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Dedication

I would like to thank foremost my parents, Teresa and David Simone for their love and support throughout many years of schooling. Their work ethic and perseverance have been examples for their children who never faced hardships as they did. To Susan Simone for her immeasurable love, support and constant teasing. I may never win an argument counselor, but that’s OK since your paying. To all my family overseas for their kindness, especially during sporadic trips to replenish my coffers with pasta and wine. To the best of friend anyone could have Frank “three-fingers” Caloroso. Thanks for all the laughs since kindergarten and many more to come. To Professor Yoshiyuki Okamoto for giving me the opportunity to work in his lab for three years. Yoroshiku onegaishimas sen-sei, I am indebted to you. To all those that passed away during the writing of this thesis especially Zio Giovanni Rana (Forza Milan), and my Golden Retriever of 15yrs.,

Goldie.

This bone is for you.

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ABSTRACT

Scope. The body of work described in this thesis focuses on the synthesis of donor-acceptor architectures of the pseudorotaxane, rotaxane, and catenane genres. The binding constants of thiophene and phenylene-ethynylene based crown ethers are determined via fluorescence quenching titrations, in an attempt to correlate structure with binding affinities. The insight obtained from the binding constant determinations allows for the proper choice of crown ether for the formation of [2]-catenanes and [2]-rotaxanes. The electronic properties of these complexes are then probed by electrochemical, spectroelectrochemical, and conductivity measurements. The potential of a poly([2]-catenane) as a photoconductive polymer is also investigated. The obstacles encountered in synthesizing poly([2]-rotaxanes) is also discussed, with emphasis on end-group strategies that aid in thwarting electrochemically induced dethreading.

Chapter 1.

This chapter provides a broad overview of the physical methods utilized in this thesis. Electrochemical methods are covered, with particular emphasis on oxidative polymerization of heteroaromatic monomers. Correlation between electrode phenomena and cyclic voltammogram waveshapes is included, in order to reinforce an understanding of the various electrochemical processes. Electroactive catenane and rotaxane supramolecules feature prominent in the literature, and a brief overview of significant examples is given. Advanced electrochemical techniques regarding in-situ conductivity measurements and spectroelectrochemistry are discussed. The elucidation of binding affinities for hosts and guest via fluorescence spectroscopy, a major theme in Chapter 2, is presented with focus on interpreting Stern-Volmer plots. A lengthy discussion of photovoltaic devices emphasizing I-V, C-V, and photoaction spectra interpretation is presented with relevant literature examples.

Chapter 2.

The synthesis of halo-functionalized crown ethers and efforts toward improving reaction yields for the macrocyclization are presented. Subsequent functionalization of
the crown ethers with acetylide and thiophene groups via cross-coupling reactions, provides a wealth of receptors for the analyte paraquat. The affinities of the macrocycles for paraquat are determined through Stern-Volmer fluorescence quenching experiments. Correlations between structure and binding constants indicate that π-stacking interactions in two parallel planes, as seen for thiophene derivatized crown ether 33, affords the greatest complimentarity with paraquat, $K_{sv} = 9665 \pm 179M^{-1}$. Acetylide functionalized crown ethers tend to have the weakest binding affinities, attributed to the poorer π-extension. Increasing the electron-donating nature of the thiophene function as seen for 23 versus 15 leads to the doubling of the binding constant. Multiple crown ether receptor 29 does not display a non-linear Stern-Volmer plot, indicating that a single binding event occurs for this molecule. Relative to its monocrown analog 25, the binding constant for 29 is 1.2x larger, hinting at cooperativity between crown ether units.

Chapter 3.

Electrochemical studies on [2]-catenane 38, its non-catenated analog 23, and their respective polymers are undertaken in an effort to quantify the electronic disparity between the differing architectures. The use of nitrosonium ion toward the oxidative polymerization of monomers is proposed as a substitute for FeCl₃. The electronic disparity between 23 and 38 is exemplified by differing oxidation potentials; 38 is harder to oxidize relative to 23. Their polymerization occurs efficiently yielding conductive polymers with conductivities for poly(23) of 11 S/cm, and that for poly(38) at 0.2 S/cm. The conductivity curve for poly(38) is parabolic in nature, decreasing at low degrees of oxidation while the curve for poly(23) does not decrease over the same potential sweep. This disparity is attributed to limited carrier formation in poly(38) due to electrostatic repulsion. Spectroelectrochemical studies for both films indicate that oxidation shifts the band-gap of the polymer from visible to IR. Reduction of the tetracationionic cyclophane reveals a blue shift in the band-gap of poly(38), attributed to the loss of the charge-transfer interaction. A concomitant increase in the absorption of the electron-poor cyclophane is realized as absorption transitions are more likely in the reduced state. Photovoltaic devices are fabricated with ITO/PEDOT:PSS as the anode and Ca as the cathode. The photovoltaic efficiency for poly(23) is determined to be 5200x greater than that for poly(38). Transport of ions through the poly(38) film coupled with trapping by the tetracationionic cyclophane are proposed as efficiency reducing phenomena.

Chapter 4.

Various strategies for the synthesis of rotaxanes and poly(rotaxanes) are discussed. Electrochemical experiments indicate that dethreading is observed for a molecular 1:1 complex when the donor is oxidized or acceptor is reduced. This behavior is also found to occur for crown ether donors that are complexed to localized-acceptor polymers. The search for a well-defined, soluble, conjugated acceptor-polymer began with attempts to synthesize soluble poly(methylpyridine-vinylene)’s (PMePyV’s). Attempts at solubilizing PMePyV failed, and attention was focused on poly(1,4-pyridinium)’s (PPy’s). The traditional deprotonation polymerization route for PPy is circumvented by utilizing an N-oxide based monomer. Multiple attempts at synthesizing well-defined and stable PPy’s were fruitless. Efforts were then refocused on applying Stoddart’s end-groups to acceptor molecules in order to hinder dethreading. The synthesis of rotaxane 51
proves that functionalized crown ethers can thread over the end-groups, and heating of the complex to 80°C does not lead to dethreading. In order to build the most robust system for use in electrochemical studies, a fully t-butylated end-group was utilized in the synthesis of 59. It was found that crown ether 23 did not form a rotaxane with 59, indicating the barrier for complexation is too high at STP. High-pressure synthesis is proposed as a future consideration for threading 23 with 59. In an effort to incorporate delocalized acceptors into rotaxanes, the PPyV based 67 was synthesized. The alkylation of this molecule with methyl iodide did not proceed to completion yielding a mixture of products primarily composed of 68.

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Chapter 1

Introduction to the Physical Methods Utilized in Characterizing Molecular and Polymeric Entities
1.1. Electrochemical Methods

1.1.1. Theory of cyclic voltammetry

Electrochemical systems involve processes that effect the transfer of charge from an electrode to an electrolyte solution. Of particular interest are the changes in current that occur while applying a potential across the electrode/electrolyte interface. There are numerous electrochemical techniques available that allow for the interrogation of the electrode interface, one of the most commonly employed is cyclic voltammetry (CV). In this experiment, a triangular voltage waveform is applied to the working electrode, Figure 1.1.¹

![Potential vs Time Diagram](image)

**Figure 1.1.** Applied potential as a function of time waveform for a cyclic voltammetric experiment.

An increase in potential to a maximum point corresponds to the forward scan half-cycle, where molecules at the electrode surface are oxidized. On the reverse scan, the molecules are reduced back to their neutral state. If the electrochemical reaction is fast enough to maintain the concentrations of the oxidized and reduced species in equilibrium
at the electrode surface, the resulting current-potential plot is assumed to obey the Nernst equation (Eq. 1) for electrochemical reversibility:

\[ E = E^0 + \frac{RT}{nF} \ln \frac{C_0(t)}{C_R(t)} \]  

(1)

As defined in electrochemical terms, reversibility is the separation in peak potentials \( \Delta E_p = E_{p,a} - E_{p,c} \), close to the value of 58/n mV, where n is the number of electrons transferred per molecule. At high scan rates, values of \( \Delta E_p \) are greater than 58/n, and reversibility becomes a function of the degree of stress applied to the system. It has been determined that any deviations from reversible behavior will be imperceptible if the value of \( k^0 \), the rate constant for the reaction, is greater than the numerical value of 0.3\( \nu^{1/2} \), where \( \nu \) is the scan rate. Redox couples whose peaks shift increasingly farther apart are known as quasi-irreversible, and if no parts of the redox couple overlap on the potential axis, then the reaction is considered totally irreversible. A subset of irreversible electrochemistry involves reactions that yield products that cannot be recycled to return the original reactants. These reactions are deemed chemically irreversible and are exemplified in electrolypolymerizable monomers.

The peak current for a reversible cyclic voltammogram is defined by the Randles-Sevcik equation:

\[ i_p = (2.69 \times 10^5)n^{3/2}AD_0^{1/2}\nu^{1/2}C_0^* \]  

(2)

where A is the electrode area, \( D_0 \) is the diffusion coefficient, \( \nu \) is the scan rate, n is the number of electrons transferred, and \( C_0^* \) is the bulk concentration. This equation
demonstrates that a reversible system has an \( i_p \sim v^{1/2} \) dependence and an independence of \( E_p \) on sweep rate.

\[ \text{Figure 1.2. Cyclic voltammogram for the reversible ferrocene/ferrocenium/ferrocene redox couple.}^2 \]

A typical reversible cyclic voltammogram is depicted in Figure 1.2. With no applied potential, only neutral molecules exist on or about the electrode surface. As the applied potential approaches \( E_{p,a} \) (a), the current begins to increase while the neutral molecules begin to oxidize. Upon continued scanning, the current reaches its peak at \( E_{p,a} \) (b), and all molecules within a depletion region from the electrode face are oxidized. Further scanning beyond (b) then leads to a decrease in current due to the formation of a large, impassable depletion layer. The direction of the potential sweep reverses at the switching potential, and the analogous processes occur in the anodic, reductive direction (c).
1.1.2. *Toward an understanding of molecular electronics*

Cyclic voltammetry is an effective technique when applied to an understanding of electronic energy states in organic molecules and conjugated polymers. By varying the energy of the electrons in the working electrode, the electron donating or accepting nature of the molecule can be ascertained, Figure 1.3.

