Conjugated Polymer Nanostructures and Supercapacitors

by

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Abstract

Controlling the nanostructure of conjugated polymers is essential for their application to functional materials. In Part 1 of this work, I present two novel methods for controlling conjugated polymer nanostructure using electrochemical polymerization in hard templates. First, we report the synthesis and characterization of a series of nanostructures and propose a mechanism whereby morphology changes as a function of building block. We show how side-chain hydrophobicity can be used to prepare nanostructures with a geometry that is different from the shape of the template. Hydrophobic side-chains result in collapsed, nonlinear, and nonrigid shapes, while hydrophilic side-chains lead to linear nanostructures. Second, I present a study of the morphology of polythiophene nanostructures synthesized in different solvent/electrolyte systems. We find that the wall thickness of such nanostructures is greatly influenced by the choice of solvent/electrolyte, which affects the rate of polymerization. Solvent/electrolyte systems that increase the rate of thiophene polymerization yield solid nanowires, whereas systems that decrease the rate of polymerization yield thin-wall nanotubes. A solvent/electrolyte system that leads to an intermediate polymerization rate yields thick wall nanotubes. The results in Part 1 open new opportunities for preparing nanostructures with greater complexity, functionality, and distinct optical properties.

Conjugated polymers that can store both a positive and negative charge can function as both the positive and negative charge storage material in a supercapacitor device, however few have been explored for this application. In part 2, I describe the synthesis of several monomers and their electrodeposited polymer electrodes. First, using different donor-acceptor molecular structures we examine the effect of electron acceptor concentration and show that device stability is
improved significantly by increasing the acceptor concentration. Supercapacitors with specific energy and power of 11 Wh/kg (at 0.5 A/g) and 20 kW/kg (at 50 A/g with an energy of 3.6 Wh/kg) are reported. Further, we provide computational insight into the important chemical requirements for achieving even better performing supercapacitors. Working from these experimental and computational results, we selected thieno[3,4-b]pyrazines as a class of molecule to explore. Thieno[3,4-b]pyrazines form narrow band gap homopolymers, storing both positive and negative charge. Initial investigations into four poly(thieno[3,4-b]pyrazine)s as charge storage electrodes is presented.
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Much knowledge is gained through the pursuit of one’s PhD. Some philosophers categorize this knowledge into three forms: personal, procedural, and propositional. One hundred and twenty one pages of this text are dedicated to my acquisition of the latter two. My acquisition of the former, and equally important, is summarized by the following quotes.

“By three methods we may learn wisdom: first, by reflection, which is noblest; second, by imitation, which is easiest; and third, by experience, which is the bitterest.”

– Confucius

“Be kind, for everyone you meet is fighting a great battle.”

– Philo

“The shortest answer is doing the thing.”

– Hemmingway
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Abbreviations

A – ampere

AAO – anodized aluminum oxide

AFM – atomic force microscopy

B3LYP – Becke, 3-parameter, Lee-Yang-Parr hybrid functional

BDTTP1 – benzo[1,2-b:4,3-b']dithiophenethieno[3,4-b]pyrazine

BF₃ – boron trifluoride

BF₃•Et₂O – boron trifluoride diethyletherate

BT – benzo[c][1,2,5]thiadiazole

CAM – Coulomb-attenuating method

CD₂Cl₂ – deuterated dichloromethane

CDCl₃ – deuterated chloroform

CV – cyclic voltammogram

D-A – donor-acceptor

D-A-D – donor-acceptor-donor

DART – direct analysis in real time

DCM – dichloromethane

DDDBT – 7,7′-bis(3,4-dimethoxythiophen-2-yl)-4,4′-bibenzo[c][1,2,5]thiadiazole

DDDQ – 8,8′-bis(3,4-dimethoxythiophen-2-yl)-5,5′-biquinoxaline

DEDQ – 8,8′-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-5,5′-biquinoxaline
DEQ – 5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline

DFT – density functional theory

DMA – dimethylacetamide

DMF – dimethylformamide

DMTP – 2,3-dimethylthieno[3,4-b]pyrazine

DPODA – 2,5-diphenyl-1,3,4-oxadiazole

EDOT – 3,4-ethylenedioxythiophene

EDX – energy dispersive X-ray spectroscopy

ESEM – environmental scanning electron microscope

Et$_2$O – diethyl ether

F – farad

FEG – field emission gun

$g$ – Earth's gravitational acceleration

H$_2$SO$_4$ – sulfuric acid

HCl – hydrochloric acid

HNO$_3$ – nitric acid

HOMO – highest occupied molecular orbital

HRMS – high resolution mass spectrometry

HSAC – high surface area carbon

Hz – hertz
ITO – indium tin oxide

K$_2$CO$_3$ – potassium carbonate

KCl – potassium chloride

KCN – potassium cyanide

kg – kilogram

KOH – potassium hydroxide

kV – kilovolt

kW – kilowatt

L – litre

LUMO – lowest occupied molecular orbital

M – molar

mg – milligram

MgSO$_4$ – magnesium sulfate

MHz – megahertz

mL – millilitre

mm – millimetre

mM – millimolar

mmol – millimole

MS-EI – mass spectrometry via electron ionization

MS-ESI – mass spectrometry via electrospray ionisation
mV – millivolt

NaOH – sodium hydroxide

nm – nanometre

NMR – nuclear magnetic resonance

PATP – phenanthrenethieno[3,4-b]pyrazine

PBDTTP1 – benzo[1,2-b:4,3-b’]dithiophenethieno[3,4-b]pyrazine

PdCl₂ – palladium dichloride

PDDDBT – 7,7’-bis(3,4-dimethoxythiophen-2-yl)-4,4’-bibenzo[c][1,2,5]thiadiazole

PDEQ – poly(5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline)

PDMTP – 2,3-dimethylthieno[3,4-b]pyrazine

PEDOT – poly(3,4-ethylenedioxythiophene)

PPATP – phenanthrenethieno[3,4-b]pyrazine

PPh₃ – triphenyl phosphine

ppm – parts per million

rpm – rotations per minute

SEM – scanning electron microscopy

TBAPF₆ – tetrabutylammonium hexafluorophosphate

TEABF₄ – tetraethylammonium tetrafluoroborate

TEM – transmission electron microscopy

TES – template-directed electrochemical synthesis
THF – tetrahydrofuran

TP – thieno[3,4-b]pyrazine

V – volt

Wh – watt hour
Chapter 1

Introductory Chapter

1.1 Thesis Overview and Background

Many types of electronic and electrochemical devices can be fabricated using conjugated polymers as the active material including chemical sensors, light emitting diodes, solar cells, transistors, and supercapacitors. Conjugated polymers are appealing for many reasons, not the least of which are the many methods available for nanostructure shape control and that both nanostructure and electronic properties can be altered through chemical modifications.

The structure of a conjugated polymer at the nanoscale affects the performance of the resultant material. Numerous methods are available to control the nanostructure of conjugated polymers. One of the most straightforward methods for synthesizing linear nanostructures is template directed electrochemical synthesis. Despite the seemingly simple approach, using different building blocks and different electrochemical conditions, I have been able to demonstrate control over the nanostructure morphology beyond the template. In the first part of my dissertation I have explored these methods by using hard templates to prepare linear nanostructures.

The electronic properties of conjugated polymers, specifically the energy of HOMO and LUMO levels, can be altered to suit the particular application. In the second part of my dissertation I present the application of conjugated polymers to supercapacitors for electrical energy storage. Here, I have designed narrow band gap polymers for use in supercapacitors that can accept both positive and negative charge.

1.1.1 Part I: Nanostructure Shape Control

Template-directed synthesis is a widely used bottom-up synthetic strategy to control the dimensions of a variety of compositions of matter on length scales that range from 10’s of nanometers to 10’s of microns. Compositions prepared by this method include encoded materials, electronic components, optoelectronic materials, sensors, nanomechanical devices, designer super structures, and gene delivery systems. In recent years, researchers have expanded syntheses to include template wetting methods, the use of block copolymer
templates,\textsuperscript{22} the preparation of hybrid nanostructures,\textsuperscript{5,11,16,23-27} and have even shown that it is possible to perform lithographic manipulations along the axis of a linear nanostructure.\textsuperscript{28,29}

Significant work has focused on the use of hard-templates such as mica or anodized aluminum oxide (AAO, Figure 1.1).\textsuperscript{1,2,4,30} The most broadly used strategy to prepare linear nanostructures is perhaps the combination of nanoscale templates and electrochemical deposition, termed template-directed electrochemical synthesis (TES). In this method, an AAO membrane is used as the template. One side of the membrane is coated with a metal such as silver or gold. This metal-coated template is then used as the working electrode in an electrochemical cell. Finally, a material is synthesized electrochemically on nanoscale metal electrodes at the base of the vertically aligned pores of the template. In general, the shape of the material adopts the shape of the template pores. Outstanding control of both diameter (by the pore diameter of the template) and length (by the amount of material deposited) is achieved by using this method.

\textbf{Figure 1.1} Scanning electron micrograph of an AAO template used in this study. Nominal pore diameter is 200 nm.

TES is widely used due to the large number of metal ions and molecules that can be deposited or polymerized by the application of an electrical potential. Thus, there exists a diversity of building blocks that can be fashioned into nanostructures by this method. To date however, most syntheses have focused on relatively simple building blocks including metals,\textsuperscript{31,32} inorganics,\textsuperscript{33,34}
and aromatic compounds such as aniline, pyrrole, 3,4-ethylenedioxythiophene, and thiophene.

Aromatic heterocycles are a versatile class of building block and are often used to prepare materials of technological importance such as semiconducting polymers. Their relatively low oxidation potential and ability to be electrochemically polymerized makes them ideal for TES. Unlike metals or inorganics, heterocycles can be extensively modified through synthetic chemistry. Studies have shown that the heterocycle’s side-chain substituents and π-conjugated core have a significant influence on the morphology of bulk films. However, the extent to which side-chain and core influence the morphology of template-synthesized nanostructures is still an open question. The answer is crucial for expanding hard-template synthesis to include more complex molecular building blocks. Desirable building blocks include those that have narrow HOMO–LUMO gaps, which allow for tunable optical properties, or pendant functionalities, which would then be imparted into the final nanomaterial. From a nanotechnology standpoint, when imparted into a linear nanostructure these properties can be exploited in electronic, sensing, and self-assembly applications. In Chapter 2 I describe the work I did with David Huesmann on controlling the shape of conjugated polymer nanostructures and the advances we made in the understanding of how molecular structure affects the shape of the resultant nanostructures. We discovered a general method for controlling nanostructure shape while being able to afford functionality to the nanostructures. When molecule-based nanostructures are prepared by TES, there is an opportunity to control the morphology beyond the dimensions that are imposed by the template. For example, diameter and shape can be affected by the choice of monomer structure given that soft nanostructures may expand or contract in various media (Figure 1.2).

Figure 1.2 Transmission electron micrographs of nanostructures prepared by TES. The morphology of the nanostructures can be affected by the monomer structure. The monomer structure is inset within the corresponding micrograph.
If one limits the study of TES to heterocycles that are known to yield linear nanostructures, a range of types of 1-D structures are possible depending on the experimental conditions employed. At one extreme, hollow structures (nanotubes) are formed, and at the other, solid structures (nanowires) result. Intermediate morphologies that consist of partially filled nanotubes (a wire that transitions into a tube) are also quite common. The mechanism that determines hollow versus solid composition, however, is still an area of investigation and debate. Initially, Martin et al. proposed that the affinity between the deposited material and the wall of template is the main driving force for nanotube, as opposed to nanowire formation. Following this, a great deal of research was carried out using templates with the desired surface charge and template-wall-functionalization as a means to control the growth of metallic, inorganic, and polymer nanotubes. For example, Martin and coworkers functionalized the pore walls of AAO templates with (2-cyanoethyl)triethoxysilane to promote the formation of gold nanotubes over gold nanowires. Mallouk and coworkers were able to select for indium tin oxide (ITO) nanotubes or nanowires by altering the surface chemistry of both the template walls and the sacrificial gold electrodes. They used AAO templates with hydrophobic walls and a hydrophilic gold cathode to achieve ITO nanowires, and hydrophilic walls and a hydrophobic gold cathode to obtain ITO nanotubes. To obtain nanowires they treated the AAO pore walls with a trichloro(alkyl)silane and the gold electrode with mercaptoethanesulfonate anions. To obtain nanotubes they treated the gold surface with an alkane-thiol and the AAO pore walls with paratungstate anions (Figure 1.3). This observation alone, however, cannot explain why in many syntheses researchers observe partially filled nanotubes, those that contain both hollow and solid segments.
Figure 1.3 Top: A diagram illustrating the methods used to alter the surface chemistry of the AAO template and the gold electrode to favour ITO nanowire (1) or nanotube (2) formation. Bottom: ITO nanowires (A, B) and an ITO nanotube (C) synthesized using the corresponding surface chemistry. Images from work by Kovtyukhova et al. Adapted from Ref 55 with permission of The Royal Society of Chemistry.

A recent study by Xiao et al. investigated partially filled poly(3,4-ethylenedioxythiophene) (PEDOT) nanostructures directly, showing that it is possible to control the hollow–solid ratio through both monomer concentration and polymerization potential. The authors propose a diffusion-based mechanism where at low monomer concentration and high
polymerization potential, tube-like structures are synthesized. Conversely, at high monomer concentrations or low polymerization potentials, wire-like structures were formed. At intermediate potentials and concentrations, partially filled nanostructures were formed (Figure 1.4).

![Graph showing tubular portion (R) vs applied potential at different monomer concentrations.](image1.png)

**Figure 1.4** Top: A plot of the measured “tubular portion” (R) for PEDOT nanotubes vs applied potential at different monomer concentrations, where R is the ratio of tube length (B) to total nanostructure length (A). Electrochemical polymerization was performed for 100 s. Bottom: A PEDOT nanowire with 10 % tubular portion at the tip (left), a fully nanotubular PEDOT nanostructure (middle), and a 50 % tubular : 50 % solid PEDOT nanostructure (right). Reprinted (adapted) with permission from Xiao, R.; Cho, S. I.; Liu, R.; Lee, S. B. Controlled Electrochemical Synthesis of Conductive Polymer Nanotube Structures. *J. Am. Chem. Soc.* 2007, 129, 4483–4489. Copyright (2007) American Chemical Society.

In another significant contribution, Cao et al. studied the mechanism of polyaniline nanostructure formation by TES. These researchers found that factors such as monomer concentration, electrolyte concentration, polymerization potential, and growth time all influence nanostructure morphology. These variables were shown to affect the rate of nucleation of the polymer and as a result influence the overall morphology. For example, increasing the concentration of the H2SO4 electrolyte from 0.25 to 1.5 M causes a shift from solid rod-like morphology to a more hollow, porous morphology (Figure 1.5).
Figure 1.5 Transmission electron micrographs of polyaniline nanowires grown electrochemically in 0.25 M (top) and 1.5 M (bottom) H₂SO₄ illustrating the effect of electrolyte concentration on nanotube morphology. Monomer concentration was 0.1 M and applied potential was 900 mV vs a saturated calomel reference electrode. Reprinted (adapted) with permission from Cao, Y.; Mallouk, T. E. Morphology of Template-Grown Polyaniline Nanowires and Its Effect on the Electrochemical Capacitance of Nanowire Arrays. Chem. Mater. 2008, 20, 5260–5265. Copyright (2008) American Chemical Society.

Selective formation of either nanowires or nanotubes is an important first step, but achieving control over the wall thickness along the length of a nanotube is ultimately necessary for developing high aspect ratio and high surface-area-to-volume ratio materials with controllable and consistent properties. The challenge with any method that uses concentration and thus diffusion to control wall thickness is the difficulty in achieving uniformity along the length of the nanotube; as the nanotube grows from the bottom to the top of the template, precursor materials need to diffuse to different depths within the template. Another complication is that diffusion rates will change as precursor materials become depleted.

While diffusion can be an important parameter, it is clear from the previous examples that polymerization kinetics play an important role in nanostructure morphology. Based on previous work in the conductive polymer field,⁵⁸-⁶⁰ we hypothesized that since electrochemical polymerization kinetics are influenced by solvent/electrolyte conditions, nanotube versus nanowire formation should be controllable by choice of solvent/electrolyte, and hence reaction kinetics alone (Figure 1.6). In Chapter 3, I describe a study that for the first time demonstrates
how the choice of solvent/electrolyte controls the wall thickness of polythiophene nanotubes. We discuss these results in detail and rationalize our observations using the mechanism for the electrochemical polymerization of thiophene.

![Figure 1.6 Illustration of the effect of polymerization rate on the wall thickness of conjugated polymer nanotubes.](image)

1.1.2 Part II: Conjugated Polymer Supercapacitors

Supercapacitors are devices that can store a significant amount of electrical energy, and can accumulate and release this energy at high rates. They can store orders of magnitude more energy than dielectric capacitors, and can be charged and discharged orders of magnitude faster than batteries. This power versus energy relationship is best visualized with a Ragone plot (Figure 1.7). Supercapacitors can also be cycled many more times than a battery. Several important commercial applications include load levelling for intermittent power sources such as wind and solar, and the recovery of energy from regenerative braking in electric vehicles.\textsuperscript{61,62}

Increasing the energy and power density will make these devices all the more useful. The energy and power of supercapacitors can be increased by increasing the capacitance of the electrode material or by increasing the operating voltage of the device. The latter method is the focus of this work.

Supercapacitor electrode materials store charge by double layer capacitance and through Faradaic surface redox reactions in a process known as pseudocapacitance. Conductive materials, most often different forms of sp$^2$ hybridized carbon, are used as electrodes in double layer devices. Redox active materials such as transition metal oxides and conjugated polymers are used in pseudocapacitive devices.

With over 1,700 articles published on supercapacitors in 2014 alone, the field of supercapacitors is far too immense to be adequately covered in this introduction. Several excellent reviews that focus mostly on carbon based materials and metal oxides are cited here$^{63-65}$ and some excellent reviews focusing mostly on conjugated polymer based supercapacitors are cited here.$^{66-70}$ The important features of different supercapacitor electrode materials, along with specific examples, are provided below.
Double layer supercapacitors fabricated from activated carbons have high specific surface area (on the order of 2000 m²/g). Although these materials are highly conductive, large pore size distributions and a non-uniform material structure limit ion diffusion, particularly at high power. Capacitance is typically limited to < 100 F/g. High surface area carbon (HSAC) supercapacitors also store energy electrostatically, but here, uniform pore size distribution and hierarchal structure lead to increased capacitance. Important advances in HSAC materials have been made recently, specifically with mesoporous carbon, carbon nanotube, and graphene based devices. In some cases, scaling these technologies may prove to be problematic.

Transition metal oxides undergo fast surface redox reactions, which enable them to be used as pseudocapacitive electrode materials. Nanostructured electrodes fabricated from these materials exhibit some of the highest specific capacitance, up to 1340 F/g for ruthenium oxide. However, to achieve such a high capacitance with a metal oxide nanomaterial, it was necessary to blend it with conductive carbon and measure the capacitance at low power. The high cost of ruthenium is also a significant drawback. Other transition metals explored recently, such as nickel oxide, have achieved capacitances as high as 900 F/g. Low cost transition metal oxides generally display even lower conductivity than ruthenium oxide. One method of circumventing the problem of low conductivity is to deposit the metal oxides on a conductive substrate such as carbon nanotubes or porous gold. Cui and coworkers reported a MnO₂/carbon nanotube composite with a capacitance of 410 F/g. TES has been used to fabricate electrodes of coaxial PEDOT/MnO₂ nanostructures which resulted in a material with a specific capacitance of 210 F/g, and better rate capability than MnO₂ alone. Depositing MnO₂ onto a highly porous gold surface resulted in a specific capacitance of 1145 F/g. One must be cautious when evaluating such figures; although essential for high performance, the mass of the supporting conductive material is often not taken into account when calculating specific capacitance.

Conjugated polymers were first discovered by Heeger, Shirakawa, MacDiarmid and coworkers in 1977. In 2000, they were awarded the Nobel Prize in Chemistry "for the discovery and development of conductive polymers". Soon after the discovery, it was recognized that conjugated polymers would be useful for energy storage. They have the ability to store charge both electrostatically, and Faradaically (formal chemical oxidation and reduction), which is an important distinction from HSACs. This combination of non-Faradaic charge separation and
Faradaic charging allows conjugated polymers to store more energy than HSAC. Oxidation or reduction occurs in a similar manner as a battery, however, the reaction quotient, or the extent of the reaction, depends on the applied potential; thus the materials are considered pseudocapacitive (Figure 1.8).

