hz), 3.54 (t, 2H, *J* = 5.5 Hz), 2.51 (t, 2H, *J* = 5.5 Hz), 2.26 (s, 6H). ¹³C NMR (120 MHz, CDCl3): δ 143.2, 129.5, 126.9, 112.6, 67.9, 58.9, 46.0. ACPI-MS *m/z* calculated for C₉H₁₄BrNOS, 263.00; found, 263.99 (M⁺).

2-(5-(5-5-5-((2-(Dimethylamino)ethoxy)methyl)tetrathiophene)methoxy)-

N,Ndimethylethanamine (7). In a dry flask that was purged with nitrogen, compound 6 (0.77 g, 2.9 mmol), 5,5'-bis(tributylstannyl)-2,2'-bithiophene (0.98 g, 1.3 mmol), tetrakis(triphenylphosphine)palladium (0.0015 g, 0.013 mmol) was dissolved in 10 mL DMF. The mixture was degassed by three freeze-pump-thaw cycles and then heated to 100°C overnight. The mixture was cooled to room temperature and diluted with dichloromethane. The organic layer was extracted with saturated NaHCO₃ three times, dried with MgSO4, and

concentrated in vacuo. The crude product was purified by column chromatography (silica gel; CH2Cl2/MeOH, 80/20) to give the desired product (0.26 g, 39%) as a red solid. ¹H NMR (CDCl3, ppm): δ 7.07 (m, 4H), 7.04 (d, 2H, J = 4 Hz), 6.92 (d, 2H, J = 3.5 Hz), 4.69 (t, 4H, J = 6.0 Hz), 2.56 (t, 4H, J = 5.5 Hz), 2.30 (s, 12H). ¹³C NMR not possible due to poor solubility. MALDI-TOF MS *m/z* calculated for C₂₇H₃₂N₂O₂S₄, 533.81; found, 533.89 (M + H⁺).

Cationic quaterthiophene (8). Compound 7 (0.1 g 0.19 mmol) was dissolved in 20 mL of dry THF. A 2 M solution of methylbromide in *t*-butyl methyl ether (5 mL, 10 mmol) was added and the mixture was stirred for 1 day at room temperature. During the stirring a yellow-orange suspension formed. The suspension was filtered to give the desired compound quantitatively as a yellow-orange solid. ¹H NMR (DMSO-*d*₆, ppm): δ 7.32 (d, 2H, *J* = 3.5 Hz), 7.29 (d, 2H, *J* = 4.0 Hz), 7.26 (d, 2H, *J* = 3.5 Hz), 7.09 (d, 2H, *J* = 4.0 Hz), 4.73 (s, 4H), 3.90 (t, 4H, *J* = 5.0 Hz), 3.60 (t, 4H, *J* = 5.0 Hz), 3.13 (s, 18H). ¹³C NMR (DMSO-*d*6, ppm): δ 140.5, 135.9, 136.1, 135.4, 128.9, 126.0, 125.8, 124.6, 67.1, 63.9, 53.7. ESI-MS *m/z* calculated for C₂₈H₃₈N₂O₂S₄ ²⁺ 281.09; found, 281.49 (M²⁺).

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