![Diagram of electron transfer](image)

**Figure 1.3.** Representation of the a) reduction and b) oxidation of a species A.

By driving the electrode to more negative potentials, the energy of the electrons is raised, until they reach a level high enough to transfer into vacant electronic states of species in solution. Similarly, the lowering of the electron energy level can be affected by applying a positive potential, and at some favorable point solute molecules will transfer electrons to the electrode. The frontier orbital energies of molecules and
valence/conduction band energies of polymers can be approximated by this redox process.\textsuperscript{1,4}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figures.png}
\caption{Electroactive molecular and supramolecular entities.\textsuperscript{5,6}}
\end{figure}

With the advent of supramolecular chemistry,\textsuperscript{30} analytical and physical characterization tools fall short of providing the necessary confirmation of structure and/or function of complex molecules.\textsuperscript{31} The electrochemical interrogation of these entities has been an invaluable tool for better understanding the electronic changes observed relative to constituent molecules. Stoddart and co-workers\textsuperscript{5} synthesized [2]-catenane and [2]-rotaxane architectures, Figure 1.4, and studied these architectures' electronic environment and molecular motion via an electrochemical approach. They found that crown ether 1 undergoes two one-electron oxidations at 1.28\text{V} and 1.37\text{V}. Taking into consideration the symmetry of the crown ether, only one two-electron oxidation would be expected. The authors rationalized that upon the first oxidation, the neutral hydroquinol group complexes with the oxidized group raising the oxidation potential for the second
oxidation. The electron-poor environment of the [2]-catenane 3 was found to raise the oxidation potential of the hydroquinol units to 1.42V and 1.72V. The electron-deficient viologen cyclophane 2 exhibited two distinct reductions at -0.283V and -0.709V corresponding to half-reduced and fully reduced forms. In the [2]-catenane, the reduction of 2 exhibits three distinct waves, and shifting to higher potentials, -0.310V, -0.437V, and -0.845V. The increased difficulty in reduction is attributed to the electron-rich environment in the [2]-catenane. The differing environments of the dication inside the crown ether cavity relative to the dication outside the cavity give rise to the three waves.

In addition to determining redox potentials and their correlation with intrinsic molecular properties, electrochemistry can be used to effect structural and electronic changes, offering control over supramolecular processes. The linear portion of rotaxane 4 was synthesized with the purpose of incorporating redox active biphenyl and benzidine moieties with distinct oxidation potentials. Initially, the viologen cyclophane 2 preferentially binds with the more electron-rich benzidine group. The selective oxidation of the benzidine unit leads to the decomplexation of 2, which then complexes with the neutral biphenyl. The net result is electrochemical control of molecular motion in a supramolecule.
1.1.3. Polymerization of electroactive monomers

The electrochemical polymerization of hetero-aromatic monomers offers advantages over traditional chemical synthesis because of the ease of isolation for study of the resulting film. Research efforts have focused on the synthesis of poly(thiophene), poly(pyrrole), poly(aniline) and their derivatives because of the high conductivity and enhanced processability relative to their inorganic counterparts.\textsuperscript{11} Numerous uses for poly(thiophenes) have been found particularly in electroluminescent devices,\textsuperscript{9b,19} photovoltaics,\textsuperscript{19} and anti-static coatings.\textsuperscript{9a} Despite the preponderance of literature dedicated to the electrochemical synthesis of conducting polymers,\textsuperscript{7,9-11} there has been little focus toward understanding the polymerization mechanism.\textsuperscript{7}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{polymerization.png}
\caption{Accepted oxidative polymerization mechanism for poly(thiophenes).}
\end{figure}

The commonly accepted mechanism of oxidation and radical combination propagation is depicted in Figure 1.5. The initiation step involves two mono-electron oxidations followed by radical coupling, with a resulting loss of protons. Further propagation
involves repeated oxidations until a polymer is formed. The mechanism is stepwise and should follow kinetics associated with an A-B type poly-condensation. Experiments concur with the resulting chemical irreversibility of the oxidation as well as an increase in electrolyte solution acidity after proton loss. The electrochemical polymerization of (3,4-ethylendioxy)thiophene in Figure 1.6 depicts the irreversibility as a decrease in current

![Graph showing electrochemical polymerization of EDOT.](image)

**Figure 1.6.** Electrochemical polymerization of EDOT.

of the monomer oxidation over successive cycles and the non-existence of the reductive half-cycle. Continuous cycling leads to an increase in current at lower oxidation potentials attributed to the growth of oligomeric and polymeric entities. The lower oxidation potential for these species corresponds to their ability to better stabilize cationic charge relative to the monomer. Once the film is deposited on an interdigitated electrode, its redox profile and conductivity can be assessed, *vide infra.*
1.1.4. Behavior of surface immobilized films

Once a polymer has been grown onto a working electrode, the electrochemical oxidation/reduction of the film can be monitored. The response obtained from an electrode coated with a monolayer of an electroactive material is shown in Figure 1.7.²

![Cyclic voltammogram](image)

**Figure 1.7.** Cyclic voltammogram for a surface-immobilized redox couple.

In the case of chemically and electrochemically reversible surface-immobilized films, the current increase and decay occur at similar rates giving rise to a symmetric half-wave. The reverse scan is a mirror image of the forward scan. The peak current for such an ideal system is given by:

\[ i_p = \frac{n^2F^2\nu}{4RT} \]  

(3)
where \( n \) is the number of electrons transferred per repeat unit, \( F \) is Faraday's constant, \( \Gamma \) is the surface coverage of the film, \( \nu \) is the scan rate, \( R \) is the universal gas constant, and \( T \) is the temperature in Kelvin. Eq. 3 reveals that a linear relationship between \( i_p \) and \( \nu \) is established in contrast to the \( i_p \sim \nu^{1/2} \) for freely diffusing species. This relationship is important because the signal-to-noise ratio will not degrade with increasing scan rate, proof that the film is immobilized and stable. If the film is deemed stable, then the charge associated with oxidizing/reducing the film should be proportional to the surface coverage by:\(^2\)

\[
\Gamma = \frac{Q_+}{nFA} \quad (4)
\]

where \( Q_+ \) is the charge associated with the oxidative half cycle obtained from the area under the curve, and \( A \) is the active area of the electrode. Having identified the surface coverage, it is possible to calculate an approximate film thickness:

\[
T = \frac{\Gamma M_w}{\rho} \quad (5)
\]

if the repeat unit molecular weight \( M_w \), and the density of the polymer \( \rho \), is known.

In the case of non-interacting functionality in the film, the full width at half-maximum (FWHM) should be \((90.6/n) \text{ mV}\).\(^2\) Larger values will indicate repulsive interactions between electroactive species, whereas smaller values indicate attractive or stabilizing interactions. When extremely sharp peaks are encountered in the cyclic voltammogram, phase transformations are operative.
The above theory holds well for monolayer films; however, electrochemically grown films can range up to thousands of monolayers and the local concentration of redox species can be much larger than which is found in solution. Charge propagation occurs via numerous processes (Figure 1.8)\(^2\), and waveforms must be analyzed on a case by case basis.

**Figure 1.8** Depiction of various aspects of charge propagation through polymer films containing electroactive groups. The processes include: 1) polymer motions; 2) transfer of cations; 3) and anions; 4) across the polymer/solution interface; 5) transport of solvent; 6) anions; 7) and cations through the polymer film; 8) electron transfer between redox partners.

A determination of the charge transport diffusion coefficient, \(D_{ct}\), can provide useful insight into the ideality of the film.\(^2\) If \(D_{ct}t/d^2\), where \(t\) is the time scale of the experiment and \(d\) is the film thickness is \(>>1\), then the voltammetric waveshape behaves as a monolayer. For \(D_{ct}t/d^2<<1\), the response is attributed to freely diffusing species in solution.
1.1.5. Spectroelectrochemistry

The amalgamation of frontier molecular orbital theory for organic molecules and band theory for periodic, crystalline materials has led to an analogous band understanding for highly conjugated organic polymers, Figure 1.9.

![Diagram of molecular orbital theory transposed to highly conjugated, semiconducting polymers.](image)

Figure 1.9. Molecular orbital theory transposed to highly conjugated, semiconducting polymers.

An iterative progression in \( \pi \)-conjugation leads to the formation of HOMO/LUMO analogs in conjugated polymers known as the valence and conduction bands. For semiconducting polymers, the valence band is filled and the conduction band is empty. The band gap, \( E_g \), represents the amount of energy required to promote an electron into the conduction band, and can be approximated as the wavelength of maximum absorption. The Fermi level, \( E_F \), corresponds to the energy level that lies in the center of
the density of states. For a metal, a continuum of energy levels exists such that there is no distinction between valence and conduction bands, hence no band gap. Very little energy is therefore required to promote electrons into empty bands, which attests to the high conductivity of metals.

It has been postulated that the oxidation of conjugated polymers results in the formation of bands within the polymer band gap. For poly(trans-acetylene) charged solitons, solitary cationic free carriers are created and occupy levels which are exactly midway between the valence and conduction bands. At low oxidation levels, radical-cationic polaron carriers prevail in poly(aromatics), and give rise to the formation of bands within the band gap, Figure 1.10. Upon further oxidation, bipolaronic cation pairs form, increasing the density of states within the band gap.

![Figure 1.10. Changes in band structure upon oxidative doping.](image-url)
Figure 1.11. Structural depiction of neutral, polaronic, and bipolaronic states as a function of oxidation.

The structural perturbation created upon oxidizing hetero-aromatic polymers (Figure 1.11), gives rise to quinoidal regions dispersed among aromatic regions. Equilibrium is attained when coulombic repulsion in polaron and bipolaron states are minimized by the smallest number of quinoid units.

Figure 1.12. Spectroelectrochemical cell configuration.
The polymer band gap continually decreases from the neutral to bipolaronic state, and the diminution can be monitored by utilizing a spectroelectrochemical cell, Figure 1.12. A polymer can be grown anaerobically in the cell in accordance with standard cyclic voltammetric experimentation. The resulting film adheres to the transparent ITO/quartz working electrode, is rinsed, and the optical absorption is monitored as a function of electrochemical oxidation. The large visible to IR absorption window for poly(heterocyclic aromatics) renders them attractive candidates for electrochromic devices.⁹
1.1.6. In-situ conductivity measurements

Structural perturbations in conjugated polymers, particularly via p or n-type doping, create significant changes in the band structure. Enhancements in conductivity from the neutral insulator/semiconductor regime to the metallic regime have been achieved by oxidative chemical or electrochemical means. The latter method allows for a rapid synthesis of polymers under anaerobic conditions, eliminating irreversible changes to polymer films from air oxidation, contamination, and mechanical damage. By synthesizing polymers on microelectrodes, the conductivity of the macromolecule can be assessed in-situ, Figure 1.13. This technique has been utilized for poly(thiophene), poly(pyrrole), poly(aniline) and derivates thereof.