Figure 1.8 An illustration of the reversible pseudocapacitive oxidation of PEDOT.

Some of the better known pseudocapacitive conjugated polymers include polythiophenes (such as PEDOT), polypyrrole, and polyaniline. Recent work has focused on blending these polymers with carbon nanotubes or graphene, as well as adding redox active pendant groups to the polymers to improve performance. Controlling the nanostructure of the polymers using hard and soft templates to increase specific capacitance, and as a result, energy, and power is also an important area of research.

All of the aforementioned polymers have early oxidation potentials and are only capable of positive (p-type), as opposed to negative (n-type) or ambipolar charging. This limits the operating voltage of the device to the positive charging voltage range of the polymer (typically 0.8–1.4 V). A polymer that can store both positive and negative charge will have a wider operating voltage window (Figure 1.9). This is important because stored energy can be increased by increasing the operating voltage window since energy is proportional to the square of the operating voltage (Equation 1.1, where E is energy and C is capacitance).
Donor acceptor copolymers are important organic electronic materials because they can be chemically modified to have a narrow band gap (the energy difference between the HOMO and LUMO levels), which effectively tunes their reduction and oxidation potentials.\textsuperscript{102-107} The donor-acceptor concept was first introduced by Havinga et al. in 1992.\textsuperscript{102,103} Alternating electron rich (donor) and electron poor (acceptor) units along the polymer backbone yields a polymer with a hybrid electronic structure. The effect is caused by monomers with high HOMO levels (the donor) located adjacent to monomers with low-lying LUMO levels (the acceptor) and generally results in a copolymer with a narrower band gap than the individual homopolymers. Control of the band gap is afforded by selection of monomers with the appropriate HOMO and LUMO energy levels.\textsuperscript{108}

Polymers with a narrow band gap are advantageous for use in supercapacitors because it means that the polymer can store both positive and negative charges allowing it to operate over a wider voltage range than many p-type polymers (Figure 1.10). In Chapter 4 I describe the use of novel donor-acceptor polymers to increase the operating voltage of supercapacitor devices.

\[ E = \frac{1}{2} CV^2 \] (1.1)
Figure 1.10 Cyclic voltammograms of PEDOT (left) and the donor-acceptor polymer 5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline (right) illustrating the increased voltage range of a donor-acceptor polymer.

Poly(thieno[3,4-b]pyrazine)s are a class of conjugated homopolymer that generally display an early oxidation potential, meaning they are readily electropolymerized, and a narrow band gap, allowing their use as both the positive and negative electrode in a supercapacitor (Figure 1.11). Their synthesis is straightforward and the HOMO and LUMO energies are altered by the electron donating or withdrawing nature of the substituents on the pyrazine ring. In Chapter 5 I describe some preliminary work on the use of thieno[3,4-b]pyrazine polymers as charge storage electrodes in supercapacitors.

Figure 1.11 The chemical structure of poly(thieno[3,4-b]pyrazine)s functionalized with either linear side-chains (left) or a fused ring system (right).

1.2 References


(61) www.maxwell.com

(62) www.nesscap.com


Chapter 2

Template-Synthesized Nanostructure Morphology Influenced by Building Block Structure

2.1 Contributing Statement

I shared nanostructure preparation and electron microscopy equally with David Huesmann. I carried out the synthesis of monomer 4, David Huesmann carried out the synthesis of monomer 3. I performed the EDX measurements and optical absorption spectroscopy. I devised and developed the nanostructure assembly methodology. X-ray diffraction was carried out by Dr. Srebri Petrov. David Huesmann and I drafted the manuscript which was edited by Prof. Dwight Seferos. Portions of this chapter have been published in J. Mater. Chem. 2011, 21, 408.

2.2 Introduction

In this study we synthesized and characterized a series of nanostructures and determine whether several distinct types of building blocks (Figure 2.1), including those with various side-chains and those with various \( \pi \)-conjugated cores, can be fashioned into nanostructures using hard-templates and electrochemical methods. During the course of these investigations we discovered that certain aspects of the molecular structure have a significant influence on the morphology of the nanostructure. We propose a mechanism by which morphology changes as a function of building block. Our results describe important considerations for designing molecules for nanostructure synthesis through template-based bottom-up approaches.

![Figure 2.1](image.png)

Figure 2.1 Molecular structures of building blocks used in this study. 1: thiophene, 2: 3-hexylthiophene, 3: 3-(2-ethyl)hexylthiophene, 4: 3-(2-(2-(2-ethoxy)ethoxy)ethoxy)methylthiophene, 5: 3-(hydroxy)methyl-thiophene, 6: thieno[3,2-b]thiophene, 7: selenophene.
2.3 Results and Discussion

Nanostructures were synthesized by the electrochemical polymerization of aromatic heterocycles within AAO templates. The procedure was adapted from literature protocols.\textsuperscript{1,2} Briefly, AAO filter discs (200 nm pore diameter) were coated with a silver backing and used as the working electrode in a three-electrode cell (Figure 2.2). A segment of silver was deposited into the pores of the membrane followed by a segment of gold using commercially available metal plating solutions and electrochemical reduction. Both silver and gold serve as sacrificial layers. The synthesis was designed so that we could take advantage of the facile etching of silver and use gold as a silver-capping layer. The capping layer prevents the formation of silver oxide\textsuperscript{3} and allows metalized templates to be stored until needed. Furthermore, the gold segment allows for the synthesis and isolation of gold–polymer heterostructures (vide infra). Heterocycles were then polymerized within the pores of the membrane using electrochemical oxidation under an inert atmosphere. To liberate the polymer portion of the nanostructures, the silver metal, aluminum oxide, and gold segments were etched by treating the template with solutions of concentrated nitric acid, sodium hydroxide, and potassium cyanide, respectively. Once the nanostructures were liberated, the suspension was washed by three consecutive centrifugation and resuspension cycles in water. The nanostructures obtained in this way appear to be tubular. The wall thickness of the tube decreases from end to end; this is observed in the transmission electron microscopy (TEM) images as a reduction in contrast along the length of the nanostructures. The wall thickness of thiophene nanostructures is approximately 45 nm near the base (the end that was previously in contact with the metal electrode; Figure 2.3).
Figure 2.2 An illustration of the preparation of the templates, and the synthesis and isolation of the nanostructures.

Figure 2.3 A scanning electron micrograph of a thiophene nanostructure cross-section. The arrows indicate the side-wall thickness near the base (the end that was previously in contact with the sacrificial metal layer) of the nanostructure (~45 nm).
We first investigated the growth kinetics of thiophene (1, Figure 2.1), the most studied building block used in this investigation.\textsuperscript{1,2,4,5} Thiophene nanostructures were synthesized at constant potential (+1.3 V vs Ag/Ag\textsuperscript{+}) over five different time intervals (20, 30, 40, 50, and 100 minutes). After the reaction time had elapsed, nanostructures were isolated and deposited onto a TEM grid for analysis. Analysis of 100 nanostructures per sample shows that nanostructures composed of thiophene grow at 72 nm/minutes in a nearly linear manner during the times examined (Figure 2.4). Regardless of length, all nanostructures prepared from thiophene appear to have a linear geometry. The base is the approximate diameter of the template \((2.4 \pm 0.4 \times 10^2 \text{ nm})\) and the structures appear to widen at the opposite end \((4.1 \pm 0.6 \times 10^2 \text{ nm})\). The larger diameter at the end opposite the base is likely due to flattening of the thinner part of the structure during the TEM sample preparation, a detail observed for 3,4-ethylenedioxythiophene\textsuperscript{3,6} and aniline\textsuperscript{7} nanotubes as well.

\textbf{Figure 2.4} A plot of nanostructure length vs reaction time and transmission electron micrographs of thiophene nanostructures grown for 20, 40, and 100 minutes.
Having determined the morphology of nanostructures composed of thiophene, we next investigated nanostructures composed of thiophenes with side-chains that have been used to promote self-organization in polymer films.\textsuperscript{8} Side-chains were incorporated into the 3-position because this regiochemistry is not expected to disrupt the polymerization reactions that occur at the 2- and 5-positions. Due to steric influences, these asymmetric thiophenes are expected to couple in a head-to-tail vs head-to-head ratio that is approximately 80 : 20.\textsuperscript{9} Interestingly, 3-hexylthiophene (2, Figure 2.1) produces nanostructures with a vastly different morphology than thiophene. Nanostructures composed of 3-hexylthiophene are curved and collapsed (Figure 2.7, center). For easy comparison, the gold segment was not etched and serves as a ruler for determining relative changes in curvature and diameter. Given that the templating methods are the same, the differences in morphology, which appear to result from differences in molecular structure, are striking and were not initially predicted. This collapsed morphology is also observed for 3-(2-ethyl)hexylthiophene (3, Figure 2.1) nanostructures (Figure 2.7, right) demonstrating that it is a property of more than one type of side-chain functionalized thiophene. The distinct morphology is a common property of all nanostructures in a sample composed of a particular building block (Figure 2.8). This structural difference does not appear to result from different degrees of organization of polymer chains within the nanostructures nor to chemical impurities. X-ray diffraction measurements indicate that both the linear thiophene and curved 3-hexylthiophene nanostructures are amorphous (Figure 2.9). Energy dispersive X-ray spectroscopy (EDX) performed on the nanostructures indicates the presence of carbon, sulfur, and minor amounts of impurities (Figure 2.5 and Figure 2.6). No major elemental differences were observed between thiophene and 3-hexylthiophene nanostructures.
Figure 2.5 Thiophene nanostructures, top left to bottom right: scanning electron micrograph; and EDX map for carbon, sulfur, boron, nitrogen, oxygen, fluorine, sodium, aluminum, potassium, silver, and gold.
Figure 2.6 3-Hexylthiophene nanostructures, top left to bottom right: scanning electron micrograph; and EDX map for carbon, sulfur, boron, nitrogen, oxygen, fluorine, sodium, aluminum, potassium, silver, and gold.
Figure 2.7 Representative transmission electron micrographs of thiophene (top), 3-hexylthiophene (middle), and 3-(2-ethyl)hexylthiophene (bottom). Building block structures are inset within the corresponding column. Micrographs were obtained prior to gold etching (left) and after gold etching (right).
Figure 2.8 Representative transmission (left) and scanning (right) electron micrographs of thiophene (top), 3-hexylthiophene (middle), and 3-(2-ethyl)hexylthiophene (bottom) nanostructures. Building block structures are inset within the corresponding row. The gold segments were not etched.
Figure 2.9 X-ray diffraction data for thiophene (left) and 3-hexylthiophene (right) nanostructures.

We next prepared nanostructures at both lower and higher potentials (Figure 2.10), which has been shown in previous studies to have an effect on nanostructure wall thickness. At the highest and lowest potentials examined, the observed morphology of 3-hexylthiophene nanostructures remains curved. The results indicate that differences in morphology are not simply due to a difference in wall thickness, but rather a property of the material. Additionally, when thiophene was grown at lower and higher potentials, the structures remained linear, suggesting that a linear geometry is a property resulting from the unfunctionalized heterocycle.
Figure 2.10  Representative transmission electron micrographs of thiophene and 3-hexylthiophene nanostructures (before gold etching) grown at various potentials. Building block structures and reaction potentials (vs Ag/Ag⁺) are inset within the corresponding column and row, respectively.
We next designed experiments to understand the origins of the differences in morphology between nanostructures composed of thiophene and 3-hexylthiophene. During aqueous work-up there is an apparent difference between the hydrophobicity of nanostructures composed of 3-hexylthiophene and those composed of thiophene. While thiophene nanostructures are easily suspended in water, the alkane-substituted structures form large aggregates (Figure 2.11; differences in other solvents were also apparent, Table 2.1). These examples show that different nanostructures interact differently with water depending on their composition. Together with the imaging results, we reasoned that tubular 3-hexylthiophene nanostructures bend and collapse to minimize interactions with water.

**Figure 2.11** Photograph of a centrifuge tube of isolated thiophene (left) and 3-hexylthiophene (right) nanostructures in water. Building block structures are given below the corresponding centrifuge tube.
Table 2.1 Behaviour of thiophene and 3-hexylthiophene nanostructures in different solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Thiophene Nanostructure</th>
<th>3-Hexylthiophene Nanostructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>suspension</td>
<td>aggregation&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>DMF</td>
<td>weak aggregation</td>
<td>dispersed</td>
</tr>
<tr>
<td>THF</td>
<td>weak aggregation</td>
<td>dispersed</td>
</tr>
<tr>
<td>DCM</td>
<td>weak aggregation</td>
<td>dispersed</td>
</tr>
<tr>
<td>Et&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>intermediate aggregation</td>
<td>partially dispersed</td>
</tr>
<tr>
<td>Toluene</td>
<td>intermediate aggregation</td>
<td>partially dispersed</td>
</tr>
<tr>
<td>Hexanes</td>
<td>strong aggregation</td>
<td>aggregation</td>
</tr>
</tbody>
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<sup>a</sup> started to disperse after 1 month

To lend support to this hypothesis, we investigated nanostructure morphology within the templates. This experiment was designed to determine morphology before contact with water. Templates were cleaved after polymerization and cross-sections were examined by scanning electron microscopy (SEM). Here nanostructures composed of thiophene and 3-hexylthiophene have a more similar morphology (Figure 2.12, left). Next, the template was etched leaving the polymer nanostructures attached to an array of metal nanorods. This treatment causes the polymer section of the nanostructures to bundle (Figure 2.12, right). Thiophene nanostructures adhere to one another in small groups but remain straight, while 3-hexylthiophene nanostructures collapse and form a large tangled mat. These observations suggest that the greatest changes in morphology occur during template dissolution, an essential step in the isolation of the material. Overall, this series of experiments further supports a mechanism where nanostructure–solvent interactions, which are significantly controlled by the structure of the building block, lead to the observed changes in morphology.
Figure 2.12 Representative scanning electron micrographs showing a cross-section of the AAO template after polymerization of thiophene and 3-hexylthiophene (left). Arrows point to polymer sections. Representative scanning electron micrographs of freestanding thiophene and 3-hexylthiophene nanostructures (right). Building block structures are inset within the corresponding row. Schemes depicting the chemical etching of the template to produce the freestanding array of nanostructures are located above the images.
The tendency of the 3-hexylthiophene nanostructures to aggregate can be exploited to produce large area sheets. Dissolution of the sacrificial metal segments results 3-hexylthiophene nanostructures embedded in the AAO template. Slow dissolution of the template results in a sheet of nanostructures free floating in water (Figure 2.13). Sheets as large as the AAO template can be formed by this method. Edge on scanning electron microscopy reveals that the sheet is composed of aligned nanostructures where the thickness of the sheet is equivalent to the length of the nanostructures.

Figure 2.13 A photograph of a sheet of assembled 3-hexylthiophene nanostructures floating in water (top left) and scanning electron micrographs of the sheet edge on.

To demonstrate that not all side-chain functionalized building blocks are detrimental for the synthesis of freely suspended linear nanostructures, we designed and synthesized a side-chain
functionalized building block that we expected would form an uncollapsed nanostructure. Specifically, we selected a thiophene with a pendent oligoethylene glycol side-chain, 3-(2-(2-(2-ethoxy)ethoxy)ethoxy)-methyl thiophene (4, Figure 2.1). This structure has a more hydrophilic side-chain relative to 3-hexylthiophene. Nanostructures were prepared as described above. Upon work-up and isolation these nanostructures exhibit a slightly expanded, but straight morphology (Figure 2.14, left). Similar morphology was observed for nanostructures fashioned from 3-(hydroxy)methyl thiophene (Figure 2.14, right), another heterocycle with a hydrophilic side-chain (5, Figure 2.1). These observations are important because they provide further support for the conclusion that the interaction of the side-chain with water is responsible for the collapse of the 3-hexylthiophene nanostructures. Moreover, they show how molecular side-chains can be incorporated into nanostructures without greatly perturbing the linear shape of the isolated material. Similar side-chain designs should allow for the incorporation of added functionality, while still taking advantage of heterocycle reactivity and template-controlled structure.

Figure 2.14 Representative transmission electron micrographs of 3-(2-(2-(2-ethoxy)ethoxy)ethoxy)-methyl thiophene (left) and 3-(hydroxy)methyl thiophene (right). Building block structures are inset within the corresponding image.

Having determined that building block structure can greatly perturb the final nanostructure morphology, we focused our attention on the preparation of new, linear-type structures. We first examined building blocks with different \( \pi \)-conjugated cores. Specifically, we selected selenophene and thieno[3,2-b]thiophene (7, 6, Figure 2.1, respectively) which are important because they have a narrow HOMO–LUMO gap relative to thiophene as determined by
absorption spectroscopy on the monomer units (Figure 2.15). When these building blocks are used to prepare bulk polymers, side-chains must be included for processing.\textsuperscript{10,11} Based upon our previous observations, we used building blocks that do not have pendent side-chains because of their greater ability to be fashioned into linear structures. Accordingly, monomers were polymerized using the methods described above. Transmission electron micrographs of these template-synthesized structures reveal a linear morphology (Figure 2.15, bottom). Interestingly, only the nanostructures composed of thieno[3,2-\textit{b}]thiophene appear to have a more red-shifted optical absorbance and thus more narrow HOMO–LUMO gap relative to thiophene. None-theless, these experiments show that it is possible to prepare and isolate linear nanostructures from a variety of π-conjugated cores including narrow HOMO–LUMO gap building blocks.

![Normalized absorbance spectra of selenophene, thiophene, and thieno[3,2-\textit{b}]thiophene monomers (top left) and the corresponding nanostructures in water (top right). Representative transmission electron micrographs of selenophene and thieno[3,2-\textit{b}]thiophene nanostructures. Building block structures are inset within the corresponding image.](image-url)
2.4 Conclusions

Overall, the advances reported in this work are: (1) the preparation of nanostructures from previously unexplored side-chain functionalized and narrow HOMO–LUMO gap molecules using the TES approach; and (2) the determination of how heterocycles with side-chains influence nanostructure morphology. Unfunctionalized heterocycles (those that do not have a side-chain) with various π-conjugated cores can be used to prepare linear nanostructures composed of both wide and narrow HOMO–LUMO gap materials. On the other hand, alkyl-substituted heterocycles lead to curved and collapsed nanostructures. These changes appear to occur during aqueous work-up, which is required for template dissolution and the isolation and purification of the nanomaterials. Given that all these building blocks are organic oils, the significant difference in the hydrophobicity of their nanostructures is very surprising.

Developing relationships that link molecular structure to nanostructure is a significant challenge in all syntheses that use a bottom-up approach. Initially, we suspected that the dimensions of the template were the sole factor in determining nanostructure morphology. We have shown however, that this is not always true and that certain functional groups influence morphology as well. Due to solvent interactions, building blocks with alkyl side-chains produce structures with nonlinear and nonrigid geometries. Due to their nonlinear shape, the resultant materials are envisioned to open up unexplored opportunities for the study of self-assembly, electronics, and biological interactions at the nanoscale. Conversely, building blocks that have pendent side-chains can be fashioned into linear nanostructures as long as the side-chains are sufficiently polar. Polar side-chains provide for a strategy to incorporate added functionality into a linear nanostructure while still taking advantage of electropolymerization and template synthesis methods.

2.5 Experimental

2.5.1 Materials

AAO discs (Anodisc 47 and Anodisc 13, 200 nm pore diameter) were purchased from Whatman Co. Silver (1025 Ag RTU) and gold (Orotemp 24 RTU) plating solutions were purchased from Technic, Inc. Thiophene was purchased from Acros, dried over KOH and distilled before use. 2-(Ethyl)hexylbromide was purchased from Acros and used as received. Boron trifluoride
diethyletherate (BF$_3$-Et$_2$O), 3-hexylthiophene, selenophene and thieno[3,2-b]thiophene were purchased from Sigma-Aldrich and used as received. All other chemicals were purchased from Fisher Scientific and used as received. Water was filtered using a Millipore (18.2 MΩ-cm) filtration system.