![Diagram](image)

**Figure 1.13.** Interdigitated microelectrode geometry and electrochemical cell setup.
In order to measure the conductivity of the polymer film, it must be brought to the desired gate potential $V_G$ by a three electrode potentiostat while a dc voltage $V_D$ is applied across the interdigitated electrode by a second potentiostat. After equilibrium is attained ($i_d=0$), the gate potential is varied and the oxidation state of the polymer changes. The drain current $i_d$ is then monitored as a function of oxidation, and is related to conductivity $\sigma$ by:

$$\sigma = \frac{i_d}{V_D} \frac{d}{N \cdot T \cdot L}$$  \hspace{1cm} (6)

where $d$ is the interdigit spacing, $L$ is the length of the microelectrode, $N$ is the number of microelectrode gaps, and $T$ is the film thickness. The polymer film thickness is difficult to calculate from the interdigitated electrode as it is hard to identify which portion of the polymer lies on top or between the electrodes. In addition, the film coverage is not expected to be uniform since the surface coverage is much less than the interelectrode spacing. A method developed by Zotti and co-workers\textsuperscript{11} was used in order to correct for non-uniform coverage. In their work, a two-electrode device was fabricated with insulated top faces, allowing for selective polymer growth between the microelectrode gap. Measured conductivity for poly(3-methylthiophene) by this method conformed to the known bulk value of 60 S/cm.\textsuperscript{11c} In our studies, the uncorrected conductivity for poly(3-methylthiophene) was determined and a normalization factor $N$ was instituted. This factor compensates for the film surface area overestimation leading to conductivity underestimation in poly(3-methylthiophene), $\sigma_{p3t}^{uncor}$.

$$N = \frac{\sigma_{p3t}^{corr}}{\sigma_{p3t}^{uncor}}$$  \hspace{1cm} (7)

The correction is then applied to any uncorrected $\sigma$ allowing for the calculation of the absolute conductivity.
1.2. Fluorescence Spectroscopy

1.2.1. Binding Constant Determination

Fluorescence spectroscopy provides for an extremely sensitive probe of fluorophores at part-per-billion (ppb) concentrations. The diminution or enhancement of fluorescence intensity observed when an analyte encounters a fluorophore, a quenching event, allows for a quantitative understanding of the analyte’s penchant for the fluorophore. A quenching event can occur by a number of processes, but of particular import to this work are the competing dynamic (collisional) and/or static (complexation) mechanisms. The Jablonski diagram in Figure 1.14 summarizes a number of possible mechanisms leading to emission or deactivation of the excited state fluorophore, $F'$.\(^{12}\)

![Jablonski Diagram](image)

**Figure 1.14.** Jablonski diagram depicting the possible deactivation pathways for the excited state fluorophore, $F'$.

Initial absorption of energy $h\nu_A$ by the fluorophore in the ground state $S_0$ leads to excitation into the $S_{1+n}$ energy levels ($n=0,1,2,...$). Solvent relaxation about the excited state specie leads to the formation of a lower energy excited state, $S_1$. In this energy state, $F'$ can decay to the ground state and emit light $h\nu_F$ that is governed by the rate of radiative decay, $\Gamma$, or it may decay via a number of non-radiative pathways, $\Sigma k_i$. In the presence of a quencher, $Q$, simple collision with $F'$ will lead to energy transfer to $Q$ and
deactivation of F' to the ground state, Figure 1.15. If Q can form a complex with F', then an excited state complex (F—Q)' will form and will decay to the ground state as F—Q. In both interactions with Q, a certain percentage of F' emission will be quenched, governed by a diffusional quenching constant for the collisional mechanism and a static binding constant for the complexation mechanism.

![Diagram of collisional and static quenching]

**Figure 1.15.** Mechanistic comparison between dynamic (collisional) quenching and static quenching.

The fluorescence intensity observed for a fluorophore is proportional to its concentration in the excited state [F']. Under continuous illumination, a constant population of excited fluorophores is established and d[F']/dt = 0. In the absence of a quencher, the equation describing [F'] is:

\[
\frac{d[F']}{dt} = f(t) - \gamma[F']_0 = 0 \quad (8)
\]

and in the presence of a quencher:

\[
\frac{d[F']}{dt} = f(t) - (\gamma + k_d[Q])[F'] = 0 \quad (9)
\]

where \(f(t)\) is the constant excitation function, and \(\gamma = \tau_0^{-1}\) is the decay rate of the fluorophore in the absence of quencher. In the absence of quenching, the excited-state
population decays at a rate \( \gamma = (\Gamma + k_{nr}) \), where \( \Gamma \) is the radiative decay rate and \( k_{nr} \) is the nonradiative decay rate. In the presence of a quencher, there is an additional decay rate, \( k_{q}[Q] \). With continuous excitation, the excited-state population is constant, so the derivative is eliminated from these equations. Division of Eq. (9) by Eq. (8) yields the Stern-Volmer equation:\textsuperscript{12}

\[
\frac{F_0}{F} = \frac{\gamma + k_{q}[Q]}{\gamma} = 1 + k_{q}\tau_0[Q] \quad (10)
\]

For a collisional quenching process, the product of \( k_{q}\tau_0 \) is \( K_D \), the diffusional quenching constant, and for a static quenching process the product is \( K_a \), the association constant. A linear Stern-Volmer plot ([F\textsubscript{0}]/[F vs. [Q]]) is generally indicative of the presence of a single class of fluorophore, all equally accessible to the quencher. If multiple fluorophore populations are present, and one class is less accessible to the quencher, then the plot will deviate from linearity toward the x-axis. Deviations will also occur if the quenching process is a result of combined dynamic and static quenching, and a Stern-Volmer plot will exhibit an upward curvature.\textsuperscript{12}

Determining whether a dynamic or static mechanism is operative requires the application of variable temperature quenching experiments or the measurement of fluorescence lifetimes, \( \tau_0 \), at each concentration of quencher. For a dynamic mechanism, and increase in temperature should increase \( K_D \), hence an increase in slope should ensue as depicted in Figure 1.16a.\textsuperscript{12} In addition, a decrease in fluorescence lifetime should occur with increasing [Q]. The decrease in lifetime occurs because quenching is an additional rate process that depopulates the excited state. The decrease in emission occurs because quenching depopulates the excited state without fluorescence emission. For the
static mechanism an increase in temperature will lead to a decrease in $K_a$ (via a less favorable $\Delta G$), and a decrease in slope will also be evident (Figure 1.16b). Unlike a dynamic process, static quenching does not decrease the fluorescence lifetime because only the fluorescent molecules are observed, and the uncomplexed fluorophores have the unquenched lifetime $\tau_0$. Hence a plot of $\tau_0 / \tau$ (quencher-free lifetime)/$\tau$ (added quencher lifetime) vs. $[Q]$ will be linear with a slope equal to 1.

**Figure 1.16.** Effect of increasing temperature on A) $K_D$, the diffusional quenching constant and B) $K_a$, the static quenching association constant with $\tau_0 / \tau = 1$.

The Stern-Volmer behavior of a number of fluorescent phenylene-ethynylene based molecular and polymeric receptors have been studied by Swager and Zhou,\textsuperscript{13} in an overall effort toward quantifying the enhanced sensitivity of polymeric receptors as apart from their molecular counterparts, Figure 1.17.
Figure 1.17. Phenylene-ethynylene based fluorophores 1-4 prepared by Swager and Zhou.\textsuperscript{13}

It has been reported\textsuperscript{5} that crown ether based receptors similar to 1 are well suited to bind paraquat 5 in a 1:1 complex. The receptor 1 was found to exhibit a $K_A$ of 1600 M$^{-1}$ with a lifetime ratio of one, hence a static quenching mechanism was operative. Its acyclic derivative 2 gave a $K_D$ of 35 M$^{-1}$ with no evolution of a charge-transfer absorption band, therefore a purely collisional quenching was observed. For the polymeric receptor 3 it was found that $K_a$ ranged from 75000 to 105000 M$^{-1}$ for polymer molecular weights ranging 31100 to 122500, relative to the receptorless polymer 4 that gave a $K_D$ of 574 M$^{-1}$. These results suggest that amplification of a fluorescence chemosensory event (quenching) occurs via receptors bound in series relative to a discrete molecular event. The utilization of quenching plots and lifetime studies provided a fundamental understanding of the operative quenching mechanisms and an insight into exciton diffusion in phenylene-ethynylene based polymers.
1.3. Photovoltaic Measurements

1.3.1. Photoconduction Theory and Photovoltaic Devices

The demand for inexpensive, renewable energy sources has fostered the development of organic semiconducting materials for photovoltaic devices.\textsuperscript{19} The lower cost and facile processing for large area production is a distinct advantage over inorganic devices.\textsuperscript{14} The flexibility of chemical tailoring allows for the synthesis of organic materials with desired properties via band gap tuning.\textsuperscript{9b} Aside from these benefits, organic solar cells have yet to attain photovoltaic efficiencies reported for Si solar cells.\textsuperscript{14a} There is still a limited understanding and lack of models available for describing charge transport in metal-semiconductor-metal (MSM) or metal-insulator-metal (MIM) polymeric devices relative to the thoroughly studied inorganic semiconductor.\textsuperscript{19,23} The discovery of electroluminescence in organic polymeric devices,\textsuperscript{15} and the field of research developed to understanding its microscopic phenomena,\textsuperscript{16} has further elevated the importance of the field of photovoltaics.\textsuperscript{17}

Photoconductivity is described by the change in conductivity of a material in the dark on the action of light is described as follows:\textsuperscript{18}

\[ \Delta \sigma = e(\Delta \mu_n \Delta n + \Delta \mu_p \Delta p) \quad (16) \]

where $e$ is the charge of the electron, $\Delta n$, $\Delta p$ are the concentration of electron and holes, and $\Delta \mu_n$, $\Delta \mu_p$ are the change in the electron and hole mobilities. The change in electron concentration under the absorbed light is described as follows:

\[ \frac{\partial \Delta n}{\partial t} = \left( \frac{\partial \Delta n}{\partial t} \right)_{\text{gen}} + \left( \frac{\partial \Delta n}{\partial t} \right)_{\text{rec}} \quad (17) \]
where the first term to the right defines the electron carrier generation and the second term defines the recombination rate; the latter is also equivalent to \((1/\tau)\Delta n\), with \(\tau\) as the mean lifetime of the charge carriers.

The photocurrent \(i_{ph}\) can be written as a function of the transit time of the charges between electrodes, \(t_{tr}\), the generation velocity of the charge carriers \(F\), and the gain coefficient \(G\), defined as the ratio of light to dark resistance.\(^{18}\)

\[
i_{ph} = eF \left( \frac{\tau}{t_{tr}} \right) = eFG \quad (18)
\]

The transit time of charge carriers is related to voltage \(V\), distance between electrodes \(L\), and mobility \(\mu\). A relationship between \(i_{ph}\) and \(V\) is obtained by combining Eq. 18 and Eq.19.

\[
t_{tr} = \frac{L}{v_{d}} = \frac{L}{E\mu} = \frac{L}{V\mu} \quad (19)
\]

\[
i_{ph} = e \left( \frac{F\mu t}{L^2} \right)V \quad (20)
\]

Eq. 20 demonstrates that the photocurrent has to be a linear function of the voltage (ohmic behavior), if \(\mu\) and \(\tau\) do not depend on the voltage. This relation works well for an ideal photodiode, however, real photodiodes deviate considerably based on carrier transport mechanisms at the metal-semiconductor junction.\(^{23}\)

A number of photovoltaic device geometries have been reported,\(^{19}\) consisting of either a single-layer conjugated polymer, a mixed donor polymer/acceptor or a heterojunction donor polymer/acceptor, Figure 1.18. In all cases, the active organic layer is sandwiched
between a low work function metal (low electron affinity) and a high work function metal (larger electron affinity).

![Diagram showing device geometries](image)

**Figure 1.18.** Device geometries a) single-layer or mixed single-layer type, b) heterojunction (p-n) type.

The difference in electrode work function creates a potential difference between the electrodes. If the potential difference is large enough to overcome the Coulomb attraction barrier of photogenerated excitons, efficient charge-generation will take place. For single-layer polymer devices, charge carrier generation was found to be rather inefficient, with an incident photon to converted electron efficiency (IPCE) of 1% and a power conversion efficiency of 0.1%.\(^{19}\) The deficiency in charge carrier formation was attributed to facile early time recombination of excitons in a device devoid of a substantial charge-separating electric field. As a result, attempts at enhancing charge carrier separation focused on incorporating an electron-accepting agent with a donor polymer, forming a heterojunction (p-n) type device (Figure 1.18b)\(^ {20}\). The electron-acceptor, typically C\(_{60}\), was found to facilitate electron-transfer from the conjugated polymer. The rectification ratio, ratio of forward bias to reverse bias current, was found to be excellent for the unidirectional geometric nature of the device. The large potential formed upon photoexcitation in this donor-acceptor (D/A) system was not exploited to its fullest because effective charge separation occurred only at the D/A interface. Charge-transport through thick junction layers (relative to nanometer carrier diffusion lengths) added to the inefficiency of this
system as transport can be wrought with numerous non-photocurrent generating pathways.\textsuperscript{24a} The net result was a power conversion efficiency of 1\% and an IPCE of 15\%.\textsuperscript{20}

In order to better exploit the strongly electron-withdrawing nature of $C_{60}$ and its derivatives, bulk heterojunction photodiodes were fabricated based on the geometry of Figure 1.18a.\textsuperscript{21} By creating an interpenetrating phase-separated D/A network, morphological control could be achieved resulting in a large interfacial area in the bulk. Since any point in the network is only a few nanometers from the D/A interface, enhanced carrier collection was expected and observed. Effective carrier generation was achieved with a quantum efficiency of charge separation close to unity and with power conversion efficiencies as high as 3.2\% and IPCE’s of 45\%.\textsuperscript{21}

Bulk heterojunction devices have been extended to donor/acceptor polymer blends exploiting the merit of having both donor and acceptor photoactive in the charge separation process. A hopping charge-transport mechanism is the only mechanism that exists for molecular acceptors, creating an imbalance relative to both hopping and diffusion mechanisms operative for the donor-polymer conjugate. The solution to this problem is the use of a polymer only D/A bulk heterojunction geometry, which would not only dispel this shortcoming, but would also operate to enhance sensitivity of the photodiode by varying the bandgap energies of the donor and acceptor polymers. Since there is almost no entropy of mixing for macromolecules, phase separation is expected in polymer blends, leading to microstructured donor-acceptor junctions. The enhanced performance of these blends is evidenced by reported power conversion efficiencies of 4.8\% and IPCE of 29\%.\textsuperscript{22}
1.3.2. *Interpretation of I-V, C-V, and photocurrent action spectra characteristics*

The simplest and most widely used model to explain the response of organic photovoltaic devices under illumination is a metal-insulator-metal (MIM) tunnel diode with asymmetrical work function metal electrodes, Figure 1.19.\(^9\)

![MIM Band Diagrams](image.png)

**Figure 1.19.** MIM band diagrams for an asymmetric device configuration, with bias defined as relative to ITO: A) reverse bias conditions; B) zero bias, short circuit conditions; C) open circuit, zero current conditions; D) forward bias conditions.
Band diagram A describes the behavior of the conduction band and valence band of a p-type polymer between asymmetric electrodes under reverse bias. Reverse bias is defined as the application of a negative voltage at the ITO electrode and a positive voltage at the metal electrode, Al. In reverse bias, the ITO electrode behaves as an electron-injecting electrode, while Al is the hole-injection electrode. Electrons are injected from ITO in the polymer conduction band (CB) and holes are injected into the polymer valence band. The barrier for injection by ITO is large in reverse bias (the energy between the Fermi energy of ITO and the conduction band), and a similar barrier is experienced by the Al electrode. As the voltage switches to forward bias, the polarity of the electrodes change as do the roles of the electrodes. The Al electrode becomes the electron-injecting electrode, while the ITO electrode is hole-injecting.

The switch to forward bias raises the Fermi energy level of the Al electrode relative to ITO, and under short-circuit conditions ($V_{\text{applied}} = 0$), the slope of the polymer bands decrease, Figure 1.19B. As the applied voltage is increased, it eventually becomes equal to the built-in voltage ($V_{\text{bi}}$) of the device, and this state defines the open-circuit voltage, $V_{\text{oc}}$, Figure 1.19C. At the $V_{\text{oc}}$, no current flows. For MIM type devices, the $V_{\text{bi}}$ is determined by the taking the difference in the work functions of the electrodes. Further application of the forward bias leads to an increase in the Fermi level of Al relative to ITO, Figure 1.19D. In this state, electron injection into the CB by Al, and hole injection by ITO is more energetically favorable than in the reverse bias case. As a result, current rectification is observed in forward bias relative to reverse bias. The MIM model assumes carrier injection occurs via tunneling through electrodes. Tunneling and non-tunneling
mechanisms play an important role in defining IV behavior, and some quantitative relations are described below.

Figure 1.20. Semilog J-V plot of an ideal diode (-----) obeying the Shockley equation for n=1, and non-ideal diode behavior (----) for n>1.

The current density-voltage behavior of a Schottky barrier contact, where injection is dominated by thermionic emission is defined by the Shockley relation: \(^{23a,24}\)

\[
J = J_0 \left[ e^{(qV/kT)} - 1 \right] \quad (21)
\]

where \(V\) is the potential across the junction, \(k\) is Boltzmann's constant, \(q\) is the elementary charge, \(T\) is temperature in Kelvin, \(n\) is the diode quality factor, with \(J_0\) as:

\[
J_0 = \Lambda^* T^2 e^{(\Phi_B / kT)} \quad (22)
\]

where \(\Lambda^*\) is the effective Richardson constant, \(\Phi_B\) is the barrier height. For an ideal diode the quality factor \(n\) equals one, and the J-V characteristics resemble the solid line plot in
in Figure 1.20. A deviation from n=1 is described by a complex curve with regions pertaining to distinct transport processes. In forward bias, the regions consist of a low field generation-recombination in region 1, a diffusion current region in 2, the high injection region, 3, and a series resistance effect in the high field region 4. In reverse bias, junction breakdown occurs at high fields, and at lower fields, a leakage current owing to generation-recombination and surface effects occurs. In non-ideal cases, it is evident that multiple models are necessary to describe the charge transport processes accurately. Once the J-V curve is modeled, valuable information can be extracted providing insight into carrier behavior and possible device efficiency enhancement.

J-V characteristics modeled on the Shockley equation are found to be very sensitive to variable temperature conditions. In the high field injection region, temperature insensitivity has been reported where a tunneling mechanism described by Fowler and Nordheim is operative. In this case the J-V shape follows this relation:25

\[ J = \frac{C}{\Phi_b} \left( \frac{V}{d} \right)^2 e^{-B \Phi_b^{3/2} (V/d)} \]  

(23)

where C and B are constants for the particular device and d is the semiconductor thickness. The charge-transport mechanisms are based on electrode carrier injection in both the Shockley and Fowler-Nordheim relations. In many reports, bulk dominated transport mechanisms such as ohmic and space-charge limited (SCL) conduction are observed.25b,26 In the ohmic case, a linear slope between J-V is found in low field regions:

\[ J = \frac{q n \mu_b V}{d} \]  

(24)
where \( n \) is the carrier density, and \( \mu_p \) is the hole mobility. SCL conduction is observed at higher fields and behaves with \( J \sim V^2 \) as per Eq. 25, giving a slope equal to 2.25b The SCL condition also allows for the direct determination of \( \mu_p \) if the semiconductor dielectric constant \( \varepsilon_s \) and the device thickness \( d \) is known.

\[
J = \frac{9}{8} \varepsilon_s \mu_p \frac{V^2}{d^3} \quad (25)
\]

Aside from charge transport behavior, J-V plots allow for the determination of device performance. The equivalent circuit of a solar cell is depicted as a current generating diode with a series and parallel (shunt) resistance, driving a load, Figure 1.21.27

![Figure 1.21. A solar cell equivalent circuit.](image)

The resistance existing between the solar cell and the load is the series resistor, while the leakage resistance between the positive and negative terminals of the cell is the parallel resistor. A solar cell’s series resistance should be as low as possible, while its shunt resistance should be very high. The fill factor (FF) is defined as the ratio of the peak power to the power calculated by multiplying the open-circuit voltage by the short circuit current and is a reflection of how much series resistance and how little shunt resistance there is in a solar cell circuit.27

\[
FF = \frac{V_m I_m}{V_{oc} I_{sc}} \quad (26)
\]
Figure 1.22. I-V characteristics and the corresponding series $R_s$ and shunt $R_{sh}$ resistance dependence: a) a high FF cell, b) excessive diode saturation current, low FF, c) low shunt resistance, d) high series resistance, e) non-ohmic contact.