2.5.2 Monomer Synthesis

3-(2-Ethyl)hexylthiophene. This reagent was prepared according to literature procedures (Scheme 2.1).$^{12}$

![Scheme 2.1](image)

Scheme 2.1 Synthetic route used to prepare 3-(2-ethyl)-hexylthiophene.

Briefly, magnesium (177 mg, 7.28 mmol) was suspended in 3 mL of diethyl ether under a nitrogen atmosphere in a dried 25 mL three-neck round-bottom flask containing a magnetic stir bar and fitted with a condenser. 2-(Ethyl)hexylbromide (1.28 mL, 7.16 mmol) in 3 mL of diethyl ether was then added dropwise to the magnesium suspension via syringe. An exothermic reaction began after 5 minutes and the mixture was stirred until nearly all magnesium had dissolved (5 h). The soluble components were then transferred into another round-bottom flask (containing a magnetic stir bar and fitted with a condenser) via syringe. 3-Bromothiophene (0.61 mL, 6.4 mmol) and Ni(1,3-bis(diphenylphosphino)propane)Cl$_2$ (15 mg, 0.028 mmol) were added and the solution was refluxed for 15 hours and then quenched with ice and 2 M HCl. The aqueous phase was extracted 3 times with diethyl ether and the organic layer was concentrated by rotary evaporation to yield an orange liquid. The crude product was purified by column chromatography in hexanes:dichloromethane (25:1) to afford a colorless liquid which was further purified by vacuum distillation to yield 755 mg (3.85 mmol, 60%) of the title compound. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.23 (dd, $J$ = 4.9, 3.0 Hz, 1H), 6.93 – 6.87 (m, 2H), 2.57 (d, $J$ = 6.9 Hz, 2H), 1.61 – 1.50 (m, 1H), 1.33 – 1.19 (m, 8H), 0.96 – 0.79 (m, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ = 142.01, 128.90, 124.92, 120.78, 40.57, 34.45, 32.69, 29.08, 25.80, 23.21, 14.28, 11.00. MS-EI: 196.1288 $\Delta$ = 1 ppm.
Scheme 2.2 Synthetic route used to prepare 3-(2-(2-(2-ethoxyethoxy)ethoxy)methylthiophene.

1-Bromo-2-(2-ethoxy)ethoxyethane (2). 2-(2-Ethoxy)ethoxyethanol (1) (10.0 mL, 73.6 mmol) was dissolved in 20 mL of chloroform under a nitrogen atmosphere in a dried 50 mL three-neck round-bottom flask containing a magnetic stir bar and fitted with a condenser. The flask was immersed in an ice bath and phosphorous tribromide (7.0 mL, 73.6 mmol) was added at which time an exothermic reaction began. Once the exothermic reaction subsided, the mixture was heated and allowed to reflux overnight. The mixture was then cooled to room temperature, poured into ice, and neutralized with 1M NaOH (150 mL). The organic phase was washed 3 times with water and concentrated by rotary evaporation. The product was purified by vacuum distillation (28.5 mm Hg). The fraction collected between 47–53°C contained 8.99 g (45.8 mmol, 62%) of the title compound (2), a colorless, strongly scented liquid. $^1$H NMR (300 MHz, CDCl$_3$) δ = 3.82 (t, $J = 6.4$ Hz, 2H), 3.70 – 3.44 (m, 8H), 1.22 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ = 71.45, 70.82, 70.01, 66.93, 30.43, 15.36. MS-ESI: 197.0171 ∆ = 2.7 ppm.

3-(2-(2-(2-Ethoxyethoxy)ethoxy)methylthiophene (3). This reagent was prepared according to literature procedures (Scheme 2.2). Briefly, 3-(hydroxy)methylthiophene (0.83 mL, 8.8 mmol) and 2 (1.76 g, 8.95 mmol) were dissolved in 25 mL of tetrahydrofuran under a nitrogen atmosphere in a dried 100 mL Schlenk flask containing a magnetic stir bar. The flask was immersed in an ice bath and sodium hydride powder (267 mg, 10.5 mmol) was added while stirring. The reaction was allowed to warm to room temperature and was then left overnight. Water was added and the mixture was filtered through Celite (acid washed standard super-cel NF). The organic phase was separated and concentrated by rotary evaporation. The product was purified by vacuum distillation (28.5 mmHg). The fraction collected between 150–160°C contained the desired product which was further purified by column chromatography in
hexanes:ethyl acetate (85:15) to afford 1.05 g (4.55 mmol, 26%) of the pure title compound (3), a colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.22 (dd, $J$ = 4.9, 3.0 Hz, 1H), 7.15 (d, $J$ = 2.2 Hz, 1H), 7.01 (dd, $J$ = 4.9, 1.0 Hz, 1H), 3.65 – 3.42 (m, 12H), 1.14 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 139.50, 127.39, 125.91, 122.85, 70.74, 70.69, 69.87, 69.35, 68.48, 66.66, 15.18. MS-EI: 230.0979 $\Delta$ = 0.9 ppm.

2.5.3 Template Preparation

To form a conductive electrode surface, 150 nm of silver was evaporated onto AAO discs using an Edwards Auto 306 evaporation system. Silver evaporation began at ~0.08 nm/s and was increased gradually to ~0.15 nm/s after 10 minutes.

2.5.4 Synthesis of Nanostructures

A BASi EC Epsilon potentiostat/galvanostat was used in all electrochemical experiments. To construct the electrochemical cells for nanostructure synthesis, the metalized AAO discs were inserted into an open-face Teflon cell. The working electrode area was defined by a Viton O-ring (9 or 19 mm diameter). The auxiliary electrode was a platinum wire and the reference electrode was Ag/AgCl (for electrochemical metal deposition in aqueous solution) or Ag/AgNO$_3$ (for electrochemical polymerization in organic solvent). To deposit the sacrificial silver segments, silver plating solution was diluted (1 : 10) with water and deposited within the template at -800 mV vs Ag/Ag$^+$ for 120–150 minutes. After deposition, the Teflon cell and electrodes were washed with water. To deposit the sacrificial gold segments, the deposition procedure was repeated using undiluted gold plating solution and a potential of -920 mV vs Ag/Ag$^+$ for 20 minutes. The cell was washed, allowed to dry, and brought into an inert atmosphere glove box. Polymerization solutions were prepared by diluting ~2 drops of monomer heterocycle with 7 mL of anhydrous BF$_3$•Et$_2$O (a concentration of 10–30 mM). Heterocycles were polymerized at +1.3 V vs Ag/Ag$^+$. After polymerization, the electrolyte solution was removed and the cell washed with acetonitrile followed by ethanol.

2.5.5 Isolation of Nanostructures

To etch the evaporated silver and sacrificial silver segments, the silver coated side of the template was treated with a few drops of concentrated HNO$_3$ for ~10 seconds and washed with water. This process was repeated two more times. To dissolve the AAO template and liberate the
gold–thiophene nanostructures, the template was treated with 2 mL of 3 M NaOH and shaken using an eppendorf Thermomixer at 1000 rpm for 1–2 hours at 40 °C. The suspension was centrifuged (6 minutes, 3400 g) to form a pellet. The supernatant was removed and 2 mL of water was added to resuspend the material. This process was repeated two more times. To etch the sacrificial gold segments, the nanostructures were suspended in 2 mL of 500 mM KCN and shaken for 15 hours at 40 °C. The final material was centrifuged, washed, and resuspended in water as above.

2.5.6 Preparation of Surface-Anchored Nanostructures

To prepare an array of surface-anchored nanostructures, the template was treated with 3 M NaOH solution in a Petri dish for 1 hour and then washed with water.

2.5.7 Preparation of Template Cross-Sections

Cross sections of AAO templates were prepared after electropolymerization. The electrochemical cell was rinsed two times with diethyl ether and the template was cleaved using two tweezers to achieve a smooth breakline.

2.5.8 Behaviour of Thiophene and 3-Hexylthiophene Nanostructures in Different Solvents

Nanostructures were suspended in a minimal amount of ethanol (10 µL) and then added to 5 mL of the corresponding solvent. The mixtures were shaken for 24 hours in a small glass vial at 500 rpm. Behaviour was determined by visually inspecting the solutions for homogeneous coloration as well as performing TEM analysis to determine whether the nanostructures were still present. The results are summarized above (Table 2.1).

2.5.9 Analysis

For analysis by electron microscopy, 5 mL of the nanostructure suspension was deposited onto a carbon-coated copper TEM grid. Transmission electron micrographs were obtained using a Hitachi H-7000 at an accelerating voltage of 75 kV. SEM images were obtained using a Hitachi S-5200 at accelerating voltages between 2 and 10 kV. For the length analysis 100 nanostructures were measured.
2.6 References


Chapter 3

Solvent/Electrolyte Control of the Wall Thickness of Template-Synthesized Nanostructures

3.1 Contributing Statement

I shared nanostructure preparation and electron microscopy equally with Ana Fokina. I devised the nanostructure wall thickness control mechanism. I performed the EDX and AFM experiments. I prepared the manuscript for publication with contribution from Ana Fokina. Prof. Dwight Seferos edited the manuscript. Portions of this chapter have been published in Chem. Mater. 2011, 23, 3787.

3.2 Introduction

In this study we used templated electrochemical synthesis (TES) to synthesize a series of polythiophene nanostructures in different solvent/electrolyte systems. Characterization of the nanostructures reveals that the formation of nanotubes vs nanowires can be controlled by selecting the appropriate solvent/electrolyte system. Various mechanisms for control over whether nanotubes or nanowires are formed by TES have been presented in the literature (see Chapter 1). Here, for the first time, we demonstrate that the rate of polymerization can be used to control nanotube vs nanowire formation and are able to achieve some control over the wall thickness of the nanotubes.

3.3 Results and Discussion

For this study, we synthesized nanostructures by electrochemically polymerizing thiophene within anodic aluminum oxide (AAO) templates. The procedure was adapted from literature protocols.\textsuperscript{1-3} Briefly, one side of the AAO filter disc (nominally 200 nm pore diameter) was coated with silver and used as the working electrode in a three-electrode electrochemical cell (Figure 3.1). A segment of silver was deposited into the pores of the membrane followed by a segment of gold using commercially available metal plating solutions and electrochemical reduction. Both silver and gold serve as sacrificial layers. The synthesis was designed to take advantage of the facile etching of silver and use gold as a silver-capping layer. The capping layer prevents the formation of silver oxide.\textsuperscript{4-6} Next, thiophene was polymerized within the pores of
the membrane using electrochemical oxidation under an inert atmosphere. To isolate the polymer nanostructures, the silver metal, aluminum oxide, and gold segments were etched by treating the template with solutions of concentrated nitric acid, sodium hydroxide, and potassium cyanide, respectively. Once the nanostructures were isolated, the suspension was washed by three consecutive centrifugation and resuspension cycles in deionized water.

Figure 3.1 An illustration of the template directed electrochemical synthesis procedure. From top left to bottom right: AAO template cross-section, AAO with evaporated silver electrode, custom-fabricated open-faced electrochemical cell, AAO with sacrificial silver and gold segments, polythiophene nanostructures synthesized on the sacrificial metal electrodes, suspension of polythiophene nanostructures after metal and template dissolution. For clarity, only half of the template is depicted.

In these studies, polythiophene was synthesized electrochemically from three different solvent/electrolyte systems. In the first example, boron trifluoride diethyletherate (BF$_3$·OEt$_2$) was used as a one-component solvent/electrolyte system. BF$_3$·OEt$_2$ is advantageous because it is a source of BF$_3$, a Lewis acid, which will coordinate to the sulfur within the thiophene ring. This coordination reduces the aromaticity of thiophene and results in a lower oxidation potential of the monomer. In the second example, acetonitrile is used as the solvent and tetrabutylammonium hexafluorophosphate (TBAPF$_6$) is used as the electrolyte. In the third example, dichloromethane is used as the solvent and TBAPF$_6$ as the electrolyte. We will describe our results using this third solvent/electrolyte system towards the end of the chapter.

Significant differences in morphology are observed between polythiophene nanostructures prepared in BF$_3$·OEt$_2$ and those prepared in acetonitrile/TBA$^+$PF$_6^-$. Specifically, nanostructures synthesized in BF$_3$·OEt$_2$ appear to be hollow (nanotubes) with very thin walls, while those prepared in acetonitrile/TBAPF$_6$ appear to be solid (nanowires). This morphological difference is
observed using bright-field TEM (Figure 3.2) as well as elemental mapping via energy dispersive X-ray spectroscopy (EDX) and atomic force microscopy (AFM; Figure 3.11). In the bright field transmission electron micrographs, nanostructures synthesized in BF$_3$·OEt$_2$ appear lighter than those prepared in acetonitrile/TBAPF$_6$ indicating that in the case of BF$_3$·OEt$_2$ there is much less material present in the interior of the structure. Additionally, the BF$_3$·OEt$_2$-prepared nanostructures appear to have a larger diameter than those prepared in acetonitrile/TBAPF$_6$. This is likely due to the walls of the BF$_3$·OEt$_2$-prepared nanotubes being so thin that the structures collapse on the TEM grids.\cite{4,6,8,9} It is interesting that a change from a hollow to a solid morphology can be achieved simply by changing the solvent/electrolyte in the reaction mixture. To understand this process as well as develop a method to control it, we systematically investigated how specific variables lead to this phenomenon, namely: applied polymerization potential, monomer concentration, and polymer formation kinetics.

![BF$_3$·OEt$_2$ and acetonitrile/TBA$^+$PF$_6$.](image)

**Figure 3.2** Transmission electron micrographs of polythiophene nanostructures synthesized in BF$_3$·OEt$_2$ (left) and acetonitrile/TBAPF$_6$ (right).

### 3.3.1 Polymerization potential

Polythiophene nanostructures were synthesized at different potentials to determine the effect of potential on nanostructure morphology. The nanostructures were synthesized according to the methods described above using BF$_3$·OEt$_2$ as the solvent/electrolyte and 30 mM of thiophene. The polymerization reaction was allowed to proceed for 10 minutes. Polymerization was carried out potentiostatically at 1.3, 1.5, or 1.8 V vs Ag/Ag$^+$. The nanostructures were isolated and compared
using TEM analysis. No significant difference in wall morphology is observed for polythiophene nanostructures prepared within this reaction potential window. Instead, a slight effect on length is observed, where the overall length decreases at the lowest potential (Figure 3.3). Nanostructures synthesized in acetonitrile/TBAPF₆ at reduced potential showed no difference in wall morphology either (Figure 3.4).

![Figure 3.3](image-url) Transmission electron micrographs of polythiophene nanostructures synthesized in BF₃·OEt₂ at 1.3, 1.5, and 1.8 V vs Ag/Ag⁺ and a plot of the length of the nanostructures as a function of synthesis potential.
3.3.2 Monomer concentration

The effect of monomer concentration on morphology was studied next. Polythiophene nanostructures were synthesized using BF$_3$·OEt$_2$ as the solvent/electrolyte at a potential of 1.5 V vs Ag/Ag$^+$ for 10 minutes. Monomer concentrations of 7.5, 15, 30, 60, and 120 mM were used in this experiment. Nanostructures were isolated and transmission electron micrographs were analyzed. Here, a significant influence of concentration on the wall morphology of the nanostructures was not observed. There is an effect of monomer concentration however, but it controls nanostructure length rather than wall thickness (Figure 3.5). The synthesis appears to be diffusion limited at low monomer concentrations (7.5 and 15 mM) where shorter nanotubes are observed. As might be expected, this effect tapers off at higher monomer concentrations ($\geq$ 30 mM), where a consistent length is observed and the reaction is no longer limited by the diffusion of the thiophene monomer to the active growth sites. Overall, monomer concentration has no observable effect on wall thickness. Nanostructures synthesized in acetonitrile/TBAPF$_6$ had a similar length dependence on monomer concentration but showed no significant change in morphology (Figure 3.6). All nanostructures synthesized in BF$_3$·OEt$_2$ appear to be tube-like, while all nanostructures synthesized in acetonitrile/TBAPF$_6$ appear to be wire-like.
Figure 3.5 Transmission electron micrographs of polythiophene nanostructures synthesized in BF₃·OEt₂ with 7.5, 15, and 60 mM of thiophene, and a plot of the length of the nanostructures as a function of thiophene concentration.
3.3.3 Reaction rate

Having concluded that applied potential or concentration (and hence diffusion) do not lead to differences in wall thickness, we next designed experiments to understand the origin of the observed differences in morphology for nanostructures synthesized in BF$_3$OEt$_2$ and acetonitrile/TBAPF$_6$ more explicitly. Specifically, we investigated the relative rate of thiophene polymerization using cyclic voltammetry in the two different solvent/electrolyte systems. Cyclic voltammetry was performed under an inert atmosphere on a platinum-disk working electrode in a three-electrode electrochemical cell. This experiment involves cycling the electrode potential...
from a reductive potential (−0.25 to 0.0 V) to an oxidative potential (1.8 V) and then back to the original potential. Eight cycles were conducted at 100 mV/s in all subsequent experiments.

Figure 3.7 Cyclic voltammograms of polythiophene synthesis (8 cycles, 100 mV/s) in BF$_3$·OEt$_2$ (left) and acetonitrile/TBAPF$_6$ (right). See the text for a description of the 3 points in the cyclic voltammograms.

In order to complete this analysis it is necessary to compare the relative rate of polymer synthesis in different solvent/electrolytes. Three points on the cyclic voltammogram are of particular importance for polymer synthesis (labeled 1−3 on Figure 3.7). Point 1 is the onset of monomer oxidation. At this potential (and higher), thiophene monomers are oxidized to radical cations. The radical cations couple to form oligomers, which in turn are oxidized and couple to form polymer chains. The polymer products deposit in the oxidized state on the working electrode once they are no longer soluble (that is at high molecular weight). Point 2 is the reduction of oxidized polymer that has been deposited on the working electrode. The magnitude of this peak increases with each successive scan as more polymer is deposited on the electrode, yielding more material which is then reduced. Point 3 is the oxidation of the polymer. The magnitude of this peak also increases with each successive scan as more material is deposited. The peaks at Point 3 and Point 2 are a measure of oxidation and reduction (doping/undoping) of the polymer, respectively. The oxidation and reduction current are mainly dependent on the amount of polymer deposited on the electrode. There may be a contribution from the monomer oxidation to the polymer oxidation peak, therefore we focus our attention on Point 2 where the increase in
peak magnitude is due to polymer reduction and thus solely dependent on the amount of polymer that is deposited on the electrode.

In these experiments we observe that the reductive current is ten times higher after the same number of cycles when the polymer is deposited in acetonitrile/TBAPF$_6$ compared to BF$_3$·OEt$_2$. The more rapid increase in reduction peak magnitude per scan (Point 2) is therefore illustrative of a significantly increased polymerization rate in this solvent/electrolyte system. While there may be differences in polymer doping level in these different solvent/electrolyte systems, which could then influence the amount of reductive current, typical doping levels for polythiophene (and other heterocycle based polymers) are on the order of 0.1 to 0.3 charge per heterocycle.\textsuperscript{7-9,11,12} This range is not sufficient to account for the factor of ten increase in Point 2. The more rapid growth rate is also observed visually; after 8 cycles, the surface of the platinum-disk electrode used for the BF$_3$·OEt$_2$ synthesis was metallic whereas the electrode used for the acetonitrile/TBAPF$_6$ synthesis was dark and has a matte texture (Figure 3.8). The dark color indicates that much more material was deposited, and hence a much more rapid polymerization rate for thiophene in acetonitrile/TBAPF$_6$ when compared with thiophene in BF$_3$·OEt$_2$.

\textbf{Figure 3.8} Photograph of platinum working electrodes used to synthesize polythiophene in BF$_3$·OEt$_2$ (left) and acetonitrile/TBAPF$_6$ (right); penny shown for scale.

The increased rate of polymer formation in acetonitrile/TBAPF$_6$ can be used to explain the observed difference in morphology; a solid rod contains more material than a thin-wall tube. Under slow polymerization kinetics, there is a limited amount of polymer formed, which
preferentially coats the walls of the membrane, an area of high surface energy. Similar effects have been observed in the case of polystyrene melts in AAO templates.\textsuperscript{10} Under rapid kinetics, there is an abundance of polymer, which coats the walls and precipitates to fill in the core of the tube.

If the reason for this difference in morphology depends on the rate at which the material is deposited, then it should be possible to synthesize nanostructures with varying wall thickness by simply changing the polymerization rate. The rate of thiophene polymerization depends on the mechanism of electrochemical oxidation and coupling of thiophene. There remains some debate as to this exact mechanism, however, in all proposed mechanisms\textsuperscript{7,11,12} proton loss from a charged intermediate is essential, and likely the rate-determining step of the polymerization.\textsuperscript{13} The importance of the proton loss step is illustrated in the proposed polymerization mechanism (Figure 3.9). The driving force for the proton loss is re-aromatization after coupling.

\textbf{Figure 3.9} Proposed mechanism for thiophene oxidation, coupling, proton loss, and polymerization.

We reasoned that a more basic solvent (such as acetonitrile) accelerates the rate of the re-aromatization step by promoting the loss of a proton. On the other hand, a Lewis acid (such as BF$_3$) slows the rate of this step by withdrawing electron density from the sulfur in the thiophene heterocycle. This reduction of electron density reduces the aromaticity of the heterocycle\textsuperscript{1-3} and reduces the energy payback for re-aromatization, which stabilizes the protonated intermediate and slows the rate of proton loss and thus polymerization.

Based on the above rationale, a solvent/electrolyte that is neither a Lewis acid nor a base would be expected to lead to an intermediate reaction rate. We postulated that such a system would yield nanostructures that are neither solid nor completely hollow. Dichloromethane and TBAPF$_6$, another common solvent/electrolyte for thiophene polymerization, is neither a Lewis acid nor
base, and was chosen to test this hypothesis. Indeed, the rate of thiophene polymerization, determined by cyclic voltammetry, in dichloromethane/TBAPF$_6$ is intermediate to that of thiophene in BF$_3$·OEt$_2$ and acetonitrile/TBAPF$_6$ (Figure 3.10, left). When polythiophene nanostructures are synthesized in dichloromethane/TBAPF$_6$ they exhibit a morphology that is intermediate to those synthesized in BF$_3$·OEt$_2$ and acetonitrile/TBAPF$_6$ (Figure 3.10, right). Transmission electron micrographs of nanostructures synthesized in dichloromethane/TBAPF$_6$ show that the structure is neither solid nor completely hollow, but a tube with well-defined walls that are much thicker than the BF$_3$·OEt$_2$ nanotubes.

![Cyclic voltammogram and TEM image](image)

**Figure 3.10** A cyclic voltammogram of polythiophene synthesis (8 cycles, 100 mV/s) in dichloromethane/TBAPF$_6$ (left, see the text for a description of the 3 points in the cyclic voltammograms) and a transmission electron micrograph of a polythiophene nanostructure synthesized in dichloromethane/TBAPF$_6$ (right) and a higher magnification image (right, inset).

To substantiate these findings we first present an illustration of the cross-section of the three nanostructures as a visual aid to interpret the mass distribution across the width of a collapsed nanotube, a hollow nanotube, and a nanowire (Figure 3.11, row 1). The mass distribution across the width of the cross-section of these structures is quite different. A collapsed tube has an even distribution of material across its width. A hollow tube with dense walls exhibits two distinct peaks where the highest density of material resides; the peaks are separated by a valley where the structure has the least mass. In a cylindrical wire cross-section, the bulk of the material is located in the center declining towards the edges and this is seen as a symmetric arc of mass distribution.
Figure 3.11 Illustration of a cross-section of a flattened nanotube, hollow nanotube, and solid nanowire (top row, left to right). Transmission electron micrographs with overlaid EDX line-scans (sulfur abundance) of polythiophene nanostructures synthesized in BF$_3$·OEt$_2$, dichloromethane/TBAPF$_6$ and acetonitrile/TBAPF$_6$ (2nd row, left to right). Tapping mode AFM images of polythiophene nanostructures synthesized in BF$_3$·OEt$_2$, dichloromethane/TBAPF$_6$, and acetonitrile/TBAPF$_6$ (3rd row, left to right); and corresponding height profile (bottom row, left to right). The line on the AFM image represents the section that was used for the height profile.

To measure actual mass distribution we used EDX. EDX is an elemental mapping technique and can be used to reveal the underlying morphology in a more quantitative manner (in this case a sulfur line-scan is shown). Using EDX we are not only able to distinguish nanotubes from nanowires, but also measure the wall thickness of polymer nanotubes.

An EDX line-scan across the width of a flattened polythiophene nanotube (synthesized in BF$_3$·OEt$_2$), a thick-wall polythiophene nanotube (synthesized in dichloromethane/TBAPF$_6$) and a polythiophene nanowire (synthesized in acetonitrile/TBAPF$_6$) yields the respective cross-sectional mass distribution curves (Figure 3.11, row 2). The measured mass distribution follows the expected distribution: the flattened nanotube has a uniform and low abundance of sulfur...
across the width of the structure, the thick-wall nanotube has a greater abundance of sulfur at the internal edges of the walls with the characteristic valley in the middle, and the solid nanowire has a greater abundance of sulfur in the center of the nanostructure tapering off towards the edges. Based on EDX analysis, the wall thickness of the structure synthesized in dichloromethane/TBAPF$_6$ is approximately 60 nm.

Further characterization of nanostructure morphology was carried out using AFM (Figure 3.11, row 3). While AFM only provides topographical information, we observe an important trend that compliments the EDX data: nanostructures synthesized in BF$_3$·OEt$_2$ are collapsed and have a short, tapered height profile (the tapering is due to thinner walls and further collapse at one end),$^{18}$ nanostructures synthesized in dichloromethane/TBAPF$_6$ have an intermediate height profile, indicating an intermediate degree of collapse and shrinking upon drying, and nanostructures synthesized in acetonitrile/TBAPF$_6$ retain a diameter that most closely matches the template pore size. The height profile in the bottom row presents this height difference more explicitly (Figure 3.11, row 4).

### 3.4 Conclusions

Electrochemically synthesized polythiophene nanostructure morphology is strongly influenced by rate of polymer formation. The rate of polymer formation can be heavily influenced by the solvent/electrolyte and this provides a method of controlling nanostructure morphology, that is whether a nanowire or nanotube is formed and even allows for some control over the wall thickness. A rapid polymerization rate leads to the formation of nanowires, a slow polymerization rate leads to thin-wall nanotubes and an intermediate polymerization rate yields thick wall nanotubes.

A rationale for the difference in polymerization rate in different solvent/electrolyte systems is based on how the rate-determining step in the electrochemical polymerization reaction is affected by the solvent/electrolyte. Understanding the mechanism responsible for the rate differences therefore allows for rational selection of a solvent/electrolyte system to achieve nanostructures with the desired morphology. These are important considerations for any researchers that use templates and electrochemical methods to prepare designer materials, including those for optics, electronics, and biochemical uses.
3.5 Experimental

3.5.1 Materials

AAO discs (Anodisc 47 and Anodisc 13, 200 nm nominal pore diameter) were purchased from Whatman Co. Silver evaporation pellets (99.99% purity) were purchased from Kurt J. Lesker. Silver (1025 Ag RTU) and gold (Orotemp 24 RTU) plating solutions were purchased from Technic, Inc. Thiophene was purchased from Acros Organics and used as received. BF$_3$·Et$_2$O was purchased from Sigma-Aldrich and used as received. Dichloromethane and acetonitrile were purified using an Innovative Technologies Pure Solv solvent system. TBAPF$_6$ was purchased from Alfa Aesar, and recrystallized from ethanol and water, and dried under vacuum at 70°C prior to use. Water was filtered using a Millipore (18.2 MΩ·cm) filtration system. All other chemicals were purchased from Fisher Scientific and used as received.

3.5.2 Template preparation

To form a conductive electrode surface, ca. 250 nm of silver was evaporated onto AAO discs using an Angstrom Engineering CoVap evaporation system. Silver evaporation began at 0.08 nm/s and was increased to 0.15 nm/s after the first 100 nm.

3.5.3 Nanostructure synthesis

A BASi EC Epsilon potentiostat/galvanostat was used in all electrochemical experiments. To construct the electrochemical cells for nanostructure synthesis, the metalized AAO discs were inserted into an open-face Teflon cell. The working electrode area was defined by a Viton O-ring (19 mm diameter). The counter electrode was a 13 mm platinum-mesh electrode and the reference electrode was Ag/AgCl (for electrochemical metal deposition in aqueous solution) or Ag/AgNO$_3$ (for electrochemical polymerization in organic solvent). To deposit the sacrificial silver segments, the silver plating solution was diluted (1:10) with water and deposited within the template at –800 mV vs Ag/Ag$^+$ for 150 minutes. After deposition, the Teflon cell and electrodes were rinsed with water. To deposit the sacrificial gold segments, the deposition procedure was repeated using undiluted gold plating solution and a potential of –920 mV vs Ag/Ag$^+$ for 20 minutes. The cell was rinsed, allowed to dry, and brought into an inert atmosphere glove box. Polymerization solutions were prepared by diluting thiophene to a concentration of 30 mM (unless otherwise stated) in BF$_3$·Et$_2$O, acetonitrile or dichloromethane (with 0.1 M TBAPF$_6$...
added to the acetonitrile and dichloromethane solutions). Thiophene was polymerized at +1.5 V vs Ag/Ag⁺ (unless otherwise stated). After polymerization, the solution was removed and the cell washed with acetonitrile or dichloromethane followed by ethanol and water.

### 3.5.4 Nanostructure isolation

To remove the evaporated silver and sacrificial silver segments, the silver coated side of the template was treated with a few drops of concentrated HNO₃ and washed with water. To dissolve the AAO template and liberate the gold–polythiophene nanostructures, the template was treated with 2 mL of 3 M NaOH and shaken using an Eppendorf Thermomixer (1000 rpm; 1–2 hours at 40°C). The suspension was centrifuged (8 min, 3400 g) to form a pellet. The supernatant was removed and 2 mL of water was added to resuspend the material. This process was repeated two more times. To remove the sacrificial gold segments, nanostructures were suspended in 2 mL of 500 mM KCN and shaken for 15h at 40°C. The final material was centrifuged, washed, and resuspended in water.

### 3.5.5 Nanostructure analysis

For analysis by electron microscopy, nanostructure suspensions were diluted with ethanol and 5 μL of this suspension was deposited onto a carbon-coated copper TEM grid. Conventional transmission electron micrographs were obtained using a Hitachi H-7000 at an accelerating voltage of 100 kV. Z-contrast transmission electron micrographs were obtained using a Hitachi HD-2000 at an accelerating voltage of 200 kV. EDX was performed using the HD-2000 coupled to an Oxford Instruments Inca EDX system. For the length analysis 100 nanostructures were measured. The error bars represent the standard deviation of 100 measurements. AFM images were obtained using a Vecco Dimension 3000 microscope operating in non-contact mode.

### 3.5.6 Cyclic voltammetry

The working electrode was a 2 mm diameter platinum-disk, the counter electrode was a 13 mm platinum-mesh electrode, and the reference electrode was Ag/AgNO₃. The solution contained 30 mM of thiophene in BF₃·OEt₂, acetonitrile, or dichloromethane (with 0.1 M TBAPF₆ added to acetonitrile and dichloromethane solutions).
3.6 References


Chapter 4


4.1 Contributing Statement

I synthesized all monomers used in this study. Philipp Klein synthesized the boronic ester precursors. I devised and developed the direct heteroarylation synthesis. I synthesized all of the polymers, performed all of the electrochemical studies, and fabricated and tested all of the supercapacitor devices. I performed the electron microscopy. I performed the computational chemistry with assistance from Theresa McCormick. Tyler Schon provided valuable discussion. I prepared the manuscript for publication which was edited by Prof. Dwight Seferos. Portions of this chapter were published in J. Phys. Chem. C 2014, 118, 8295.

4.2 Introduction

The donor-acceptor (D-A) design is extremely attractive for narrow band gap conjugated polymers because the redox properties of the donor and acceptor moieties can be chemically tuned.1-15 These narrow band gap polymers are typical in certain organic electronic applications16-26 but atypical in supercapacitor research. When fabricated into a Type III polymer-based supercapacitor (a symmetric supercapacitor that operates with one electrode oxidized and one electrode reduced) they can significantly increase the operating voltage by storing both positive and negative charge depending on the applied potential. The distinction between Type I, II, and III supercapacitors was formulated by Rudge, et al.27 and Type IV was introduced by Irvin, et al.28

Only a handful of conjugated polymers have been applied to Type III devices27,29-35 and to the best of our knowledge, there is only one example of an alternating donor-acceptor copolymer used in a Type III device configuration. In that important study, the device degraded relatively rapidly due to the instability of the polymer in the reduced form, although the polymer was very stable under positive bias.36 Earlier work has shown that p-type polymers can be used in Type III devices when a large negative potential is applied. Despite larger bias, these earlier studies report better cycle stability than D-A polymers.
We have designed a series of donor-acceptor polymers, characterized their electrochemical properties, synthesized electroactive films, and fabricated Type III supercapacitors to gain fundamental insight into their electrochemical charge-storage ability. While positive charge delocalization within donor-acceptor polymers is well established, negative charge delocalization is somewhat ambiguous. Estrada et al. observe localization of the LUMO on the acceptor moiety and charge-pinning upon reduction. We explore the use of several EDOT-acceptor polymers and demonstrate that certain designs of electron-accepting units can improve negative charge delocalization, negative charge capacity, and the performance of D-A polymers in a Type III device.

4.3 Results and Discussion

4.3.1 Molecular Design

We examine five donor-acceptor monomers: 5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline (DEQ), 8,8'-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-5,5'-biquinoxaline (DEDQ), 8,8'-bis(3,4-dimethoxythiophen-2-yl)-5,5'-biquinoxaline (DDDQ), 7,7'-bis(3,4-dimethoxythiophen-2-yl)-4,4'-bibenzo[c][1,2,5]thiadiazole (DDDBT), 2,5-diphenyl-1,3,4-oxadiazole (DPODA), as well as 3,4-ethylenedioxythiophene (EDOT) (Figure 4.1). The monomers were selected to study the effect of increasing the acceptor to donor ratio in the polymers (Table 4.1). Synthesis as well as three important molecular design factors are considered: solubility, film formation, and electrochemical potential range.

![Figure 4.1](image_url) Structures and abbreviations of the monomers used in this study. Donor units are coloured blue, acceptor units are coloured red.
4.3.1.1 Synthesis

Donor-acceptor-donor (D-A-D) monomers with EDOT or other thiophene-like end groups, like DEQ, are important compounds for organic electrochromic applications, and more recently have been applied to photovoltaic, field-effect transistor, and sensing applications. Most syntheses involve at least three steps, require an organolithium reagent, and include the preparation of an organostannane reagent. The organostannane compounds, which are less desirable due to toxicity concerns, are used in excess (up to 2.5 times the stoichiometric requirement). Here, we use direct heteroarylation for the synthesis of a D-A-D monomer eliminating the use of organolithium and organostannane reagents, the need for cryogens, and achieve yields comparable to Stille coupling with much higher atom economy. Direct heteroarylation is a one-step, one-pot reaction conducted at moderate temperature (Scheme 4.1). Although not the focus of this report, this technique is very straightforward and will be useful to others synthesizing similar D-A-D monomers.

Scheme 4.1 Synthesis of DEQ by direct heteroarylation and Suzuki-type synthesis of DDDBT. DEDQ and DDDQ were synthesized in a similar fashion to DDDBT.

The donor-acceptor monomers, DEDQ, DDDQ, and DDDBT were synthesized using Suzuki-Miyamura coupling. First EDOT or 3,4-dimethoxythiophene was treated with an organolithium reagent followed by isoproxyboronic acid pinacol ester to yield the corresponding boronic ester. The boronic ester was then treated with the dibrominated acceptor molecule
(5,8-dibromoquinoxaline or 4,7-dibromobenzo[c]-1,2,5-thiadiazole) in a one to one ratio. The mono-brominated product was then subjected to a one-pot \textit{in situ} boronic esterification and coupling using half an equivalent of bis(pinacolato)diboron to generate the boronic ester in the presence of the bromo species, allowing for conventional Suzuki-Miyamura coupling.\textsuperscript{54}

4.3.1.2 Solubility and Solubilizing Side-Chains

Solubility is an important parameter for any solution-based approach to polymerization. Side-chains increase the solubility of the monomer, however alkyl side-chains act as insulators and are not electrochemically active, thus the side-chain size should be minimized. For electopolymerized materials it is sufficient for the monomer to be soluble and not the corresponding oligomers/polymers, as deposition of insoluble oligomers/polymers is desired. No solubilizing groups are required for the D-A-D monomers, however we found that the D-A-A-D monomer DEDQ was not suitably soluble to undergo electropolymerization from solution. Dimethoxythiophene has similar electronic properties to EDOT, but has free rotation of the methoxy groups and more conformational degrees of freedom. Replacing EDOT with dimethoxythiophene in the DDDQ and DDDBT monomers increased the solubility significantly and allowed for the preparation of appropriately concentrated solutions (5 mM).

4.3.1.3 Film Formation

Electrochemical polymerization\textsuperscript{55-57} affords several advantages for polymer film formation: polymers are formed directly on the electrode surface and films several micrometers thick can be readily deposited. However, certain electronic factors will make electrochemical polymerization extremely challenging and thus judicious selection of monomers is essential. For example, DPODA has a reversible reduction wave, as does the alternating poly(phenylene-alt-1,3,4-oxadiazole),\textsuperscript{58,59} and appears to be a good candidate for an n-type polymer, it is synthesized in high yield, and the ionization energy is predicted to be -6.40 eV by DFT, the same as 3-methylthiophene which is readily electropolymerized.\textsuperscript{32} However, we found that it cannot be polymerized electrochemically because the oxidation potential of the monomer is too high. On the other hand DEQ and DDDBT are readily polymerized by cyclic voltammetry in an analogous manner to EDOT (Figure 4.2), and several micrometer thick films of oligomers/polymers are formed.
Figure 4.2 Left column: electrochemical polymerization and deposition of polymers by cyclic voltammetry (the corresponding monomer is inset). Right column: cyclic voltammograms of PEDOT, PDEQ and PDDDBT films (solid lines) and the respective monomers (dotted lines).

The cross-sections of the PDEQ and PDDDBT films indicate that the morphologies of the two films are quite different (Figure 4.3). The PDEQ film is composed of small clusters of material with very small grain sizes. The PDDDBT film is composed of much larger domains of oligomer/polymer. This is likely due to faster grain nucleation for DEQ compared with DDDBT.
To our surprise, although structurally similar to DDDBT, DDDQ cannot be polymerized electrochemically. Irreversible oxidation is observed but the peak fails to increase with subsequent oxidation scans (Figure 4.4, left). A very thin film is observed on the electrode surface. Because the monomer is oxidized but only produces a very thin film, we hypothesize that the film is not suitably conductive for subsequent growth. This is likely the result of steric hindrance that leads to a large dihedral angle between adjacent quinoxaline groups and disrupts the conjugation along the molecule. The predicted dihedral angle between the two quinoxalines in DDDQ is 49.0° (DFT calculation) compared to only 31.2° between the benzothiadiazoles in DDDBT (Figure 4.4, right). We focus on the three electropolymerizable monomers: EDOT, DEQ, and DDDBT.
4.3.2 Capacitive Properties

The electrochemical response of PEDOT, PDEQ, and PDDDBT was investigated using cyclic voltammetry in a standard three-electrode electrochemical cell (Figure 4.2, Table 4.1). Charge carrier delocalization and pseudocapacitance are important criteria for conjugated polymer supercapacitors. A shift of the oxidation onset (or reduction onset) to potentials of lower magnitude as the monomer is converted to the oligomer/polymer is indicative of delocalization, which is due to the formation of low energy states.