A healthy fill factor for a solar cell ranges from 0.6 to 0.8. As a solar cell degrades with age, its series resistance increases, resulting in a lower fill factor. Figure 1.22a represents the square shape of a good cell with high shunt resistance, low series resistance and a good fill factor. The curve of a junction with excessive diode saturation current $I_s$, hence, a poor FF is shown in Figure 1.22b. The $V_{oc}$ is not usually effected under this condition except in extreme cases. A low $R_{sh}$, Figure 1.22c, and high $R_s$, Figure 1.22d, both reduce the FF, with the $V_{oc}$ affected in the former case and the $I_{sc}$ in the latter case under extreme conditions. The effect of a high $R_s$ becomes more pronounced at higher illumination intensities while the effect of a poor shunt is predominant at lower illumination levels. The intensity dependence of the I-V curve provides a means for distinguishing and separating the two resistance terms. A non-ohmic contact manifests itself as curvature near the $V_{oc}$ or $I_{sc}$ point, Figure 1.22e. The $R_{sh}$ value of a device can be obtained from the
inverse of the slope of the I-V curve in the third quadrant, and the $R_s$ can be determined from the linear portion of the I-V curve in the first quadrant, Figure 1.23.  

Figure 1.23. I-V curve depicting linear regions in quadrant I for the determination of $R_s$, and quadrant III for $R_{sh}$.

Once the fill factor has been determined and optimized, the power conversion efficiency $\eta_c$ of the solar cell can be calculated if the incident light power, $P_{in}$ (W/cm$^2$) is known.  

$$\eta_c(\%) = \frac{V_{oc} I_{sc} \text{FF}}{P_{in}} \times 100 \quad (27)$$

The spectrally resolved efficiency $\eta_\lambda$, relating the incident photon to converted electron (IPCE) is given by Eq. 28, where I is the light intensity in W/m$^2$ at wavelength $\lambda$.  

$$\eta_\lambda(\%) = \frac{1240 I_{sc}}{\lambda I} \times 100 \quad (28)$$
Figure 1.24. J-V characteristics for a photovoltaic in the dark (----) and illuminated (——).

Irradiation of a photovoltaic device leads to an increase in the $I_{sc}$ and an increase in $V_{oc}$ relative to the dark I-V characteristic, Figure 1.24. The large reverse bias photocurrent is most likely due to the collection of holes at the irradiated ITO electrode that are accelerated by the increased barrier height $q(V_{bi} - V_{R})$. The conclusion is that the hole carrier is most responsible for generating photocurrent and the potential that is created upon charge separation leads to a shift in $V_{oc}$ of about 0.3V.

Capacitance-voltage measurements allow for a determination of the depletion region width. From the relation:

$$C = \frac{S_{E_a}}{x_d} \quad (29)$$
the depletion width can be calculated if the semiconductor dielectric constant $\varepsilon_s$, and the area of the Schottky barrier contact S are known.\textsuperscript{23a}

$$C_v = \left( \frac{q \varepsilon_s N_D}{2 (V_{bi} - V)} \right)^{1/2} \quad (30)$$

A plot of $1/C^2$ against applied bias gives a slope that is equal the dopant concentration $N_D$ (Eq. 31).

$$N_D(x) = -\frac{2}{q \varepsilon_s} \frac{1}{d(1/C^2)/dV} \quad (31)$$

The capacitance-voltage plot can be used to derive the charge density $\rho(x)$ vs distance from the junction x, profile as in Figure 1.25.\textsuperscript{23a} The built-in potential $V_{bi}$ can be determined from the intercept with the abscissa.

![Graphs showing various possible space-charge profiles and the corresponding $C^2$ vs. V characteristics.](image)

**Figure 1.27.** Various possible space-charge profiles and the corresponding $C^2$ vs. V characteristics.

The relationship between the photocurrent and absorption spectra for organic semiconductors can be classified in one of two possible categories. If a good correlation exists between the photocurrent action spectra and the absorption spectra such that a
maximum photocurrent is obtained for the most strongly absorbed light, then the photocurrent is said to be symbatic with the absorption spectrum. If instead the maxima of the photocurrent action spectrum occurs for photon energies where the absorption is weakest, then the photocurrent response is said to be antibatic. Antibatic behavior is thought to arise from the reduced penetration depth for higher energy wavelengths such that absorption produces a high density of charge carriers or excitons within a narrow penetration depth. The carriers or excitons undergo more rapid recombination, resulting in a reduced photocurrent yield. For thick films based on poly(phenylenevinylene), antibatic behavior occurs when the ITO interface is irradiated at reverse bias, or when the metal electrode is irradiated in forward bias. When the device is biased such that hole current can only be produced from excitons which dissociate at the far electrode, self-absorption by the intervening polymer film gives rise to an internal filter effect. The antibatic response is less pronounced for thinner films as a result of reduced self-absorption.
1.4. References


Chapter 2

Synthesis and Binding Constant Determination for Cyclophane Monomers
2.1. Introduction

The ability of molecular entities to organize into large supramolecular architectures via additive, weak, non-covalent interactions, attests to the power and elegance with which biological systems have utilized toward self-assembly and self-replication.\(^1\) The science of supramolecular chemistry, directed toward the understanding of the role of the non-covalent bond, has attracted a frenzy of research activity since the awarding of the Nobel Prize in 1987 to Pederson, Cram, and Lehn.\(^2\) Crown-ether based receptors have found their niche in this field ranging from highly selective metal-ion sensors to logic based molecular circuits.\(^3\) Of particular interest is the work of Stoddart, who found that crown ether 9 is a receptor for the herbicide paraquat (PQ\(^{2+}\)), Figure 2.1.\(^4\)

![Figure 2.1. Binding of paraquat, within the cavity of crown-ether 9.](image)

From X-ray, NMR, and UV spectrophotometric titration data, Stoddart's group found that PQ\(^{2+}\) is bound within the crown ether cavity with an association constant of 730 M\(^{-1}\) (\(\Delta G = -3.9 \text{ kcal/mol}\)) measured in acetone. The major contributors to the favorable binding constant were: electrostatic interactions between the electron-rich hydroquinol groups on the crown ether and the electron-poor pyridiniums, a charge-transfer interaction giving rise to an absorption band at \(\lambda_{CT}\) at 435nm, and hydrogen bonding between the third oxygen of 9 and the methyl protons of paraquat. That basic understanding of the binding process obtained via spectrophotometric titrations allows for the optimization of host-guest complimentarity and the elimination of extraneous
functionality on the receptor. The development of complex architectures of the catenane and rotaxane genre are examples of extending the utility of self-assembly toward higher order targets. In this chapter, the binding affinity of various pherylene-ethynylene and phenylene-thiophene based crown ethers is examined via fluorescence quenching titrations with paraquat. The most efficacious receptors in binding paraquat, as determined from this study, are then utilized toward the synthesis of electropolymerizable catenane and rotaxane architectures as reported in future chapters.

2.2. Results and Discussion

2.2.1 Cyclopane Synthesis

The synthesis of crown ether receptors is founded upon functionalizing the hydroquinol periphery of 9 with ethynylene and thiophene moieties as they are useful precursors in the synthesis of poly(phenylene-ethynylene)'s and poly(phenylene-thiophene)'s. The facility with which Migita-Kosugi-Stille and Hagihara-Sonogashira couplings afford these precursors, requires that the base cyclophanes have either iodo or bromo substituents. Initial efforts were focused upon the synthesis of a pentaethylene glycol derivative that has a cavity size exceeding 9, Scheme 2.1. It was rationalized that in order to realize an effective rotaxane architecture, a larger than 9 crown ether would be required. The synthesis of 2 can be obtained via a one-pot process or through the syringe-pump technique. The diiodohydroquinone 1 is doubly alkylated with pentaethylene glycol bistosylate followed by intramolecular cyclization affording 2. The role of Cs$^{2+}$ has been postulated to aid in templating the formation of the crown ether, hence Cs$_2$CO$_3$ has been utilized as the base. Irrespective of approach, the yield for 2 never exceeded 10% for the
four alkylation steps, which is most likely due to the greater entropy of formation for the larger crown ether.

Scheme 2.1. Synthesis of pentaethylene glycol derivative crown ether 2.

The synthesis of iodo-hydroquinone tetraethylene glycol derived crown ethers 4a and 4b was undertaken, Scheme 2.2. The one-pot alkylation of 3 leads to the formation of constitutional isomers in poor yields with no preference for formation. The isomers are inseparable via chromatographic techniques and derivatives were not synthesized. The role of crown ethers 4a and 4b in future projects was deemed limited, if ever useful.

Scheme 2.2. Mono-iodo periphery tetraethylene glycol derived crown ethers isomers 4a and 4b.

Aside from functionalizing both hydroquinol units with halides, functionalization of only one unit affords precursors that are amenable to catenane formation, Scheme 2.3.
Scheme 2.3. Synthesis of tetaethylene glycol derivative crown ethers 6, 8, and 9.

The synthesis of diiodo crown ether 6 occurs via alkylation of 1 with bistosylate 5 in a 48% yield. This is a marked improvement over previous efforts that afforded 6 in a 15% yield.\textsuperscript{8b} The cyclization gives the greatest yield of 6 when the reactant concentrations are between 7-8 mM. If the concentration is too high, the formation of a polymer is observed. The use of fresh bottles of acetone and degassing the reaction solution with argon before heating also contribute to the enhanced yield. The iodo-bromo derivative 8 was conceived to be an excellent building block due to the selectivity of organometallic coupling reactions toward iodo groups relative to bromo. Under the same conditions for the formation of 6, the 45% yield of 8 is comparable. As a reference, Stoddart’s crown
ether, 9, was synthesized in 59% yield, which was an improvement over his literature yield of 47%.

Tetraiodo substituted triethylene glycol based crown ether 11, and tetaethylene glycol analog 13 have been synthesized by co-worker Dr. D.K. Fu, Scheme 2.4, and derivatives have been synthesized and characterized by the author of this thesis. A discussion of the synthesis of 11 and 13 has been included for the purpose of completeness.