PEDOT has a wide, rectangular cyclic voltammogram, indicative of charge delocalization. Similarly, the cyclic voltammogram of PDEQ exhibits a broad flat current response at oxidative potentials, which indicates gradual positive charging over a relatively broad potential range. However, at reductive potentials a much narrower peak is observed. Comparing the area of the oxidative wave to the reductive wave of PDEQ, it is apparent that the material can store more positive charge than negative charge. In contrast to a large stabilization of the HOMO energy level (ca. 750 mV), the reduction onset increases only slightly (ca. 20 mV) and thus there is very little LUMO stabilization upon polymerization. These observations indicate that there is good delocalization in the positively charged film, but poor delocalization in the negatively charged film, and although PDEQ is reducible, it more closely resembles a redox couple than an ambipolar pseudocapacitive material.
Table 4.1 Physical data of monomers used in the study.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Monomer Structure</th>
<th>Molecular Weight (g/mol)</th>
<th>Film Formation</th>
<th>Oxidation Potential [V vs Ag/Ag⁺]</th>
<th>Reduction Potential [V vs Ag/Ag⁺]</th>
<th>Largest Dihedral Angle [degrees]</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDOT</td>
<td><img src="image" alt="EDOT Structure" /></td>
<td>142.18</td>
<td>Yes</td>
<td>1.08</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>DEQ</td>
<td><img src="image" alt="DEQ Structure" /></td>
<td>410.47</td>
<td>Yes</td>
<td>0.47</td>
<td>-1.55</td>
<td>10.1</td>
</tr>
<tr>
<td>DEDQ</td>
<td><img src="image" alt="DEDQ Structure" /></td>
<td>538.60</td>
<td>No</td>
<td>n/a</td>
<td>n/a</td>
<td>48.4</td>
</tr>
<tr>
<td>DDDQ</td>
<td><img src="image" alt="DDDQ Structure" /></td>
<td>542.63</td>
<td>No</td>
<td>0.52</td>
<td>-0.87</td>
<td>49.0</td>
</tr>
<tr>
<td>DDDBT</td>
<td><img src="image" alt="DDDBT Structure" /></td>
<td>554.68</td>
<td>Yes</td>
<td>0.86</td>
<td>-1.38</td>
<td>31.2</td>
</tr>
<tr>
<td>DPODA</td>
<td><img src="image" alt="DPODA Structure" /></td>
<td>222.24</td>
<td>No</td>
<td>n/a</td>
<td>-1.94</td>
<td>0.0</td>
</tr>
</tbody>
</table>

PDDDBT was designed with two electron acceptor heterocycles to increase electron delocalization along the polymer backbone and to better match the amount of positive and negative capacitance of the material. The cyclic voltammogram of PDDDBT reveals several interesting results. First, the reduction onset of the DDDBT monomer is decreased in magnitude relative to DEQ. However, in contrast to a large stabilization (ca. 600 mV) of the HOMO energy level upon polymerization, there is almost no LUMO level stabilization. On the other hand, the dual acceptor units result in multiple reduction processes over a wide potential range.

Taken together it is clear that the width of the positive charging range decreases with increasing acceptor concentration. For PEDOT, PDEQ, and PDDDBT the positive charging range is 1400 mV, 980 mV, and 840 mV respectively. This reduces the capacitive contribution of the positive electroactive range to the device. However, introducing two acceptor moieties in PDDDBT allows for more negative charge to be accepted compared to PDEQ and causes the charge stored in the negative electroactive range to much better match the positive range. Finally, the voltage from the edge of the positive charging range to the edge of the negative charging range...
range is 2.9 V and 3.2 V for PDEQ and PDDDBT, respectively. This will equate to a device that has a higher operating voltage than PEDOT.

4.3.3 Supercapacitors

Supercapacitors composed of conjugated polymers are fabricated in four configurations, termed Types I–IV. In this study we focus on Type I and Type III supercapacitors, referred to as symmetric devices because both electrodes are composed of the same material. In a Type I device, both electrodes operate in either the positive or negative electrochemically active voltage range of the material, but not both. As p-type conjugated polymers are the most common, Type I conjugated polymer devices are most commonly operated by each electrode accepting and donating positive charges. In this configuration, the negative electrode operates in the lower half of the potential range while the positive electrode operates in the higher half of the potential range. When the device is discharged, the chemical potential across the device is zero and both electrodes retain the same partial positive charge. When the device is charged, the positive electrode becomes fully positively charged and the negative electrode is neutral. The cell voltage of a Type I PEDOT device is limited to 1.4 V, the electrochemically active range of the polymer and the difference between the fully charged and fully discharged potential.

In a Type III device, the positive electrode operates by accepting and donating positive charges, while the negative electrode operates by accepting and donating negative charges. When the device is discharged, both electrodes are neutral and the cell voltage is zero. Charging the device causes the positive electrode to become positively charged and the negative electrode to be negatively charged. This cell voltage is higher that what can be achieved in a Type I device. These two different operating mechanisms are illustrated on the device cyclic voltammograms by the coloured circles (Figure 4.5).
Figure 4.5 Electrochemical characterization of Type I PEDOT (left column), Type III PDEQ (middle column), and Type III PDDDBT devices (polymer structure inset in corresponding column). Top row: cyclic voltammetry at 50, 100, 200, 500, 750, 1000 mV/s. The electrodes where the electron donor material stores charge are in blue, and where the electron acceptor stores charge is in red, a neutral electrode is white. The state of charge on the electrode for the discharged and charged device is indicated by “+” and “-”s. Middle row: peak capacitance vs scan rate. Bottom row: charge/discharge at 1 A/g current density.

Type III supercapacitors were fabricated using PDEQ and PDDDBT as the charge storage material and Type I devices were made using PEDOT to illustrate the differences in electrode materials and device performance. Briefly, each device was fabricated by polymerizing monomers using cyclic voltammetry on two platinum button electrodes. The electrodes were rinsed in monomer free electrolyte solution. The cyclic voltammogram of the polymer in a three-electrode cell is used as a guide for conditioning the electrodes prior to device fabrication. First, the operating voltage of the device is determined (2.5 V for PDEQ and PDDDBT, 1.4 V for PEDOT) and then the electrodes are charged to the midpoint of the operating voltage range (-0.80 V, -0.51 V, and 0.30 V vs Ag/Ag⁺ for the PDEQ, PDDDBT, and PEDOT devices respectively). This allows for the best overlap of the electroactive range(s). The electrodes were then coated with a poly(methyl methacrylate)/tetrabutyl ammonium
hexafluorophosphate/acetonitrile electrolyte. One electrode was placed into one end of a custom made Teflon casing (Figure 4.6), a porous paper disk separator was placed on top of the electrolyte coated electrode, and the second electrode coated with polymer electrolyte was inserted to create a sandwich-type device.

Figure 4.6 Photograph of the platinum button electrodes, the separator, and the Teflon casing (top) used to prepare the devices. Illustration of the assembled capacitor device (bottom). The Teflon casing is cut away for clarity.

The performance of the Type III PDEQ and PDDDBT devices were measured over 2.5 V and the Type I PEDOT device was measured over 1.4 V (Figure 4.5). Devices were cycled at various scan rates (50 mV/s to 5 V/s). From the cyclic voltammogram it is apparent that the Type III devices only exhibit pseudocapacitance at potentials above 1.5 V. However, due to the energy-voltage relationship (Equation 1.1) 75% of the energy in a capacitor is stored in the highest 50% of the operating voltage. This is advantageous because the vast majority of the charge on the devices is extracted at potentials above 1.5 V. The current of the PDEQ device begins to diminish after 2.0 V, whereas the PDDDBT has a broader current profile up to 2.5 V. This is due to better capacitance matching of the negative and positive electrode. Peak capacitance measured from the discharge scan is plotted as a function of scan rate (Figure 4.5). The device electrodes exhibit excellent capacitance even at scan rates as high as 5 V/s with a maximum value of
201 F/g and 91 F/g (obtained at 100 and 50 mV/s) for the PDEQ and PDDDBT devices respectively.

Charge-discharge measurements were performed on the devices at current densities of 0.2–50 A/g (the 1 A/g measurements are presented). The typical triangular charge-discharge curve is observed for the Type I PEDOT device. However, for both Type III devices, the shape is different due to the initial, fast, non-Faradaic (double layer) charging at potentials too low for pseudocapacitance. This causes the potential of the Type-III device to increase sharply, followed by a more gradual increase in potential as the pseudocapacitive charging of the electrodes takes place. Average capacitance for the electrodes was calculated from the discharge measurement at 0.5 A/g. Measuring average capacitance over the entire voltage range (1.4 V for PEDOT and 2.5 V for PDEQ and PDDDBT) yields average specific capacitances of 41 F/g for PEDOT, 88 F/g for PDEQ, and 17 F/g for PDDDBT. Most supercapacitors are operated from $V_{\text{max}}$ to $V_{1/2}$, and using $dV = V_{\text{max}} - V_{1/2}$, the average specific capacitance is 37 F/g for PEDOT, 30 F/g for PDEQ, and 25 F/g for PDDDBT. Finally, using $dV = V_{\text{max}} - V_{\text{pseudo}}$, where $V_{\text{pseudo}}$ is the onset voltage of the pseudocapacitive region for the donor-acceptor polymers, gives a specific capacitance of 72 F/g for DEQ (over a range of only 0.3 V) and 40 F/g for PDDDBT (over a range of 0.675 V).

The PEDOT and PDDDBT devices are nearly symmetric upon charging/discharging, however the PDEQ device is not. The device efficiency, as measured by the difference in area of the charging and discharging curve (measured 1 A/g), is 98% for PEDOT, 38% for PDEQ and 60% for PDDDBT. The adjacent electron acceptors improve the device efficiency of the D-A devices. The lower efficiency, longer charging time, and rapid potential drop upon discharge for the PDEQ device are attributed to negative charge leakage.

The specific energy and power for the devices are extracted from the charge/discharge plots and both exceed the specific energy of PEDOT (Figure 4.7, Table 4.2). The specific energy and specific power of the PDEQ device are 11 Wh/kg (at 0.5 A/g) and 20 kW/kg (at 50 A/g with a specific energy of 3.6 Wh/kg) respectively. The PDDDBT device has a specific energy of 4.8 Wh/kg (at 0.5 A/g) and a very high specific power of 55 kW/kg (at 50 A/g with a specific energy of 0.76 Wh/kg) respectively. For ease of comparison to other published figures for new materials, only the mass of the active material is considered in these calculations. The mass
of the active layers was estimated by the charge passed during electrochemical deposition.\textsuperscript{64} We assumed that the deposition is 100\% efficient, however, the coulombic efficiency of electrochemical polymerization can be as low as 16\%,\textsuperscript{66,67} which means that performance values are an \textit{underestimation} of the true values. The volumetric performance is reported for the PDEQ and PDDDBT devices as their respective polymerization efficiencies are likely different. The energy and power density of the PDEQ device are 0.84 Wh/L (at 0.5 A/g) and 1.5 kW/L (at 50 A/g with an energy density of 0.28 Wh/L) respectively. For the PDDDBT device the values are 1.0 Wh/L (at 0.5 A/g) and 12 kW/L (at 50 A/g with an energy density of 0.16 Wh/L) respectively. Thus, on a volumetric scale, PDDDBT performs slightly better than PDEQ.

\textbf{Figure 4.7} Ragone plots of PDEQ (black stars), PDDDBT (red circles), and PEDOT (green squares) devices compared to a commercial lithium ion battery (blue triangles) and a commercial double-layer supercapacitor (purple diamonds). The polymer devices were measured at 0.2, 0.5, 1.0, 2.0, 5.0, 10, 20, 50 A/g. Data points for the 0.2 and 50 A/g measurements are labeled.

\textbf{Table 4.2} Performance metrics of supercapacitor devices.

<table>
<thead>
<tr>
<th>Material</th>
<th>Peak Capacitance ([\text{F/g}]^{b})</th>
<th>Specific Energy ([\text{Wh/kg}]^{b})</th>
<th>Specific Power ([\text{kW/kg}]^{c})</th>
<th>Energy Density ([\text{Wh/L}]^{d})</th>
<th>Power Density ([\text{kW/L}]^{d})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT</td>
<td>49</td>
<td>2.8</td>
<td>31</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PDEQ</td>
<td>201</td>
<td>11</td>
<td>20</td>
<td>0.84</td>
<td>1.5</td>
</tr>
<tr>
<td>PDDDBT</td>
<td>91</td>
<td>4.8</td>
<td>55</td>
<td>1.0</td>
<td>12</td>
</tr>
</tbody>
</table>

Although higher energy values have been reported for electrodeposited polymer Type III supercapacitors, ranging from 6–53 Wh/kg,\textsuperscript{27,30,31,33} most use highly porous carbon fabric as the current collector and are measured in a flooded cell rather than as an assembled device.
Improved specific energy and very high specific power can be achieved by nanostructuring the polymer.\textsuperscript{68}

Cycle stability measurements were performed on the supercapacitor devices (Figure 4.8). PEDOT is well known to be highly stable and does not significantly degrade after 2000 cycles at 1.4 V. The multi-cycle CV of PDEQ illustrates the importance of good negative charging stability. The pseudocapacitive peak of the PDEQ capacitor shifts to higher potentials with increasing scan number while a low voltage peak begins to appear. This effect is due to current leakage from the negative electrode. Initially, when the device is at 0 V, each electrode is at -0.80 V vs Ag/Ag\textsuperscript{+}, a conditioning voltage in the middle of the band gap. When the device is scanned, the positive electrode collects and holds positive charge, and the negative electrode collects an equivalent amount of negative charge, however some of this charge leaks and the negative electrode never achieves a full charge. Over multiple scans, the 0 V point drifts out of the band gap into the positive charging range of the electrodes. Eventually the device acts as a Type I capacitor from 0 V to ca. 0.75 V and then a Type III capacitor from 2 V to 2.5 V.

![Figure 4.8](image.png)

**Figure 4.8** Cyclic voltammogram of a PEDOT (left), PDEQ (middle), and PDDDBT (right) supercapacitors from 2 to 1000 cycles at 500 mV/s. Cycles 2, 50, 100, 250, 1000 shown.

Installing a second acceptor unit in the polymer backbone allows better charge stabilization and prevents significant charge leakage. Peak shifting due to charge leakage is not seen in the PDDDBT device. Although the performance of the device itself does diminish with cycling it
maintains 75% initial capacity after the first 100 cycles and 30% of initial capacity after 1000 cycles. Estrada et al. reported an electrodeposited Type III device based on poly(bis-EDOT-isoindigo) films prepared on gold electrodes that achieve 15 Wh/kg which was fully degraded after 200 cycles.\textsuperscript{36} When compared to a Type I supercapacitor the stability is not impressive, however it is clear that in Type III device configuration adjacent acceptor units improve the cyclability. Type III devices are very distinct from Type I devices because the polymer must accept both a positive and negative charge, a much more challenging materials design requirement. Materials development for Type III devices is imperative to achieve stable operation above 1–1.4 V, which increases energy and power densities. In contrast to the hundreds of papers on donor-acceptor polymers in photovoltaics, little is known about the performance of these materials in supercapacitors and the wide variety of acceptor moieties available promise significant potential for improvement. This report represents an important step forward in the development and advancement of Type III supercapacitors. Although more improvement is required, this is the first time a Type III donor-acceptor supercapacitor has been shown to have stability beyond \textasciitilde 200 cycles.

The decrease in current with cycling is likely due to slow degradation of the polymer during reduction. It is possible that the reduced state can be further stabilized by blending the active polymer with an appropriate material to stabilize it through specific chemical interactions as was recently demonstrated with a polyaniline:polyacid blend.\textsuperscript{69} Mastragostino et al. reported an electrodeposited poly(3-methylthiophene) Type III device prepared on platinum which achieved an energy density of 13 Wh/kg, however, stability was only achieved after the polymer was coated onto a stainless steel grid electrode and blended with a binder and carbon black.\textsuperscript{32} Similar methods are expected to improve the stability of the new polymers presented here, but are beyond the scope of the present study.

4.3.4 Theoretical Modeling

Theoretical modeling provides important insight into the observed electrochemical differences and future materials design. Capacitance matching of the positive and negative charging ranges is important when designing materials for Type III supercapacitors. It is also important that there is charge delocalization in both the oxidized and reduced state of the polymer. The extent of charge delocalization across the polymers was examined using computational chemistry.
Geometry optimizations (density functional theory)\textsuperscript{70} of model oligomers with twelve aromatic moieties were performed using Gaussian 09\textsuperscript{71} on PEDOT, PDEQ, and PDDDBT, as well as a hypothetical block copolymer version of PDDDBT (EDOT-\textit{b}-BT; six monomers per block). Here we are interested in how the bond lengths along backbone of the polymer change in the +1 and -1 oxidation and reduction states relative to the neutral ground states. Smaller bond length changes (in the +1 or -1 state compared to the ground state) that are spread over several repeat units indicate that the charge (positive or negative) is also spread over multiple repeat units and are thus indicate delocalization of the oxidized or reduced form. Larger bond length changes that are isolated indicate greater localization. For clarity, only the bond length changes within the acetylene backbone are shown (Figure 4.9). The calculated HOMO and LUMO orbital distributions for the neutral polymer are presented with the +1 and -1 bond length change plots respectively.

\textbf{Figure 4.9} Change in bond length along the acetylene backbone from neutral to +1 (blue, top row) and neutral to -1 (red, bottom row) doublet states for PDEQ, PDDDBT, P(EDOT-\textit{b}-BT) models (left to right). The orbital diagrams of the HOMO and LUMO of the neutral polymer are above the neutral minus +1 and neutral minus -1 plots respectively.

For PEDOT, the bond length change in the +1 doublet state is spread over many repeat units (Figure 4.10), which we interpret as a great deal of charge delocalization. The models for PDEQ and PDDDBT are more localized in both the +1 and -1 states. It is apparent that the positive
charge resides mostly on the electron rich heterocycles whereas the negative charge resides on the electron deficient heterocycles. This reinforces the hypothesis that delocalization of charge carriers in donor-acceptor copolymers is not as great as in homopolymers like PEDOT. Further, based on the model compounds, there is greater delocalization of the negative charge when the number of adjacent acceptors is increased, as predicted for PDDDBT. Considering all bond lengths but excluding those to hydrogen shows identical trends (Figure 4.11).

![Bond length change for PEDOT model neutral minus +1 for all bonds excluding those to hydrogen.](image)

**Figure 4.10** Bond length change for PEDOT model neutral minus +1 for all bonds excluding those to hydrogen.

![Bond length change for PDEQ, PDDDBT, P(EDOT-b-BT) (top to bottom) model neutral minus +1 (left) and neutral minus -1 for (right) all bonds excluding those to hydrogen.](image)

**Figure 4.11** Bond length change for PDEQ, PDDDBT, P(EDOT-b-BT) (top to bottom) model neutral minus +1 (left) and neutral minus -1 for (right) all bonds excluding those to hydrogen.

We performed the same computational analysis on a hypothetical donor-acceptor block-copolymer. Here, the positive charge resides exclusively on the donor block while the negative
charge resides on the acceptor block. Bond length change is well distributed along each block indicating that there is good delocalization of the oxidized and reduced form within. A solution to the poor charge delocalization of alternating donor-acceptor copolymers might be the use of a block copolymer where each block acts independently to store positive and negative charge. This system is beyond the scope of the present study, but provides guidance for future work in this field. Moreover, based on the agreement between the modeled and experimental data for PDEQ and PDDDBT, computational chemistry appears to provide rational design principles for future organic energy storage materials.

4.4 Conclusion

Donor-acceptor polymers have the unique ability to hold both a positive and negative charge at relatively modest potentials. Incorporating equal concentrations of donor and acceptor units in the polymer backbone results in improved capacitance matching in the positive and negative electroactive potential ranges, which is imperative for high performance and stable devices. Negative charges are poorly delocalized across the polymer backbone but incorporating two adjacent acceptor groups improves negative charging stability and the ambipolar characteristic of the material. Ambipolar charging allows the polymer to be used as the sole charge storage material in a Type III supercapacitor with the advantage of having a higher operating voltage than typical p-type conjugated polymers. The high operating voltage translates into specific energy and power values much higher than the reference PEDOT Type I device. Improved ambipolar character of the polymer dramatically improves the stability of the device.

Future work to develop high performance donor-acceptor polymers for supercapacitors may be directed at developing donor-acceptor block copolymers to achieve good delocalization under both positive and negative charging. The development of very low band gap materials with early oxidation and reduction potentials will also be important as they will display pseudocapacitance over a greater potential range that will increase the capacity of the device.

4.5 Experimental

*General Considerations:* Reagents were purchased from Sigma-Aldrich and used as received unless otherwise noted. THF, DMF, dichloromethane, and acetonitrile were purified and dried using an Innovative Technology Pure Solv system. All electrochemical experiments were
performed in an Innovative Technology Pure Lab nitrogen filled glove box using a BioLogic SP-200 potentiostat. Acetonitrile and dichloromethane used for electrochemistry were stored over molecular sieves in the glove box. 2-(tributylstannyl)-3,4-(ethylenedioxy)thiophene was prepared according to a literature procedure.\textsuperscript{72}

4.5.1 Synthesis

5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline (DEQ):

\textit{Stille-type coupling procedure (adapted from Durmus et al.}\textsuperscript{39}: 5,8-Dibromoquinoxaline (0.513 g, 1.78 mmol) was added to a dry 3-neck flask fitted with a condenser, a rubber septum, and a glass plug, under a nitrogen atmosphere. Anhydrous THF (100 mL) and 2-(tributylstannyl)-3,4-(ethylenedioxy)thiophene (2.3 g, 5.3 mmol) were added to the flask. The solution was deoxygenated with bubbling nitrogen for 30 minutes. PdCl\(_2\)(PPh\(_3\))\(_2\) (0.118 g, 0.176 mmol) was suspended in a small amount of THF and added to the reaction mixture by a syringe. The mixture was heated to reflux for 36 hours where it turned from light yellow to dark orange/red as the reaction proceeded. The mixture was allowed to cool and the solvent was removed under vacuum to yield a red solid. Column chromatography on silica gel (3:1 dichloromethane:hexanes) afforded the desired product, a bright orange solid (0.240 g, 33%).

\textit{Direct heteroarylation method:} A 10 mL Schlenk flask was flame dried under vacuum and backfilled with nitrogen three times. 5,8-Dibromoquinoxaline (0.432 g, 1.50 mmol), palladium (II) acetate (0.034 g, 0.15 mmol), pivalic acid (0.046 g, 0.45 mmol), and potassium carbonate (0.621 g, 4.5 mmol) were added to the flask under a nitrogen atmosphere. DMA (3 mL) and 3,4-(ethylenedioxy)thiophene (0.80 mL, 7.5 mmol) were added to the flask by syringe. The mixture darkened quickly and an orange solid appeared. The mixture was allowed to stir at 100 °C for 70 minutes and then left to cool to room temperature. The mixture was diluted with dichloromethane, washed with water (3X), brine, and the organic phase was separated, dried over MgSO\(_4\), and filtered. The solvent was evaporated to yield the crude product, which was subsequently purified by column chromatography on silica gel (dichloromethane) to yield a bright orange solid (0.268 g, 44%).

\(^1\)H NMR (400 MHz, CDCl\(_3\), δ): 8.94 (s, 2H), 8.57 (s, 2H), 6.56 (s, 2H), 4.39–4.29 (m, 8H); HRMS (DART) \(m/z\): [M + H]\(^+\) calcd for C\(_{20}\)H\(_{15}\)N\(_2\)O\(_4\)S\(_2\), 411.04732; found, 411.04746.
2-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (I):

Synthesized as previously reported.\textsuperscript{73} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, \(\delta\)): 6.62 (s, 1H), 4.35–4.13 (m, 4H), 1.34 (s, 12H).

5-bromo-8-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)quinoxaline (2):

5,8-Dibromoquinoxaline (1.00 g, 3.47 mmol) and 1 (1.33 g, 3.47 mmol) were added to a flame-dried, 250 mL 3-neck flask equipped with a condenser under an argon atmosphere. Toluene (140 mL) and water (8 mL) were added and the solution was degassed by three freeze-pump-thaw cycles. Potassium carbonate (1.08 g, 7.81 mmol), tetrakis(triphenylphosphine)palladium(0) (0.200 g, 0.173 mmol), and Aliquat 336 (0.4 mL) were added to the flask and the reaction mixture was allowed to stir at 84 °C for 64 hours. The solution was diluted with dichloromethane and washed with water three times. The aqueous phase was extracted with dichloromethane. The combined organic phases were washed with brine, dried over magnesium sulfate, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (dichloromethane) to yield the title compound (0.105 g, 9% yield). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, \(\delta\)): 8.99 (d, \(J = 1.8\) Hz, 1H), 8.94 (d, \(J = 1.7\) Hz, 1H), 8.44 (d, \(J = 8.3\) Hz, 1H), 8.10 (d, \(J = 8.3\) Hz, 1H), 6.59 (s, 1H), 4.40–4.28 (m, 4H); HRMS (DART) \(m/z\): [M + H]\textsuperscript{+} calcd for C\textsubscript{14}H\textsubscript{10}Br\textsubscript{1}N\textsubscript{2}O\textsubscript{2}S\textsubscript{1}, 348.96464; found, 348.96579.

8,8'-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-5,5'-biquinoxaline (DEDQ):

Potassium carbonate (0.081 g, 0.59 mmol) and 2 (0.068 g, 0.20 mmol) were added to a flame dried 10 mL Schlenk flask under an nitrogen atmosphere. The flask was transferred into a nitrogen filled glove box and 1,1'-bis(diphenylphosphino)ferrocene-palladium(II)dichloride (0.0044 g, 0.006 mmol) and bis(pinacolato)diboron (0.027 g, 0.11 mmol) was added to the flask. The flask was removed from the glove box and dry DMF (1.2 mL) was added. The mixture was stirred at 90 °C for 26 h, cooled to room temperature, diluted with methanol, and the solids were collected on a glass frit. The solids were washed with methanol, followed by water, allowed to dry on the frit, collected, suspended in dichloromethane, and washed by three centrifugation/resuspension cycles to yield the title compound (0.027 g, 52 %). \textsuperscript{1}H NMR (500 MHz, CD\textsubscript{2}Cl\textsubscript{2}, \(\delta\)): 8.87 (d, \(J = 1.6\) Hz, 2H), 8.69 (d, \(J = 1.6\) Hz, 2H), 8.66 (d, \(J = 7.7\) Hz, 2H), 7.91 (d, \(J = 7.7\) Hz, 2H), 6.59 (s, 2H), 4.43–4.30 (m, 8H); HRMS (DART) \(m/z\): [M + H]\textsuperscript{+} calcd for C\textsubscript{28}H\textsubscript{19}N\textsubscript{4}O\textsubscript{4}S\textsubscript{2}, 539.08477; found, 539.08347.
2-((3,4-dimethoxythiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3): Prepared in an analogous manner as 1 using 3,4-dimethoxythiophene (4.975 g, 34.50 mmol) to give a mixture of 3,4-dimethoxythiophene and the title compound (10 g, 89% crude yield), which was used in the next step without further purification. \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 6.46 (s, 1 H), 4.00 (s, 3 H), 3.82 (s, 3 H), 1.31 (s, 12 H); \(^13\)C NMR (100 MHz, CDCl\(_3\), \(\delta\)): 154.62, 150.58, 147.82, 103.27, 96.29, 83.97, 61.34, 57.72, 24.66; HRMS (DART) m/z: [M + H\(^+\)] calculated for C\(_{12}\)H\(_{20}\)B\(_1\)O\(_4\)S\(_1\), 217.11753; found, 217.11666.

5-bromo-8-(3,4-dimethoxythiophen-2-yl)quinoxaline (4): Prepared in an analogous manner as 2 using 3 (0.619 g, 2.29 mmol) and excess 5,8-dibromoquinoxaline (1.980 g, 6.876 mmol). Column chromatography on silica gel (dichloromethane) allowed for recovery of the excess 5,8-dibromoquinoxaline and isolation of the title compound (0.416 g, 52%). \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 8.99 (d, \(J = 1.7\) Hz, 1H), 8.95 (d, \(J = 1.8\) Hz, 1H), 8.19 (d, \(J = 8.1\) Hz, 1H), 8.14 (d, 1H), 6.42 (s, 1H), 3.91 (s, 3H), 3.79 (s, 3H); \(^13\)C NMR (101 MHz, CDCl\(_3\), \(\delta\)): 150.65, 145.69, 145.28, 144.41, 141.70, 140.85, 133.66, 132.36, 130.90, 123.06, 119.30, 98.80, 60.36, 57.43; HRMS (DART) m/z: [M + H\(^+\)] calculated for C\(_{14}\)H\(_{12}\)Br\(_1\)N\(_2\)O\(_2\)S\(_1\), 350.98029; found, 350.97989.

8,8’-bis(3,4-dimethoxythiophen-2-yl)-5,5’-biquinoxaline (DDDQ): Prepared in an analogous manner to DEDQ using 4. The compound was purified by Soxhlet extraction (hexanes, dichloromethane) through a glass frit. The title compound was isolated by concentrating the dichloromethane extracts (0.340 g, 53%). \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 8.91 (d, \(J = 1.7\) Hz, 2H), 8.73 (d, \(J = 1.7\) Hz, 2H), 8.41 (d, \(J = 7.6\) Hz, 2H), 7.94 (d, \(J = 7.6\) Hz, 2H), 6.44 (s, 2H), 3.94 (s, 6H), 3.88 (s, 6H); \(^13\)C NMR (101 MHz, CDCl\(_3\), \(\delta\)): 150.67, 145.52, 144.36, 143.75, 142.34, 140.85, 137.55, 132.52, 132.20, 130.28, 120.37, 98.40, 60.52, 57.42; HRMS (DART) m/z: [M + H\(^+\)] calculated for C\(_{28}\)H\(_{23}\)N\(_4\)O\(_4\)S\(_2\), 543.11607; found, 543.11697.

4-bromo-7-(3,4-dimethoxythiophen-2-yl)benzo[c][1,2,5]thiadiazole (5): Prepared in an analogous manner as 2 using 4,7-dibromobenzo[c][1,2,5]thiadiazole (0.979 g, 3.33 mmol) and 3 (1.00 g, 3.33 mmol). Column chromatography on silica gel (dichloromethane:hexanes 8:2) followed by trituration with methanol afforded the title compound (0.262 g, 22%). \(^1\)H NMR (600 MHz, CDCl\(_3\), \(\delta\)): 8.17 (d, \(J = 7.8\) Hz, 1H), 7.88 (d, \(J = 7.8\) Hz, 1H), 6.44 (s, 1 H), 3.91 (s, 3 H), 3.89 (s, 3 H). \(^13\)C NMR (126 MHz, CDCl\(_3\), \(\delta\)): 153.50, 152.34, 150.89, 132.50, 127.79,
125.76, 119.74, 112.14, 98.56, 60.12, 57.34; HRMS (DART) m/z: [M + H]^+ calcd for C_{12}H_{16}Br_1N_2O_2S_2, 356.93717; found, 356.93735.

7,7'-bis(3,4-dimethoxythiophen-2-yl)-4,4'-bibenzo[c][1,2,5]thiadiazole (DDDBT): Prepared in an analogous manner as DEDQ using 5. The product was purified by Soxhlet extraction (hexanes, dichloromethane) through a glass frit. The title compound was isolated by concentrating the dichloromethane extracts (0.219 g, 56%). $^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 8.50 (d, J = 7.7 Hz, 2H), 8.45 (d, J = 7.6 Hz, 2H), 6.46 (s, 2H), 3.96 (s, 6H), 3.94 (s, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$, $\delta$): 154.00, 153.39, 151.10, 145.91, 131.58, 128.22, 127.67, 126.22, 120.72, 98.62, 60.43, 57.50; HRMS (DART) m/z: [M + H]^+ calcd for C$_{24}$H$_{19}$N$_4$O$_4$S$_4$, 555.02891; found, 555.02843.

2,5-diphenyl-oxadiazole (DPODA): Synthesized as previously reported. $^{74}$ $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 8.18–8.13 (m, 4H), 7.61–7.48 (m, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$, $\delta$): 164.74, 131.86, 129.23, 127.09, 124.12; HRMS (DART) m/z: [M + H]^+ calcd for C$_{14}$H$_{11}$N$_2$O$_1$, 223.08714; found, 223.08756.

**Electrochemical Polymerization and Measurement:** Electrochemical polymerization was performed in a standard 3-electrode electrochemical cell with a platinum disk working electrode (2 mm diameter), a platinum wire counter electrode, and a Ag/Ag$^+$ reference electrode. The polymerization solution contained 5 mM of the appropriate monomer and 0.1 M TBAPF$_6$ in dichloromethane. Deposition was stopped when the charge required to deposit a 5–10 µm thick film had passed, ca. 30 cycles for the donor-acceptor monomers and 50 cycles for EDOT. Electrochemical measurements on polymer films were performed in a 3-electrode cell in acetonitrile with 0.1 M TBAPF$_6$. The ferrocene redox couple Fc$^+/Fc$ has a half-wave potential of 0.09 V vs the reference electrode in the acetonitrile solution. Herein, the terms reduction and oxidation refer to the process of electron injection from the current collector to the polymer and the process of electron injection from the polymer to the current collector, respectively.

4.5.2 Polymer Electrolyte Preparation

The polymer electrolyte was prepared in a nitrogen filled glove box by first making a solution of 1 M TBAPF$_6$ in acetonitrile. Poly(methyl methacrylate) (10% by weight; relative to the acetonitrile solvent) was added in small portions with stirring, waiting for each portion to fully
dissolve before further addition. As the viscosity increased the solution was heated slightly to facilitate polymer dissolution.

4.5.3 Device Fabrication

After electrochemical polymerization, polymer coated electrodes were rinsed twice in dichloromethane and twice in acetonitrile. The electrodes were then immersed in a solution of 0.1 M TBAPF$_6$ and held at the midpoint of the operating voltage of the polymers vs Ag/Ag$^+$ (0.30 V for PEDOT, -0.80 V for DEQ, and -0.51 V for PDDDBT) until the current decayed to zero (2 minutes). One electrode was inserted into a Teflon casing and coated with the electrolyte. An oven dried paper circle cut from a Kimwipe was placed on top of the electrolyte-coated electrode. A second electrode was coated with the polymer electrolyte and pressed against the first within the Teflon casing with the paper separator held in between each electrode. The polymer electrolyte is viscous and will not leak from the device.

4.5.4 Device Characterization

The mass of the polymer films was estimated by the amount of charge passed during film formation. The total mass of both polymer electrodes was used to calculate specific energy and specific power. Energy was calculated by integrating the area under the discharge cycle of the charge-discharge curve and multiplying by the current density. Power was calculated by dividing the energy by the discharge time. Peak specific capacitance of the electrodes was determined by multiplying the current peak of the discharge CV scan of the device by the scan rate (a correction factor 4 was used to account for the series connection and the mass difference between the device and a single electrode). Electron microscopy was performed using a Quanta FEG 250 ESEM.

4.5.5 Computational Methods

The geometries of the oligomers 12 rings long of PEDOT, PDEQ, and PDDDBT, as well as a block copolymer version of PDDDBT (EDOT-b-BT) were optimized with the nonlocal hybrid Becke three-parameter Lee-Yang-Parr$^{75}$ with Handy and coworkers’ long range corrected version using the Coulomb-attenuating method (CAM-B3LYP)$^{76}$ functional and the 6-311g(d) basis set on the Gaussian 09 suit of programs.$^{71,77}$ The geometry of oxidized and reduced versions of each oligomer was optimized with the same basis set and level of theory (+1 doublet,
-1 doublet). Coordinates for optimized geometries are listed in the supporting information. The frontier orbitals are visualized with an isocontour value of 0.03. Bond length change plots were made by taking difference of the optimized bond lengths of the neutral geometry and the oxidized or reduced geometries. The plots show the bond length change down the conjugated backbone is indicative of the changes seen if all bonds are considered.

4.6 References


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Chapter 5

Thieno[3,4-\textit{b}]pyrazines as Electrode Materials for Electrochemical Supercapacitors

5.1 Contributing Statement

I devised the computational methodology and performed the computational chemistry experiments. I synthesized all of the monomers used in this study. I synthesized all of the polymers and performed all of the electrochemical characterization. I performed all of the electron microscopy. I fabricated all of the supercapacitors and performed all of the characterization of the supercapacitor devices.

5.2 Introduction

Supercapacitors are energy storage devices capable of high charge and discharge rates and are finding many important applications. Both the energy and power of a supercapacitor is proportional to the square of the operating voltage, thus increasing the operating voltage of a supercapacitor is of great interest.

Using conjugated polymers as the charge storage material in a supercapacitor allows for greater energy density due to the phenomenon of pseudocapacitance.\textsuperscript{1-3} Most conjugated polymers are p-type,\textsuperscript{4-7} meaning that they are electron rich hole conductors and are only able to store positive charge. This limits the operating voltage of the supercapacitor to the stable positive charging range of the polymer, between 0.8 and 1.4 V depending on the polymer. Conjugated polymers that can hold both a positive charge and negative charge allow for a greater operating voltage. When fabricated into a Type III supercapacitor, each electrode is coated with the polymer. On the positive electrode the polymer is oxidized during charging, on the negative electrode the polymer is reduced during charging. The polymer, however, is not pseudocapacitive over the voltage range of the band gap and thus stores very little charge in that range. A narrow band gap polymer mitigates this issue because it will store pseudocapacitive charge over more of the operating voltage range of the device, increasing the total energy stored.

Thieno[3,4-\textit{b}]pyrazines are a class of molecule that form narrow band gap polymers.\textsuperscript{8-19} The pyrazine ring contributes more strongly to the LUMO than the HOMO and this leads to some
interesting electronic effects. For example, substitution on the pyrazine ring has a greater effect on the LUMO energy than the HOMO energy.\textsuperscript{18,20} Thieno[3,4-\textit{b}]pyrazines are easily synthesized by double condensation of an alpha-dione with 3,4-diaminothiophene.

![Structures](image.png)

**Figure 5.1** Structures, names, and abbreviations of the monomers selected for this study.

### 5.3 Results and Discussion

#### 5.3.1 Monomer Selection Process

Thirty different monomers were screened using DFT for use as narrow band gap conjugated polymers (Figure 5.2, Table 5.1). Criteria included that they must have a narrow HOMO–LUMO gap and a HOMO no more stable than 3-methylthiophene. Known monomers were selected from literature references and some novel monomers hypothesized to have narrow HOMO–LUMO gaps were modeled. The modeling experiments indicate that thieno[3,4-\textit{b}]pyrazines tend to have elevated HOMOs and relatively low LUMOs. We focused our attention on this class molecule as thieno[3,4-\textit{b}]pyrazines are known to be electropolymerizable, the LUMO energy can be modified by substitution of the pyrazine ring, and a variety of them can be synthesized in one step from commercially available reagents.
Figure 5.2 DFT calculated HOMO and LUMO levels and HOMO–LUMO gaps of the monomers screened for use in narrow band gap electrochemical supercapacitors. The dotted line indicates the HOMO energy of 3-methylthiophene.

Table 5.1 Legend of compounds modeled using DFT and their associated abbreviation.

Four thieno[3,4-b]pyrazine monomers were selected for this study: thieno[3,4-b]pyrazine (TP), 2,3-dimethylthieno[3,4-b]pyrazine (DMTP), to keep with the thienopyrazine naming convention dibenzo[f,h]thieno[3,4-b]quinoxaline will be referred to by an abbreviation for
phenanthrenethieno[3,4-\textit{b}]pyrazine (PATP), and trithieno[3,4-\textit{b}:2',3'-\textit{f}:3'',2''-\textit{h}]quinoxaline will be referred to by an abbreviation for benzo[1,2-\textit{b}:4,3-\textit{b'}]dithiophenethieno[3,4-\textit{b}]pyrazine (BDTTP1).

Geometry optimizations were performed on model oligomers of the four compounds selected for study. Hexamers of TP and DMTP, as well as trimers of PATP and BDTTP1 were optimized. The molecular orbital diagrams of the HOMO and LUMO for all four compounds are extended over the entire length of the model oligomer, indicating a delocalized electronic structure, which is desirable for pseudocapacitive applications (Figure 5.3 and Figure 5.4). The position of the molecular orbitals on the model compounds with extended pi-systems indicate that the majority of the electron density lies on the main thieno[3,4-\textit{b}]pyrazine oligomer backbone.

\textbf{Figure 5.3} Model hexamers of TP and DMTP with the HOMO (bottom row) and LUMO (top row) molecular orbitals represented.
Figure 5.4 Model trimers of PATP and BDTTP1 with the HOMO (bottom row) and LUMO (top row) molecular orbitals represented.