![Chemical structures and reactions](image)

**Scheme 2.4.** Crown ethers 11 and 13 synthesized by Dr. D.K. Fu.

The synthesis of crown ethers 11 and 13 proceed from the alkylation of the bistosylate derivatives 10 and 12 with 1 in 30% yields. The restricted geometry of the triethylene glycol derivative 11 makes it an interesting target, allowing for the better understanding of cavity-size limitations toward binding. The synthesis of derivatives of 13 allow for the study of the effect on binding with both hydroquinol units functionalized.
2.2.2. Functionalization of crown ethers

The substitution of thiophene groups to crown ether 2 via a Stille cross-coupling with an excess of commercial tributylstannythiophene yields 14 in excellent yield, Scheme 2.5. The crystal structure depicts the large size of the cavity, and is the largest cavity crown ether studied herein. Upon treating a concentrated solution of 14 with paraquat a purple color ensues, indicating the formation of a charge-transfer band. All functionalized crown ethers studied in this chapter have had this observed behavior; the only variation being the color of the charge-transfer band. The net result is the quenching of the crown ether fluorescence when large concentrations of paraquat are added.

Scheme 2.5. Functionalization of 2 with thiophene moieties; the crystal structure represents 30% ellipsoids.

The synthesis of bis-functionalized crown ethers of the tetraethylene glycol variety is depicted in Scheme 2.6. The synthesis of thiophene functionalized crown ethers 15, 17, 21, and 23 are all achieved utilizing a Pd(II) catalyst, an excess of tin reagent, and air free conditions. The extent of the reaction was found to be strictly dependent on the exclusion of air. The reaction yields tend from 80% upwards, the only issue being the removal of tin byproducts in the workup. Tin reagents 16, 20, 22 have been synthesized according to modified literature procedures. The functionalization of 6 with acetylenic
Scheme 2.6. Bis-functionalized tetraethylene glycol based crown ethers.

groups is achieved via a Hagihara-Sonogashira cross-coupling utilizing diisopropylamine (DIPA) as a base, an excess of trimethylsilylacetylene, CuI as a deprotonation catalyst, and Pd(II) as the active catalyst. The yield for the conversion of 6 to 18 was rather low most likely indicative of poor degassing or loss during recrystallization. The reaction was run only once, yielding over a gram of product; enough for thorough characterization and study. The removal of the trimethylsilyl groups affords a chemically polymerizable terminal acetylene crown ether, and allows for the understanding of the steric influence on binding by large groups on the crown ether. The conversion of 18 to 19 occurs in excellent yields, and can also be achieved using NaOH as the base.
Scheme 2.7. The synthesis of crown ethers 25 and 26.

The determination of the binding constant of a molecule containing multiple crown ether groups allows for the understanding of whether a cooperative or non-cooperative interaction exists. Toward this purpose, crown ethers 25 and 26 were synthesized, Scheme 2.7. The coupling of 6 with a slight excess of acetylide 24 gave crown ether 25 and 26 in 25% and 31% yields respectively. The low yields are attributed to the statistical nature of the coupling and the loss of 24 to diacetylide formation. The yield of the monocoupling can be improved to 70% if the iodo-bromo crown ether 8 and Pd(0) are used, Scheme 2.8.
Scheme 2.8. Improved synthesis of monocoupled product 27.

The synthesis of crown ether 29 was achieved in 20% yield by coupling two equivalents of 26 to one of diacetylide 28 in the presence of a Pd(0) source, Scheme 2.9. Under similar conditions (at 100°C), the bromo derivative 27 gave trace amounts of crown ether 29 (<<1%). The low yields in both reactions might be attributed to the less active nature of 27 toward coupling and the steric constraints in the final coupling step to form 29.

Scheme 2.9. Synthesis of the double crown ether 29.
Scheme 2.10. Acetylide functionalization of crown ether 13.

The functionalization of tetraiodo crown ether 13 with acetylide groups follows the synthesis mentioned previously for the diiodo crown ether 6, Scheme 2.10. The desilylation of 30 yields an insoluble white fluorescent solid purported to be compound 31. The poor solubility of 31 (soluble in hot sulfolane) did not allow for spectrophotometric titration. Compound 13 and its triethylene glycol counterpart 11 can undergo coupling reactions with tributylstannylthiophene to form derivatives 32 and 33, Scheme 2.11. These compounds, synthesized by Dr. D.K. Fu, were recrystallized, characterized, and binding studies were performed by the author.
Scheme 2.11. Synthesis of crown ethers 32 and 33 undertaken by Dr. D.K. Fu.

Other quenching agents besides PQ\textsuperscript{2+} are also of interest for use in the formation of rotaxanes. Compound 34 encorporates the electron-deficient nature of PQ\textsuperscript{2+} and reactive hydroxy end-groups. 34 can be utilized toward the formation of electron-deficient polymers via poly-condensation chemistry as shown in Chapter 4. Crystallization of 1:1 complexes of the chiral PQ\textsuperscript{2+} derivative 35 and crown ether receptors were attempted in order to induce electronic unidirectionality in crystals. Attempts at obtaining X-ray quality crystals for analysis were not successful. The molecular analog to head to tail poly(pyridinium vinylene) (PPyV) was synthesized in order to determine whether the crown ethers synthesized had an affinity for the PPyV repeat unit.

The spectrophotometric titration of electron-deficient analyte 36 was limited due to its large absorptive overlap with the crown ether receptors and its highly emissive nature. Mixing large concentrations of 36 and 23 did not lead to the formation of the prerequisite charge-transfer band for complexation.
2.2.3. Binding Constant Determination

The affinities of the various crown ether receptors synthesized for PQ\(^{2+}\) were measured by utilizing the Stern-Volmer relationship described in Chapter 1. A solution of optically dilute fluorescent crown ether is titrated with quencher PQ\(^{2+}\) and the decrease in fluorescence intensity as a function of quencher concentration is monitored. If the assumption is made that quenching occurs predominantly via a static process (binding within the cavity), then a Stern-Volmer plot of the ratio of \(F_0/F\) vs. quencher concentration \([Q]\) should be linear. Stoddart's analysis of 9 confirms that binding occurs within the cavity of the crown ether,\(^4\) and the results of Swager and Zhou\(^{3c}\) attest to the virtual non-existence of competitive collisional quenching in acyclic analogs.

The studies undertaken herein were performed exclusively in CH\(_3\)CN, taking advantage of the solvent's short-wavelength absorption (190nm) and low volatility. The solutions were ideally dilute (10\(^{-6}\) M) with absorption maxima at 0.2 units or less, titrations were performed 2 to 3 times in each study. The binding constant for cyclophane 9 was measured using UV titration, and the growth of the charge-transfer band was monitored with increased PQ\(^{2+}\) concentration. For all other binding measurements fluorescence titrations were implemented. The absorption-emission spectra and Stern-Volmer plots have been summarized in Figure 2.2 and Table 2.1.
Figure 2.2. Fluorescence quenching titrations and Stern-Volmer plots for the cyclophane receptors.

In CH$_3$CN, the binding constant for 9 was measured to be 400 M$^{-1}$, 1.8 times weaker than that measured via UV titration by Stoddart in acetone, 730 M$^{-1}$.$^4$ The discrepancy is attributed to the greater polarity of CH$_3$CN leading to a larger solvation energy for the analyte and receptor, hence a diminished binding affinity. A similar trend is observed for cyclophane 25 where fluorescence titration in acetone revealed a binding constant of 1600 M$^{-1}$ in acetone and 466 ± 2 M$^{-1}$ for CH$_3$CN. Extending the π-conjugation on the receptor periphery of 9 with thiophene groups leads to a remarkable 24-fold increase in the binding constant for 33 of 9665 ± 179 M$^{-1}$. The increased affinity for the analyte is indicative of the importance of extended π-conjugation in driving the binding process, coupled with the electron-donating nature of the thiophene groups.

A decrease or increase in cavity size relative to 33 leads to diminished binding affinities, affirming the greatest complimentarity of PQ$^{2+}$ for 33. By increasing the cavity size by two ethylene glycol groups as in 14, the binding constant decreases 25-fold relative to 33 to 386 ± 5 M$^{-1}$. The unfavorable increase in entropy for binding in 14 is attributed to this diminution. If the cavity size decreases by two ethylene glycol groups,
then static and collisional quenching mechanisms compete, as seen for cyclophane 32. The Stern-Volmer plot for 32 displays the typical curvature toward the y-axis for multiply competing mechanisms. The magnitude of the quenching and binding constants cannot be inferred from this plot, and further study toward quantifying the constants was not pursued.
<table>
<thead>
<tr>
<th>Crown Ether</th>
<th>$\lambda_{\text{ex}}$ (nm)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
<th>$K_A$ (M$^{-1}$)</th>
<th>$-\Delta G$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>$\lambda_{\text{CT}} = 420$</td>
<td>--------</td>
<td>400 M$^{-1}$ (730 M$^{-1}$)</td>
<td>3.55 (3.9)</td>
</tr>
<tr>
<td>14</td>
<td>365</td>
<td>396, 414</td>
<td>386 ± 5 M$^{-1}$</td>
<td>3.529 ± 0.008</td>
</tr>
<tr>
<td>15</td>
<td>360</td>
<td>392, 412</td>
<td>1160 ± 7 M$^{-1}$</td>
<td>4.181 ± 0.004</td>
</tr>
<tr>
<td>17</td>
<td>411</td>
<td>459, 487</td>
<td>626 ± 3 M$^{-1}$</td>
<td>3.815 ± 0.003</td>
</tr>
<tr>
<td>18</td>
<td>360</td>
<td>375</td>
<td>166 ± 6 M$^{-1}$</td>
<td>3.029 ± 0.02</td>
</tr>
<tr>
<td>19</td>
<td>346</td>
<td>367</td>
<td>320 ± 6 M$^{-1}$</td>
<td>3.418 ± 0.011</td>
</tr>
<tr>
<td>21</td>
<td>385</td>
<td>451</td>
<td>357 ± 6 M$^{-1}$</td>
<td>3.483 ± 0.01</td>
</tr>
<tr>
<td>23</td>
<td>365</td>
<td>392, 412</td>
<td>2912 ± 28 M$^{-1}$</td>
<td>4.726 ± 0.006</td>
</tr>
<tr>
<td>25</td>
<td>369</td>
<td>394, 414, 435sh</td>
<td>466 ± 2 M$^{-1}$ (1600 M$^{-1}$)</td>
<td>3.64 ± 0.003 (4.4)</td>
</tr>
<tr>
<td>29</td>
<td>390</td>
<td>434</td>
<td>567 ± 23 M$^{-1}$</td>
<td>3.757 ± 0.025</td>
</tr>
<tr>
<td>30</td>
<td>350</td>
<td>395</td>
<td>158 ± 4 M$^{-1}$</td>
<td>3.0 ± 0.015</td>
</tr>
<tr>
<td>32</td>
<td>365</td>
<td>400sh, 415</td>
<td>Non-linear</td>
<td>--------</td>
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<tr>
<td>33</td>
<td>365</td>
<td>400sh, 414</td>
<td>9665 ± 179 M$^{-1}$</td>
<td>5.437 ± 0.011</td>
</tr>
</tbody>
</table>