5.3.2 Electrochemical Polymerization and Measurement

5.3.2.1 Polymerization on Platinum Button Electrodes

All polymers explored in this study were synthesized by electrochemical polymerization. Briefly, a solution of acetonitrile containing 0.01 M of monomer and 0.1 M electrolyte (either tetrabutylammonium hexafluorophosphate, TBAPF$_6$, or tetraethylammonium tetrafluoroborate, TEABF$_4$) was prepared. In the case of PATP and BDTTP1, a saturated solution of monomer was prepared. Electropolymerization was performed by cyclic voltammetry in a standard 3-electrode electrochemical cell with a platinum button electrode (circular, 2 mm diameter), a Ag/Ag$^{+}$ pseudo reference electrode, and a platinum counter electrode.

Electrochemical deposition of TP was attempted first. The initial scan on the cyclic voltammogram shows a large current wave with an onset of ca. 1.1 V. However, on subsequent scans, the oxidation potential shifts to higher and higher voltages, in the direction of the arrow (Figure 5.5, left). The polymer oxidation wave on the forward scan and the polymer reduction wave on the reverse scan are both very small, indicating that the film is not being charged and
that it is poorly conductive. This is likely because the oxidation potential of the monomer is higher than the voltage under which the polymer is stable. Thus, any polymer deposited is quickly degraded by overoxidation. This phenomenon is known in the literature and is referred to as the “polythiophene paradox”.21

A dark film was present on the electrode and electrochemical measurements were made on the film in a monomer-free solution (Figure 5.5, right). The lack of a broad charging wave and poor reversibility of the cyclic voltammogram are not characteristic of a good conductive polymer capable of becoming positively charged.

Figure 5.5 Attempted electrochemical deposition of TP (left) and the electrochemistry of the deposited film (right) in a monomer-free solution.

The solution often applied to the polythiophene paradox is to electrochemically polymerize the thiophene dimer 2,2'-bithiophene because the dimer has a much lower oxidation potential than the monomer. 5,5'-bithieno[3,4-b]pyrazine, the thienopyrazine dimer, is not a known compound. Numerous attempts to synthesize this compound were not successful.

Installing electron donating groups on a monomer is another method to decrease the oxidation potential. DMTP was selected for this reason. DMTP has a lower oxidation potential than TP (ca. 900 mV vs Ag/Ag⁺) and cyclic voltammetry in a monomer containing solution yields a cyclic voltammogram typical of electrodeposition of a conjugated polymer (Figure 5.6, left). Very little current passes in the first scan until the oxidation potential of the monomer is reached (indicated by arrow 1). The polymer is deposited in the oxidized state, and on the reverse scan a new peak grows in which is the reduction of the oxidized polymer (indicated by arrow 2). On subsequent scans the polymer is oxidized at a lower potential than the monomer (indicated by arrow 3). The peaks resulting from the oxidation and reduction of the polymer (arrows 2 and 3) grow with each
scan indicating that more polymer is being deposited on the electrode. Cyclic voltammetry on the polymer film indicates a broad positive and negative pseudocapacitive region (Figure 5.6, right).

![Graph](image)

**Figure 5.6** Electrochemical polymerization of DMTP by cyclic voltammetry (left) and cyclic voltammetry of PDMTP (right) in a monomer-free solution.

Installing electron donating methyl groups on the pyrazine ring has the effect of lowering the oxidation potential, allowing for electrochemical polymerization, however, the methyl groups also have the effect of increasing the reduction potential of the monomer (Figure 5.8). This is undesirable for Type III supercapacitors as the band gap of the polymer will be increased, reducing the amount of pseudocapacitive charge that can be stored.

PATP and BDTTP1 were chosen for study next. PATP is known to have low oxidation and reduction potentials. BDTTP1 was modeled using DFT calculations and is predicted to have an even more stabilized LUMO than PATP. The two monomers were polymerized electrochemically on platinum button electrodes and cyclic voltammetry was performed on the polymers formed in monomer-free electrolyte solution (Figure 5.7).
Figure 5.7 Top Row: Electrochemical polymerization of PATP (left) and a cyclic voltammogram of the corresponding polymer (right) in monomer-free solution. Bottom Row: Electrochemical polymerization of BDTTP1 (left) and a cyclic voltammogram of the corresponding polymer (right) in monomer-free solution.

Varying the substituent on the pyrazine ring has a pronounced effect on the LUMO energy of the monomer (Figure 5.8). The electron donating methyl groups on DMTP destabilize the LUMO relative to the parent TP. The fused phenanthrene ring on PATP however stabilizes the LUMO relative to TP, and the fused benzodithiophene ring stabilizes the LUMO even further.

Figure 5.8 Cyclic voltammograms of the reduction of the monomers used in this study. Conditions for TP, DMTP: 0.01 M monomer, 0.1 M TEABF₄ in acetonitrile. Conditions for PATP and BDTTP1: 0.1 M TEABF₄ in acetonitrile saturated with monomer.
High cycling stability is important for supercapacitor electrodes. The cycling stability of both PPATP and PBDTTP1 was measured in 0.1 M TEABF$_4$/acetonitrile (Figure 5.9) at a scan rate of 500 mV/s scanning between -800 mV and -1800 mV vs Ag/Ag$^+$. Coulombic efficiency is calculated as the ratio of charge extracted on the anodic scan to charge input on the cathodic scan. Both materials exhibited good coulombic efficiency over the negative potential scanning range, both above 95% and either increasing or staying relatively constant over 500 cycles (Figure 5.10, left). The capacity retention, represented as percent of maximum charge (on discharge), is approximately 70% for PPATP and 80% for PBDTTP1 after 500 cycles (Figure 5.10, right).

![Figure 5.9](image1.png) Cycling stability of PPATP (left) and PBDTTP1 (right) in 0.1 M TEABF$_4$/acetonitrile.

![Figure 5.10](image2.png) Coulombic efficiency (left) and capacity retention (right) of PPATP and PBDTTP1 measured for 500 cycles on platinum button electrodes in 0.1 M TEABF$_4$/acetonitrile.

### 5.3.2.2 Electrochemical Polymerization on Carbon Fibre Paper Electrodes

The use of carbon fibre paper, herein referred to as carbon paper, current collectors was explored for this project. Carbon paper offers a high surface area and three-dimensional network of
conductive carbon on which conjugated heterocycles can be electropolymerized (Figure 5.11). Fabricating a conjugated polymer supercapacitor on carbon paper allows for a very high mass loading over a given surface area, without requiring a thick film. The carbon paper acts as a 3-dimensional electrode, and coating it with polymer yields a thick electrode with a high internal surface area. The mass loading in the device can be high without having a polymer film so thick that the performance is affected. Rather, it is the carbon paper that is thick and the polymer coats the paper in a thin shell.

**Figure 5.11** Scanning electron micrograph of the carbon paper used as the electrode for electrochemical polymerization of monomers.

A potentiostatic pulse method was used for electropolymerization on carbon paper electrodes. Briefly, the carbon paper is immersed into 3-electrode electrochemical cell filled with a solution of monomer and electrolyte. The carbon paper acts as the working electrode. A potential greater than the oxidation potential of the monomer is applied for a brief period of time ($t_{on}$) and then the potential is switched to a lower potential for a brief period of time ($t_{off}$). Previous studies have shown that a pulsed technique leads to polymer with higher electrochemically accessible surface area and higher capacitance than potentiostatic methods.\(^{22}\) In addition, during the $t_{on}$ period monomer concentration is decreased in the vicinity of the electrode as it is polymerized, particularly in the interior of the carbon paper. The $t_{off}$ period allows monomers to diffuse into the interior of the carbon paper, allowing for a more uniform polymer deposition throughout the thickness of the carbon paper.

Before thienopyrazines were polymerized on carbon paper electrodes, 3,4 ethyленedioxythiophene (EDOT) was used as a test compound to optimize the deposition
process. EDOT is commercially available and has previously been polymerized on carbon paper electrodes fabricated into supercapacitors.\textsuperscript{23}

EDOT was electropolymerized on carbon paper using the potentiostatic pulse method. Increasing the number of pulses increases the polymerization time and the amount of charge passed. Mass loading of the polymer shows a linear relationship with current density (Figure 5.12). The rate of mass loading is approximately 0.6 mg/C. From these experiments it was determined that the PEDOT loading level for a supercapacitor electrode should be approximately 0.6 mg/cm\textsuperscript{2}. This allows for the highest mass loading without compromising the film quality. When more polymer is deposited, the polymer tends to flake off the electrode.

![Figure 5.12](image-url) A plot of mass loading as a function of charge passed for EDOT electropolymerized on carbon paper.

To ensure reproducibility, three trials of EDOT electropolymerization were performed with a charge density of 0.96 C/cm\textsuperscript{2}. The mean mass of polymer deposited was 0.62 mg/cm\textsuperscript{2} with a standard deviation of 0.063 mg/cm\textsuperscript{2}.

DMTP, PATP, and BDTTP1 were all deposited on carbon paper with varying degrees of loading. The rate of mass loading for PDMTP is approximately 0.2 mg/C (Figure 5.13). Scanning electron micrographs of the PDMTP on carbon paper reveal good coverage on the carbon paper. A compact polymer layer is formed on the surface of the fibres with nodules distributed on top of the compact layer.
Figure 5.13 Mass loading vs charge passed of DMTP electropolymerized on carbon paper and scanning electron micrographs of PDMTP on carbon paper with a mass loading of ca. 0.57 mg/cm².

PATP and BDTTP1 are less soluble than EDOT and DMTP. A mass-loading curve was not obtained for PATP. SEM images of PPATP on carbon paper reveal a very high density of polymer nodules overtop of the compact layer on the outer surface fibres of the carbon paper (Figure 5.14). The inner fibres, however, are sparsely coated. This is likely due to the poor solubility of the monomer and low concentration of monomer in the interior of the electrode.
Figure 5.14 Scanning electron micrographs of PPATP on carbon paper with a mass loading of ca. 0.84 mg/cm².

Omitting the final data point, the rate of mass loading for PBDTTP1 is approximately 0.5 mg/C (Figure 5.15). It is likely that the non-linearity observed at higher charge densities is due monomer depletion, a result of the limited solubility of the monomer. Similar to PPATP, scanning electron micrographs show that there is good coating of polymer on the fibres in the outer layer of the carbon paper, but polymer loading on the interior of the carbon paper is significantly lower. In instances where the monomer is of limited solubility, $t_{\text{off}}$ can be increased to allow for monomer to diffuse into the inner portions of the carbon paper electrode allowing for more uniform polymer deposition through the thickness of the carbon paper. However, in this case the low solubility of the monomer was the limiting factor.
Figure 5.15 A plot of mass loading vs charge passed of BDTTP1 electropolymerized on carbon paper and scanning electron micrographs of PBDTTTP1 on carbon paper with a mass loading of ca. 0.27 mg/cm².

5.3.3 Carbon Paper Supercapacitors

Before conjugated polymer supercapacitors were fabricated with thieno[3,4-b]pyrazines, poly(3,4-ethylenedioxythiophene) on carbon paper was fabricated into a supercapacitor device (Figure 5.16).

Figure 5.16 An illustration of a carbon paper supercapacitor device.

The device was fabricated to test the design before proceeding with thieno[3,4-b]pyrazine coated carbon paper. The PEDOT-carbon paper supercapacitor exhibits excellent specific capacitance and capacitance retention over the 10,000 cycles and appears to stabilize after about 8000 cycles,
although longer measurements would be required to confirm this (Figure 5.17). The coulombic efficiency is near 100% for the entire 10,000 cycles which indicates that capacitance losses are not due to trapped charge or parasitic redox reactions occurring within the device, but likely due to polymer delamination from the carbon paper.

![Figure 5.17](image)

**Figure 5.17** Specific capacitance of a PEDOT-carbon paper supercapacitor (left), coulombic efficiency and capacitance retention of the PEDOT-carbon paper supercapacitor (right).

## 5.4 Conclusions

Thieno[3,4-\(b\)]pyrazines polymers are promising for use in narrow band gap organic electronic applications and appear well suited for use as electrodes in Type III supercapacitors. The cycling stability of PPATP and PBDTTP1 are the highest observed for all of the materials studied as a part of this dissertation.

We demonstrated that thieno[3,4-\(b\)]pyrazines functionalized with a fused ring moiety can significantly narrow the HOMO–LUMO gap of the monomers and leads to polymers with very narrow band gaps. The novel compound BDTTP1 had the most stabilized LUMO of all monomers explored in this study.

This chapter is meant to be used as a guide for others to continue this work. Given the low solubility of the PATP and BDTTP1 monomers, and the difficulty in obtaining uniform deposition of the polymer throughout the thickness of the carbon paper, it is recommended that gold coated Kapton electrodes be used for electropolymerization. Films of 5–10 µm in thickness can be readily synthesized.

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1 Data for cycles 1833–4464 was not collected due to a computer malfunction. The cycles did run but the data was not stored.
5.5 Experimental

*General Considerations*: Reagents were purchased from Sigma-Aldrich and used as received unless otherwise noted. THF, dichloromethane, and acetonitrile were purified and dried using an Innovative Technology Pure Solv system. Anhydrous ethanol was stored over molecular sieves. All electrochemical experiments were performed in an Innovative Technology Pure Lab nitrogen-filled glovebox using a BioLogic SP-200 potentiostat. Acetonitrile used for electrochemistry was stored over molecular sieves in the glovebox. AvCarb MGL190 carbon paper (0.19 mm thick, 0.44 g/cm$^3$ dense, 78 % porosity, no Teflon treatment) was purchased from Fuel Cell Earth.

5.5.1 Computational Methods

The geometries of the modeled compounds were optimized with the nonlocal hybrid Becke three-parameter Lee-Yang-Parr$^{24}$ functional and the 6-311g(d) basis set on the Gaussian 09 suite of programs.$^{25,26}$ The isocontour value was set to 0.20 for the molecular orbital diagrams.

5.5.2 Synthesis

\[
\text{H}_2\text{N}\begin{array}{c}
\text{NH}_2 \\
\text{S} \\
\end{array} \cdot 2\text{HCl} \quad \xrightarrow{1} \quad \begin{array}{c}
\text{K}_2\text{CO}_3/\text{EtOH} \\
\text{R} \\
\text{O} \\
\text{R} \\
\end{array} \quad \xrightarrow{2} \quad \begin{array}{c}
\text{TP} \\
\text{DMTP} \\
\text{PATP} \\
\text{BDTTP1} \\
\end{array}
\]

**Scheme 5.1** General method for the synthesis of thieno[3,4-b]pyrazines.

*Thieno[3,4-b]pyrazine (TP)* was prepared according to a modified literature procedure.$^{15}$ Glyoxal (40 % in H$_2$O, 1.19 mmol, 0.1727 g) was diluted to 5 mL and added to 10 mL of 5 % K$_2$CO$_3$. 3,4-Diaminothiophene dihydrochloride (1.08 mmol, 0.2020 g) was then added and the solution was stirred for 5 hours. The reaction mixture was washed thoroughly with diethyl ether. The combined ether fractions were washed with KCl brine, dried over MgSO$_4$, filtered, and concentrated under vacuum at room temperature. Further purification was not necessary. The title compound was obtained as an orange solid (0.1015 g, 69 % yield).$^1$ H NMR (400 MHz,
CDCl$_3$) δ 8.53 (s, 2H), 8.06 (s, 2H). HRMS (DART) m/z: [M + H]$^+$ calcd for C$_6$H$_5$N$_2$S$_1$, 137.01734; found, 137.01739.

2,3-Dimethylthieno[3,4-b]pyrazine (DMTP) was prepared according to a modified literature procedure.$^{15}$ K$_2$CO$_3$ (5.4 mmol, 0.74 g) was added to 62 mL of anhydrous ethanol. 3,4 Diaminothiophene dihydrochloride (1.336 mmol, 0.2500 g) was added to the solution with stirring. Diacetyl (1.389 mmol, 0.1196 g) was diluted with 1 mL of ethanol and added to the reaction mixture. After 3 hours, the ethanol was removed under reduced pressure. The residue was rinsed thoroughly with ether. The combined ether fractions were washed twice with water and once with brine. The ether was removed under reduced pressure at room temperature to yield an orange solid (0.1868 g, 85% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 (s, 2H), 2.63 (s, 6H), $^{13}$C NMR (101 MHz, CDCl$_3$) δ 153.30, 141.83, 116.12, 23.75.

Dibenzo[f,h]thieno[3,4-b]quinoxaline (PATP) was prepared according to a modified literature procedure.$^{18}$ K$_2$CO$_3$ (4.0 mmol, 0.55 g) was added to a 25 mL Schlenk flask equipped with a stir bar and septum. The flask was flame dried and purged with argon. 10 mL of anhydrous ethanol was added via syringe and the mixture was sparged with argon for 10 minutes. The solution was cooled to 0 °C and 3,4-diaminothiophene dihydrochloride (1.0 mmol, 0.1932 g) was added with stirring. 9,10-Phenanthrenequinone (1.0 mmol, 0.2082 g) was added to the reaction mixture, which was then sparged with argon for 10 minutes. The reaction was left to stir overnight. The solvent was removed under reduced pressure at room temperature. The crude mixture was dissolved in a minimum amount of dichloromethane and purified by column chromatography (dichloromethane) to yield the title compound (0.1600 g, 56%). $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 9.19 (d, $J$ = 8.0 Hz 2H), 8.48 (d, $J$ = 8.2 Hz, 2H), 8.22 (s, 2H), 7.76 (t, $J$ = 7.5 Hz 2H), 7.68 (t, $J$ = 7.5 Hz, 2H). HRMS (DART) m/z: [M + H]$^+$ calcd for C$_{18}$H$_{11}$N$_2$S$_1$, 287.06429; found, 287.06489.

**Scheme 5.2** Synthetic method for benzo[1,2-b:4,3-b']dithiophene-4,5-dione.
1,2-Di(thiophen-2-yl)ethane-1,2-dione (1) was prepared according to a modified literature procedure. Three solutions are required for this synthesis. Solution A (Flask A): A 100 mL Schlenk flask was oven dried, equipped with a stir bar and septum, evacuated, and purged with argon. 40 mL of dry THF and 2-bromothiophene (50 mmol, 4.84 mL) was added to the flask via syringe. The solution was cooled to -78 °C. n-Butyllithium (1.36 M, 50 mmol, 36.8 mL) was added with stirring via syringe, dropwise. Solution B (Flask B): Copper(I) bromide (50 mmol, 7.17 g) and lithium bromide (50 mmol, 4.34 g) were added to an oven dried 1 L Schlenk flask, subsequently equipped with a stir bar and rubber septum, inside a glovebox. The flask was then evacuated and purged with argon. Dry THF (275 mL) was added via cannula. The mixture was stirred to dissolve the bromide salts, then cooled to < -80 °C with a liquid nitrogen/methanol mixture. Solution C (Flask C): A 100 mL Schlenk flask was flame dried, evacuated, and purged with argon. THF (40 mL) was added via syringe. The flask was cooled to -78 °C and oxalyl chloride (22.5 mmol, 1.93 mL) was added via syringe. Solution A was added to Flask B via cannula being very careful to keep the temperature < -80 °C. Solution B turned from dark green to lime green upon addition of solution A. Solution C was then added to Flask B dropwise via cannula. The solution in Flask B turned from lime green to amber with the addition of Solution C. The solution was left to warm to room temperature overnight. The solution was treated with saturated ammonium chloride, washed with water until the copper salts were removed and then dried over MgSO₄. The crude material was purified by column chromatography (10:1 hexanes:ethyl acetate) to yield the title compound (2.0994 g, 43 %). \(^1\)H NMR (400 MHz, CDCl₃) δ 8.07 (dd, \(J = 3.8, 1.2\) Hz, 1H), 7.84 (dd, \(J = 4.9, 1.2\) Hz, 1H), 7.21 (dd, \(J = 4.9, 3.9\) Hz, 1H), \(^13\)C NMR (100 MHz, CDCl₃) δ 182.51, 138.71, 137.61, 137.37, 128.79.

Interestingly, starting with 3-bromothiophene led to the same product (1). Arroyave, et al. started with 3-bromothiophene, followed a similar procedure and obtained the 3-substituted product, 1,2-di(thiophen-3-yl)ethane-1,2-dione. However, Fragnelli, et al. attempted to synthesize both the thiophene-2-yl and thiophene-3-yl products, starting with 2- and 3-bromothiophene respectively. They reported a successful conversion in both cases, however the reported NMR peaks and splitting were identical and match the NMR peaks reported above.

**benzo[1,2-b:4,3-b']dithiophene-4,5-dione (2)** was synthesized according to modified literature procedures for benzo[1,2-b:6,5-b']dithiophene-4,5-dione synthesis. In a glove box, FeCl₃ (26.2 mmol, 4.25 g) was added to a dry 100 mL Schlenk flask, subsequently equipped with a stir
bar and rubber septum. Nitromethane (12 mL) was added to the Schlenk flask via syringe. In a separate flask 1 (5.24 mmol, 1.16 g) was dissolved in dry dichloromethane (30 mL). The solution of 1 was added to the FeCl₃ solution via syringe. The combined solution was heated to reflux for 48 hours. The reaction was allowed to cool and was treated with saturated ammonium chloride. The organic layer was washed with water followed by brine. The organic layer was dried over MgSO₄, filtered, and concentrated under reduced pressure. The product was purified by column chromatography (1:1 dichloromethane:ethyl acetate) to yield the title compound (0.4615 g, 40 %). ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, J = 5.0 Hz, 2H), 7.29 (d, J = 5.0 Hz, 2H), ¹³C NMR (101 MHz, CDCl₃) δ 173.95, 142.59, 138.64, 135.15, 124.96. HRMS (DART) m/z: [M + H]+ calcd for C₁₀H₅O₂S₂, 220.97310; found, 220.97320.

*trithieno[3,4-b:1'-2',3'-f:2''-h]quinoxaline (BDTTP1)* was synthesized in an analogous method to PATP. The crude material was purified by column chromatography (100:1 dichloromethane:ethyl acetate) to yield the title compound (0.0614 g, 21 %). ¹H NMR (400 MHz, CDCl₃) δ 8.22 (s, 2H), 7.77 (d, J = 5.2 Hz, 2H), 7.67 (d, J = 5.2 Hz, 2H). HRMS (DART) m/z: [M + H]+ calcd for C₁₄H₇N₂S₃, 298.97714; found, 298.97812.

### 5.5.3 Electrochemistry

Potentials in a 3-electrode electrochemical cell are referenced to a Ag/Ag⁺ reference electrode. Cycling stability experiments were performed at 500 mV/s.

### 5.5.4 Electrochemical Polymerization

The pulse times used for electrochemical polymerization on carbon paper electrodes was t_{on} = 0.5 s and t_{off} = 0.1 s unless otherwise stated. A platinum mesh electrode was used as the counter electrode in all experiments performed in a 3-electrode cell.

EDOT polymerization was performed in a solution containing 0.01 M EDOT, 0.1 M TBAPF₆ in acetonitrile. The DMTP polymerization solution contained 0.01 M DMTP, 0.1 M TEABF₄ in acetonitrile. For PATP, a saturated solution of the monomer was prepared with 0.1 M TEABF₄ in acetonitrile. For BDTTP1, a saturated solution of the monomer was prepared in either a 0.1 or 0.2 M TBAPF₆ in a mixture of benzonitrile and acetonitrile (1:3 w/w).
The mass of the polymer coating was found by weighing the carbon paper before and after polymerization. The bare carbon paper was washed thoroughly with acetonitrile and dichloromethane prior to weighing. After polymer deposition, the polymer was undoped at an appropriate potential, rinsed thoroughly with acetonitrile, and dried under vacuum.

5.5.5 General Device Fabrication

Before device fabrication it is important to charge both electrodes to the correct level. For example, PEDOT exhibits uniform pseudocapacitive behaviour over a voltage range of ca. 1.4 V (i.e. capacitance is constant over the voltage range). Assuming ideal capacitive behaviour of both electrodes over that voltage range, in a 2-electrode device the positive electrode will increase in voltage by 0.7 V and the negative electrode will decrease in voltage by 0.7 V relative to the discharged state of 0 V when the device is charged to 1.4 V. In a 3-electrode cell, PEDOT has near-ideal capacitive behaviour between -0.4 V and + 1.0 V vs Ag/Ag⁺. Thus, charging two PEDOT electrodes to +0.3 V vs Ag/Ag⁺ means that there is no potential difference between them and fabricating a 2-electrode device from them in this state yields a measured voltage of 0 V. The device can now be charged and will display capacitive behaviour over a voltage range of up to 1.4 V.

5.5.6 Carbon Paper Device Fabrication

Carbon paper supercapacitor devices were fabricated by first depositing the conjugated polymer onto half of a 1 x 2 cm piece of carbon paper, yielding a 1 x 1 cm area of conjugated polymer coated carbon paper. This single piece of carbon paper was immersed in a monomer-free electrolyte solution and charged potentiostatically to the required voltage for the initial conditions of the device. At no point is the polymer coated carbon paper allowed to dry.

PEDOT-coated carbon paper was charged to a voltage of 0.3 V vs Ag/Ag⁺. The carbon paper was then cut in half lengthwise to yield two pieces 0.5 cm wide x 2 cm long with half of the paper coated with PEDOT. The two electrodes were placed onto two separate gold/Kapton™ films which function as current collectors. The ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide was pipetted onto each electrode. A piece of Celgard polypropylene separator was placed on one electrode, the other electrode was rotated 180° to ensure only the PEDOT coated portion of the electrode overlapped, and sandwiched on top (Figure 5.16).
5.5.7 Data Processing

Adjacent-averaging was used to smooth the cyclic voltammograms of polymer deposition due to some noise in the signal. The overall shape of the signal was not affected.

5.6 References


(25) Frisch, M. J.; et al. Gaussian 09, revision B.01; Gaussian, Inc.: Wallingford, CT, 2009.*


(30) Mei, C.-Y.; Liang, L.; Zhao, F.-G.; Wang, J.-T.; Yu, L.-F.; Li, Y.-X.; Li, W.-S. A Family of Donor–Acceptor Photovoltaic Polymers with Fused 4,7-Dithienyl-2,1,3-

Chapter 6

Conclusions

6.1 Summary and Future Work, Part 1

Controlling the morphology of conjugated polymers at the nanoscale is important for optimizing electronic properties, for elucidating structure-function relationships, and for synthesizing solution suspended nanostructures with desired shape and packing properties. Templated electrochemical synthesis (TES) is perhaps the most straightforward method of controlling nanoscale morphology and generating conjugated polymer nanostructures. One of the main advantages of this technique is that polymerization and nanostructure formation occur simultaneously; chemical polymer synthesis is not required. TES can be used to synthesize polymer nanostructures from any monomer that can be electropolymerized. Some common examples include thiophene,\(^1\) 3,4-ethylenedioxythiophene,\(^2\) pyrrole,\(^3\) and aniline.\(^4\)

In Chapter 2 we demonstrated that thiophene and many of it derivatives functionalized at the 3 and 4 positions and narrow HOMO–LUMO gap monomers like selenophene and thieno[3,2-\(b\)]thiophene can be formed into nanostructures using TES as well. Although TES was discovered over 40 years ago,\(^5\) and first applied to conjugated polymers in 1986,\(^3\) this is the first work to examine and demonstrate the effect of side-chain substituents on nanostructure morphology and to demonstrate optical property modification by using monomers with different absorption properties. We are able to use side-chains to control whether the nanostructure is a linear, hollow nanotube or a collapsed nanowire. Building blocks without side-chains or with hydrophilic side-chains yield linear, tubular nanostructures. Building blocks with hydrophobic side-chains cause the nanotubular structure to collapse upon aqueous work-up. The methods we have developed are general and will allow for morphological control of any conjugated polymer by substituting the monomer with an appropriate side-chain. Also demonstrated for the first time is the assembly of template synthesized nanostructures into free-floating arrays of aligned nanowires. The hydrophobic nature of the hexyl side-chains causes the collapsed nanostructures to assemble into these arrays.

In Chapter 3, for the first time, we demonstrate that nanotube versus nanowire formation by TES is controlled by the rate of electropolymerization. Solvent/electrolyte systems that increase the
rate of thiophene polymerization yield solid nanowires, whereas systems that decrease the rate of polymerization yield thin-wall nanotubes. A solvent/electrolyte system that leads to an intermediate polymerization rate yields intermediate structures, namely thick wall nanotubes.

Our group has already expanded upon the work presented in Chapters 2 and 3. Colin Bridges has used these polythiophene nanostructures as sacrificial internal templates for gold nanotube synthesis. Briefly, polythiophene nanostructures were synthesized by TES, then gold was electrodeposited around the polythiophene nanostructures generating core-shell structures. The polythiophene core was then etched. He was able to control the wall thickness of the gold nanotubes by using polythiophene nanotubes that collapsed to different degrees based on their side-chain and wall thickness. These gold nanotubes have been demonstrated as highly sensitive refractive index sensors and as a surface enhanced Raman spectroscopy substrate.

One important application of this work is to use the metal-coated AAO template embedded with polymer nanotubes as a pseudocapacitive electrode in supercapacitors. Sang-Bok Lee and coworkers have demonstrated this using PEDOT nanotubes as electrodes in a supercapacitor device. They were able to achieve higher power densities than are typical with a polymer film due to fast ion diffusion into the thin nanotube walls. The total energy that can be stored in a device is dependent on the amount of redox active material present; however, the power is largely reliant on accessible surface area for ion diffusion. Achieving control over the thickness of the nanotube walls will allow for optimization of energy and power density. Further, the polymers presented in Part 2 could be formed into nanotubes using TES, and Type III supercapacitors with nanotubular electrodes could be demonstrated.

Other future work could be done on the assembled arrays of polymer nanowires. Being composed of conductive polymers, they may be useful as electronically switchable membranes.

### 6.2 Summary and Future Work, Part 2

Supercapacitors are important devices for storing electrical energy. Applications include electric vehicles, renewable energy storage (e.g. solar and wind), aerospace, military, consumer electronics, and the Smart Grid. Increasing the energy and power density of supercapacitors is thus an important area of research. Using pseudocapacitive materials as the electrodes allows for approximately a 10-fold increase in energy stored. Most pseudocapacitive conjugated
polymers are p-type, meaning that they can only be positively charged. Supercapacitors fabricated from p-type polymers are termed Type I. Type I supercapacitors have a voltage range limited to the positive charging voltage range of the polymer. Applying ambipolar conjugated polymers, polymers that can hold both positive and negative charge, increases the voltage range and in turn increases both the energy and power density of the device (Equation 1.1). Supercapacitors fabricated from ambipolar polymers are termed Type III.

Rudge et al. first studied polymers often considered as p-type, polythiophene, poly(3-phenylthiophene), and poly(3-(4-fluorophenyl)thiophene), for use in Type III supercapacitors. These polymers can hold negative charge at relatively high negative potentials. Devices fabricated from the most promising material, poly(3-(4-fluorophenyl)thiophene), operated at 3 V but due to the wide band gap only stored significant charge from ca. 2.4–3.0 V. A handful of other conjugated polymers have been electrodeposited and applied to Type III supercapacitors with operating voltages between 2 and 3 V. Energy densities ranging from 0.25–53 Wh/kg were reported. In all but one example, cycling stability is problematic.

Donor-acceptor polymers are narrow band gap and can be both positively and negatively charged. In Chapter 4, I fabricated and tested Type III supercapacitor devices from PDEQ and the novel polymer PDDDBT. The PDEQ device has a specific energy of 11 Wh/kg (at 0.5 A/g) and a specific power of 20 kW/kg (at 50 A/g with a specific energy of 3.6 Wh/kg). The PDDDBT device has a specific energy of 4.8 Wh/kg (at 0.5 A/g) and a specific power of 55 kW/kg (at 50 A/g with a specific energy of 0.76 Wh/kg). While higher values have been reported, most use high surface area carbon fabric as the current collector and are measured in a flooded cell rather than as an assembled device. This was only the second report of alternating donor-acceptor polymers used in Type III supercapacitors. Recently, John Reynolds and co-workers demonstrated a poly(bis-EDOT-isoindigo) donor-acceptor polymer in a Type III device with specific energy of ca. 9–15 Wh/kg. The device lost 50 % of its electroactivity after 100 cycles and was completely degraded after 200 cycles. The stability was in part limited due to localization of the LUMO on the acceptor unit. We demonstrated that extending the acceptor unit, or increasing the acceptor to donor ratio, yields more stable Type III supercapacitor devices, with the PDDDBT device retaining 75 % initial capacity after the first 100 cycles and 30 % of initial capacity after 1000 cycles. The computational study of the model oligomers indicated that
increasing the number of adjacent acceptor units could further increase the extent of negative charge delocalization.

With the experimental and computational results of Chapter 4 in mind, I screened thirty potential monomers for polymerization and use as positive and negative charge storing materials in supercapacitors. Thieno[3,4-b]pyrazines were focused upon because of their narrow HOMO–LUMO gap and straightforward synthesis. DFT prediction of the molecular orbitals on model oligomers indicates good delocalization of both the HOMO and the LUMO. I demonstrated the synthesis of one new thieno[3,4-b]pyrazine, BDTTP1, and electrochemical polymerization of three thieno[3,4-b]pyrazines on carbon paper. The thieno[3,4-b]pyrazines, particularly PPATP and PBDTTP1, have a very narrow band gap and show excellent negative charging reversibility. The electrochemistry indicates that both positive and negative charges are highly delocalized on the polymer, as predicted by the DFT calculations. These two polymers need to be fabricated into supercapacitors and tested for specific energy, specific power, and cycling lifetime. Type I devices operating in the negative voltage range should be fabricated to demonstrate the n-type stability. Type III and/or Type IV devices should be fabricated to achieve operating voltages of 2–2.5 V. The monomers are too insoluble to adequately coat a carbon paper electrode, so I recommend depositing the polymer on gold-coated Kapton. Films 5–10 µm thick should be achievable.

Moving forward from here, it is important to find both materials and device architectures that will yield Type III supercapacitors that are stable for thousands of cycles. Finding new materials with a less negative onset of reduction may reduce deleterious side reactions happening at the negative electrode. 2,3-dicyanothieno[3,4-b]pyrazine is a good candidate with the least negative reduction onset of all thieno[3,4-b]pyrazines studied to date (-0.93 V vs Ag/Ag⁺ for the monomer). The oxidation potential is too high for electrochemical polymerization, thus chemical methods may be required. Alternatively, a dimer or trimer of 2,3-dicyanothieno[3,4-b]pyrazine could be chemically synthesized as the oxidation potential of an extended conjugated molecule will be significantly lower than the monomer.

The most stable Type III supercapacitor to date (the only device with considerable stability beyond 1000 cycles) is a poly(3-methylthiophene) device, where the polymer was prepared electrochemically and blended with activated carbon and a polymer binder. This composite was
then coated on a stainless steel mesh current collector. Future work must consider blending the polymer with a conductivity enhancing agent as well as a binder. Different current collectors should also be tested for their effect on the stability of the polymer.

Finally, it would be instructive to analyze the chemical breakdown mechanism of the supercapacitor electrodes, and the effect of these changes on specific elements of device performance. Information on the chemical transformations happening to the electrode material would be useful in designing more stable materials. Analytical techniques suitable for measuring thin organic films, such as infrared spectroscopy would be useful and electrochemical impedance spectroscopy may provide insight into the specific effects of the degraded electrode material on device performance. Further information could be obtained by measuring the electrode breakdown products at various potentials.

6.3 References


Appendix 1

Supercapacitor Characterization Methods

A1.1 General Comments

Accurate and consistent testing of supercapacitor devices is essential for characterization of new materials. To acquaint oneself with the methods presented below, the author suggests experimenting on a commercial dielectric capacitor or supercapacitor device. These devices can be purchased cheaply at any electronics store.

A1.2 Measuring Capacitance

Capacitance $C$ is a measure of the quantity of charge $Q$, measured in coulombs, stored in a device at a given voltage $V$ (Equation A1.1). The SI units for capacitance are farads $F$.

$$C = \frac{Q}{V} \quad (A1.1)$$

Capacitance can be measured by several methods including electrochemical impedance spectroscopy (EIS), cyclic voltammetry, and charge/discharge. The latter two methods will be outlined below. Details on EIS techniques for supercapacitor measurement, as well as an overview of the techniques covered here, can be found in Supercapacitors: Materials, Systems, and Applications, Béguin, F.; Frąckowiak, E., Eds.; 1st ed.; Ch. 3, Electrochemical Techniques, Taberna, P.-L., Simon, P.; Wiley-VCH Verlag GmbH & Co. KGaA: 2013.

A1.2.1 Cyclic Voltammetry

Cyclic voltammetry allows one to increase the voltage across a supercapacitor device at a constant rate, measured in $V/s$. Current is measured as a function of voltage as the electrodes accumulate charge. An ideal supercapacitor will exhibit a rectangular cyclic voltammogram. The PEDOT device in this work behaves in a near-ideal manner (Figure 4.5). The donor-acceptor devices display peaks in the cyclic voltammograms as the pseudocapacitance of the materials, particularly of the negative electrode, is voltage dependent.

The capacitance of the device can be found using the following equation:
\[ C = \frac{i}{dV/dt} \]  \hspace{1cm} (A1.2)

where \( i \) is the current measured in amperes, and \( dV/dt \) is the scan rate. Scan rates suitable for conjugated polymer based devices range from ca. 20 – 5000 mV/s.

This calculation provides the average capacitance over the measured voltage range. For an ideal device, capacitance is not voltage dependent and this calculation provides straightforward measure of capacitance. However, when a device displays voltage dependent pseudocapacitance, averaging over the entire voltage range may not be the most instructive method. In Chapter 4, for example, the maximum specific capacitance, the capacitance from maximum voltage to half maximum voltage \((V_{\text{max}} - V_{1/2})\), and the capacitance over only the pseudocapacitive region \((V_{\text{max}} - V_{\text{pseudo}})\) were presented. The specific capacitance of the device can be calculated by dividing the measured capacitance by the total mass of the electrode material.

### A1.2.2 Charge/Discharge

The constant current method for measuring capacitance is known as charge/discharge. Here, a current is applied to the device until the device reaches some predetermined voltage (charge), at which point the current is reversed (discharge). The results are displayed on a graph of voltage versus time (or charge). For an ideal capacitor the shape of curve for one charge/discharge cycle is triangular. Capacitance can be calculated by using (Equation A1.2) where \( i \) is the applied current, \( dV \) is the voltage change on discharge, and \( dt \) is the discharge time. The specific capacitance is typically obtained by dividing the current by the mass of the electrode material before running the experiment. Typical values of applied current for a pseudocapacitor are in the range of ca. 0.1 – 50 A/g.

### A1.2.3 Reporting Capacitance

Capacitance values for materials are generally reported for one electrode itself, rather than the entire device. If the specific capacitance was calculated using the mass of both electrodes, the capacitance is multiplied by two to account the fact that we are interested in the specific capacitance of just one electrode in the two-electrode device. To account for the fact that both electrodes are arranged in series (Equation A1.3), the specific capacitance is multiplied again by two. This method assumes that both electrodes have equal capacitance (i.e. \( C_1 = C_2 \)).
A1.3 Efficiency

The efficiency of the charging and discharging process can be calculated by integrating the charge/discharge curve. The ratio of the discharge to charge area is the efficiency of the device.

A1.4 Energy and Power Calculation

Most advanced software packages allow automatic calculation of the energy of the device. The most straightforward method for calculating the energy of the device manually is using the charge/discharge data. As we are interested in how much energy the device can deliver, we will use the discharge curve. We begin by integrating the area under the discharge curve of the device. This gives a quantity in units of V•s. Multiplying by the applied current, in units of amperes/g, yields the specific energy of the device in V•C/g, or J/g. Conversion to units of Wh/kg is common.

The power can then be calculated by dividing the energy (J/g) by the discharge time (seconds) to yield the power in units of W/g. Often, specific power is reported in units of kW/kg.

Converting values of specific energy and specific power to the volumetric quantities of energy and power density can also be useful. In all cases, it is important to report the thickness of the capacitive electrode.

A1.5 Ragone Plots

Ragone plots are useful for illustrating the power of a device as a function of energy. Although plotting power versus energy, and vice-versa are both common in the literature, the original plots that Ragone published were of the form power versus energy.\(^1\) A straightforward method for generating a Ragone plot is to perform charge/discharge measurements at increasing discharge currents. Specific energy and specific power are calculated at all measured specific currents and then plotted. For example, in Chapter 4 of this work, specific currents of 0.2, 0.5, 1.0, 2.0, 5.0, 10, 20, 50 A/g were suitable for generating the Ragone plot data.
A1.6 References