Table 2.1. Spectrophotometric titration data for the cyclophane receptors.
Extended conjugation with ethynyl groups has also been studied in an effort to understand the extent of π-stabilization imparted by acetylenic functionality. Cyclophanes 30 and 31 were synthesized with this purpose in mind. The tetra-substituted trimethylsilyl ethynyl crown ether 30 displayed a weak affinity for the analyte with a $K_{\text{sv}}$ of $158 \pm 4 \text{ M}^{-1}$. It can be inferred that the steric demand of the trimethylsilyl groups imposes the cost of decreased binding relative to a desilylated analog. The binding affinity of 30 is essentially identical to that for 18, indicating that the steric demand of only two trimethylsilyl groups is necessary to decrease binding. The limited π-doniong on the part of the ethynyl substituted crown ether is evident in comparison with the thiophene derivative 33. Furthermore, the smaller extension of conjugation with ethynyl groups may not be sufficient to afford the complimentarity achieved with 33, leading to the observed 61-fold decrease in binding for 30.

Crown ether receptors were also functionalized on only one hydroquinol unit affording derivatives 15 through 29. The thiophene derivative 15 displays a binding constant of $1160 \pm 7 \text{ M}^{-1}$, 8-fold less than the tetrasubstituted 33. It is therefore evident that extended conjugation on both hydroquinol units in the crown ether is critical in order to maximize the binding affinity of the receptor. If bithiophene aromatics are substituted for thiophene 17, the binding constant ($626 \pm 3 \text{ M}^{-1}$) is effectively halved. A limit is attained in 17, where further extension of conjugation relative to 15 competes sterically with the binding process. On substitution with head to head hexylbithiophene units as in 21, the binding constant is halved further to $357 \pm 6 \text{ M}^{-1}$. If the electron-donating nature of the thiophene group is increased as in cyclophane 23, the $K_{\text{sv}}$ increases 2.5-fold to $2912 \pm 28 \text{ M}^{-1}$. It can be inferred that the degree and nature of π-extension is extremely important for binding; without extended conjugation the crown ether's penchant for binding diminishes, with
over-extension steric factors playing a pivotal role. The oxidation potentials of receptors 15, 17, and 23 (0.8V, 0.6V, 0.35V vs. Fc/Fc\(^+\)) affirms the effect of the electron-donating nature of the thiophene substituents, but does not parallel the respective binding affinities of each receptor. It is therefore evident that highly electron-donating substituents may enhance binding, but has only a minor effect in enhancing the degree of complimentarity between host and guest.

The trimethylsilyl ethynyl derivative 18 displays a binding constant of 166 ± 6 M\(^{-1}\), almost identical to the 158 ± 4 M\(^{-1}\) observed for 30. It can be concluded that inhibition toward binding is fully affected by incorporating hindering groups on one aromatic periphery. Upon removal of the trimethylsilyl group, the binding constant doubles to 320 ± 6 M\(^{-1}\) for 19. From these findings, it would be expected that the binding constant for 31 would be greater than that for 19 due to extended conjugation on both hydroquinol units for 31.

The role of electron-donating phenoxyethynyl groups toward binding was also studied. The binding ability of cyclophane 25 was found to increase 1.5-fold relative to the phenoxy-less 19. The marginal binding increase may be a combination of electron-donation countered with steric hinderance. If two crown ether receptors are incorporated into one molecule as in 29, the binding constant is found to maintain a 1:1 relationship as observed via a linear Stern-Volmer plot. Furthermore, the measured binding constant of 567 ± 23 M\(^{-1}\) is only a 1.2-fold increase over that measured for 25. The increase is mostly likely a function of the increased electron-rich nature of 29 over 25, however, the exact nature of the binding process is not clear (i.e. cooperativity between crown ether units). The analyte could bind in one of the two crown ethers, or in an intermediate complex between both crown ethers.
2.3. Conclusion

Cyclophane receptors that incorporate functionality on both hydroquinol rings have been found to exhibit larger binding constants than when functionality is solely on one ring. The extended \( \pi \)-conjugation afforded by thiophene aromatics has the proper spacial orientation for effective \( \pi \)-stacking relative to ethynyl analogs. Within the thiophene-derivitized crown ether genre, increases in cavity size lead to decreased binding due to increased entropy, and smaller cavity sizes lead to competition between static and dynamic quenching processes. Ethynyl-based crown ethers exhibit improved binding when sterically encumbering groups such as trimethylsilyl are removed, and are good candidates for the synthesis of poly(phenylene-ethynylene)'s. When incorporating two crown ether receptors in one molecule, a small increase in binding is observed, which follows a 1:1 binding behavior. Increasing the electron richness of the aromatic scaffold on the receptor leads to modest increases in the binding ability of the crown ether. Overall, thiophene based crown ethers were observed to better compliment the size of the analyte relative to ethynyl derivatives.
2.4. Experimental

General Methods. Air- and moisture-sensitive reactions were carried out in oven-dried glassware using standard Schlenk line techniques under an inert atmosphere of dry argon. All chemicals used were of reagent grade or better and were purchased from Aldrich unless otherwise noted. Anhydrous DMF was used directly from Aldrich Sure-Seal bottles. Anhydrous CH$_3$CN was prepared by a literature procedure involving activated alumina and CaH$_2$. Anhydrous toluene was obtained from a solvent purification system utilizing drying columns under an inert atmosphere of argon. (3,4-ethylenedioxy)thiophene was obtained from Bayer and used as is. Trimethylsilylacetylene was obtained from GFS chemicals and was used as is. Diethynylbenzene (28), 1,4-diiodo-2,5-dihydroxybenzene (1), 1-iodo-4-bromo-2,5-dihydroxybenzene (7), 7,10,13,16,19,26,29,32,35,38-decaoxa[13.13]paracyclophane (9), 2-tributylstannyl-bithiophene (16), and (2-tributylstannyl-3,4-ethylenedioxy)thiophene (22), were prepared according to literature procedures. [1-Tributylstannyl-5-(9-hexyl)-thiophene]-3-hexylbithiophene (20), 1-dodecyloxy-4-ethynylbenzene (24), 1,4,21,24-tetraiodo-7,10,13,16,19,26,29,32,35,38-decaoxa[13.13]paracyclophane (13), 1,4,18,21-tetrathiophenyl-7,10,13,16,26,29,32-octaoxa[10.10]paracyclophane (32), 1,4,21,24-tetrathiophenyl-7,10,13,16,19,26,29,32,35,38-decaoxa[13.13]paracyclophane (33), were obtained from co-workers and were used as is. $^1$H NMR and $^{13}$C NMR spectra were acquired with a Varian INOVA 500 spectrometer at 500 MHz (125.66 MHz $^{13}$C) and a Bruker Mercury 300 MHz spectrometer, and were taken in CDCl$_3$, and CD$_3$CN with $^1$H chemical shifts reported relative to internal tetramethylsilane (0.00 ppm) and $^{13}$C chemical shifts reported relative to CDCl$_3$ (77.23 ppm) and CD$_3$CN (1.39 ppm). Thin-layer chromatography (TLC) was performed on cut glass slides (2.5 x 5 cm) coated with Merck 5715 Kieselgel
Developed plates were air-dried, scrutinized under a UV lamp and, if necessary, developed in an iodine tank. Baker 7024 (40μm mesh) silica gel was used to perform flash column chromatography. Fast atom bombardment mass spectroscopy (FABMS), using a xenon primary atom beam in conjunction with a 3-nitrobenzyl alcohol matrix was performed on a Finnigan MAT 8200.


To a 500ml round bottom flask with magnetic stirring was added Cs₂CO₃ (27.02g, 83 mmol, 3 equiv.) and 250ml of acetone. 1 (10.02g, 28 mmol) and pentaethylene glycol bistosylate (15.31g, 28 mmol) were dissolved in a 100ml solution consisting of 15ml DMF and 85ml acetone. This solution was added to the Cs₂CO₃ mixture via dropping funnel while refluxing over several days. After 4 days addition was completed and the solution was allowed to reflux for another four. TLC of the reaction mixture after this period (1:4 EtOAc/CH₂Cl₂) indicated complete consumption of the starting materials. The reaction solution was then rotary evaporated yielding an orange-brown solid. Methylene chloride was then added to this solid and the slurry was acidified with an aqueous solution of HCl. Upon acidification the aqueous phase was extracted with methylene chloride (3x60ml). All organic layers were combined, dried with MgSO₄, filtered, and the resulting solution was rotary evaporated. The resulting oil was subjected to high vacuum in order to remove residual DMF. The resulting solid was dry loaded onto silica gel and chromatography was initiated with 15:85 EtOAc/CH₂Cl₂ and slowly graded 20:80, 25:75, 35:65, 1:1 until the most polar third spot was eluted and isolated as a white solid (1.5506g, 1.37 mmol, 10% yield): FABMS 1262 (M–Cs)⁺, 1152 (M+Na)⁺; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.21 (s, 4H), 4.07-4.09 (m, 8H), 3.85-3.88 (m, 8H),
3.76-3.78 (m, 8H), 3.68-3.75 (m, 16H); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ (ppm) 69.9, 70.5, 71.0, 71.1, 71.5, 86.7, 123.5, 153.2

1,21-Diiodo-7,10,13,16,19,26,29,32,35,38-decaoxa[13.13]paracyclophane isomers (4a-4b). To a 500ml Schlenk flask equipped with a condenser and magnetic stirring was added 200ml of acetone and Cs$_2$CO$_3$ (13.93g, 42.6 mmol, 3 equiv.). To this mixture was added via syringe pump at 1.67ml/hr (for a 60ml syringe setting) a solution of iodohydroquinone (3) (3.35g, 14.2 mmol) and tetraethylene glycol bistosylate (7.14g, 14.2 mmol) in 40ml of acetone. The syringe contents were slowly added (one 50ml syringe) over two days in refluxing solution and after complete addition was allowed to reflux for another two days. The reaction was then cooled to room temperature and the reaction solution was filtered and washed with methylene chloride. The organic phase was washed with saturated NaCl solution, and was rotary evaporated. The crude product consisted of three compounds upon TLC eluted sequentially with 1:9 EtOAc/CH$_2$Cl$_2$, 1:1 EtOAc/CH$_2$Cl$_2$, 9:1 CH$_2$Cl$_2$/MeOH via silica gel chromatography. The most polar third spot determined to be the product was isolated as a gummy solid and recrystallized from a methylene chloride/petroleum ether solution yielding a white solid (250mg, 0.32 mmol, 2.5% yield): FABMS 921 (M+Cs)$^+$, 811 (M+Na)$^+$, 788 (M$^+$); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ (ppm) 7.29-7.30 (d, 2H, $J = 3$ Hz), 6.74-6.78 (m, 2H), 6.66-6.69 (d, 2H, $J = 8.7$ Hz), 4.01-4.04 (m, 4H), 3.96-4.01 (m, 4H), 3.86-3.89 (m, 4H), 3.76-3.83 (m, 8H), 3.70-3.71 (m, 12H); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ (ppm) 68.5, 68.5, 69.8, 69.8, 70.2, 70.9, 71.0, 71.0, 71.0, 71.1, 71.2, 87.2, 113.8, 113.8, 115.7, 115.8, 125.7, 125.7, 152.4, 152.4, 153.8, 153.9

1,4-Bis[2-(2-(2-toluenesulfonyloxy) ethoxy) ethoxy] ethoxy)-benzene (5). A 1 L round-bottomed flask equipped with a stir bar and a condenser was charged with hydroquinone (2.97g, 27 mmol, 1 equiv), tetra(ethylene glycol)di-p-tosylate (53.78g, 107
mmol, 4 equiv), anhydrous K$_2$CO$_3$ (37.1 g, 268 mmol, 10 equiv) and acetone (400 mL). The flask was then capped with a septum and argon was bubbled through the solution for 30 min. with stirring. The golden-yellow solution was then heated to reflux under a gentle stream of argon for 6 days. The reaction mixture was then cooled to room temperature, rotary evaporated, and the residue washed with 3.2 M HCl (3 x 200 mL). The gummy insoluble residue was then extracted from the aqueous phase with EtOAc (4 x 200 mL). The organic phase was separated, dried with MgSO$_4$ and concentrated in vacuo. The resulting viscous oil was then dissolved in acetone, dry-loaded onto silica gel, and subjected to flash column chromatography [SiO$_2$: EtOAc-hexanes-EtOH (30:20:1)]. The fractions containing the product (as monitored by TLC) were concentrated under vacuum yielding the title compound as a yellow oil (7.18 g, 35%): FABMS 770 (M$^+$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$(ppm) 7.76-7.77 (d, 4H, $J = 8$ Hz), 7.31-7.33 (d, 4H, $J = 8$ Hz), 6.82 (s, 4H), 4.12-4.13 (t, 4H, $J = 5$), 4.03-4.05 (t, 4H, $J = 5$), 3.78-3.80 (t, 4H, $J = 5$), 3.55-3.67 (m, 20H), 2.40 (s, 6H); $^{13}$C NMR (500 MHz, CDCl$_3$) $\delta$(ppm) 21.3, 67.7, 68.3, 69.1, 69.5, 70.2, 70.3, 70.4, 115.2, 127.6, 129.6, 132.6, 144.6, 152.8

1,4-Diiodo-7,10,13,16,19,26,29,32,35,38-decaoxa[13.13]paracyclophane (6). A 3 L round-bottomed flask equipped with a stir bar and a condenser was charged with 1,4-diiodo-2,5-dihydroxybenzene (1) (3.37 g, 9.3 mmol, 1 equiv), 5 (7.18 g, 9.3 mmol, 1 equiv), Cs$_2$CO$_3$ (33.37 g, 102 mmol, 11 equiv), and acetone (1.2 L). The flask was then capped with a septum and argon was bubbled through the solution for 30 min. with stirring. The golden-yellow solution was heated under reflux under a gentle stream of argon for 7 days. The reaction mixture was then cooled to room temperature, rotary evaporated, and the residue washed with 3.2 M HCl (3 x 200 mL). The gummy insoluble residue was then extracted from the aqueous phase with EtOAc (4 x 200 mL). The organic phase was separated, dried with MgSO$_4$ and concentrated in vacuo. The resulting
brown solid was dissolved in CH₂Cl₂, dry-loaded onto silica gel, and subjected to flash column chromatography [SiO₂: EtOAc/hexanes/EtOH (30:20:1)]. The fractions containing the product (as monitored by TLC) were concentrated under vacuum yielding a white crystalline solid (3.5g, 48%, mp 107.5-108°C): FABMS 788 (M)+; ¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.18 (s, 2H), 6.74 (s, 4H), 4.02-4.04 (t, 4H, J = 9.5 Hz), 3.98-4.00 (t, 4H, J = 9.5 Hz), 3.87-3.98 (t, 4H, J = 9.5 Hz), 3.82-3.83 (t, 4H, J = 9.5 Hz), 3.70-3.78 (m, 16H); ¹³C NMR (500 MHz, CDCl₃) δ (ppm) 68.4, 69.8, 70.0, 70.5, 71.0, 71.1, 71.2, 71.3, 86.6, 115.7, 123.5, 153.2, 153.3

1-Iodo-4-bromo-7,10,13,16,19,26,29,32,35,38-decaoxa[13.13]paracyclophe (8). To a 3 liter flask equipped with condenser and magnetic stirrer was added 5 (9.15g, 11.9 mmol), Cs₂CO₃ (42.5g, 130 mmol, 14 equiv.), and 1.46 liters of acetone. The reaction mixture was stirred for 15 minutes with a purge of argon through the solution. 1-iodo-4-bromohydroquinone (7) (2.97g, 9.43 mmol) was then added in a solution of 100ml of acetone. The reaction was heated to reflux for 10 days. After this period the reaction was allowed to cool and was rotary evaporated. The solid residue was then acidified with concentrated HCl. The aqueous phase was then extracted with methylene chloride (4x150ml), and the organic phases were dried with MgSO₄, filtered and rotary evaporated. The resulting solid was recrystallized from EtOAc yielding a white solid (3.14g, 4.25 mmol, 45% yield): FABMS 763 (M+Na)+; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.27-7.28 (d, 1H, J = 2.1 Hz), 6.97-6.98 (d, 1H, J = 2.1 Hz), 3.98-4.04 (m, 8H), 3.70-3.88 (m, 24H); ¹³C NMR (300 MHz, CDCl₃) δ (ppm) 68.4, 69.7, 70.0, 70.5, 71.0, 71.1, 71.1, 71.2, 71.3, 71.3, 85.1, 112.9, 115.7, 117.7, 124.9, 150.7, 153.0, 153.2

7,10,13,16,19,26,29,32,35,38-Decaoxa[13.13]paracyclophe (9). To a three-necked 3 liter flask with magnetic stirring was added 5 (5.27g, 6.84 mmol), hydroquinone
(0.7535g, 6.84 mmol) in 900ml of acetone. The reaction solution was purged with argon for 30 minutes after which Cs₂CO₃ (24.53g, 75.3 mmol, 11 equiv.) was added. The solution was heated to reflux with stirring for 7 days. After this period the solution was rotary evaporated and the crude solid was acidified with 2M HCl. The aqueous solution was then extracted with CH₂Cl₂ (3x200ml). The organic fractions were collected, dried with MgSO₄ and rotary evaporated. The resulting viscous oil was subjected to high vacuum and chromatography (68:30:2 Et₂O/CHCl₃/MeOH) yielded a white solid. Upon recrystallization from ethyl acetate a white solid was isolated (0.6124g, 1.25 mmol, 59% yield): FABMS 559 (M+Na)⁺; ¹H NMR (300 MHz, (CD₃)₂CO) δ (ppm) 6.79 (s, 8H), 3.97-4.0 (m, 8H), 3.78-3.81 (m, 8H), 3.64 (s, 16H); ¹³C NMR (300 MHz, (CD₃)₂CO) δ (ppm) 68.9, 70.5, 71.4, 71.6, 116.2, 154.1

1,4,21,24-Tetraiodo-7,10,13,16,19,26,29,32,35,38-decaoxa[13.13]paracyclophane (13). FABMS 1063 (M+Na)⁺; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.18 (s, 4H), 4.05-4.08 (m, 8H), 3.87-3.89 (m, 8H), 3.72-3.78 (m, 16H); ¹³C NMR (300 MHz, CDCl₃) δ (ppm) 69.8, 70.5, 71.2, 71.4, 86.7, 123.5, 153.1

1,4,24,27-Tetrakis(thiophenyl)-7,10,13,16,19,22,29,32,35,38,41,44-dodecaoxa[16.16]paracyclophane (14). To a 25ml Schlenk flask equipped with magnetic stirrer was added 2 (0.277g, 0.25 mmol), PdCl₂(PPh₃)₂ (10mg, 0.0146mmol, 5 mol %), and 10ml of DMF. Tributylstannylthiophene (0.773g, 2.07 mmol, 8.3 equiv.) was added and the solution was heated to 120ºC for 3 hours. After this period the reaction was cooled and diluted with 10ml of deionized water. The aqueous solution was then extracted with methylene chloride (3x40ml), the organic phases were collected and dried with MgSO₄. The organic phase was then filtered and rotary evaporated yielding a yellow colored oil that was subjected to high vacuum yielding a yellow solid. The solid
was washed with hot hexanes and filtered yielding a yellow solid (0.222g, 0.233 mmol, 95% yield). FABMS 976 (M+Na)^+, 953 (M)^+; ^1H NMR (300 MHz, CDCl₃) δ (ppm) 7.46-7.48 (dd, 4H, J = 2.4 Hz), 7.25-7.26 (dd, 4H, J = 2.7 Hz), 7.16 (s, 4H), 7.00-7.03 (dd, 4H, J = 1.5 Hz), 4.10-4.13 (m, 4H), 3.84-3.88 (m, 4H), 3.62-3.67 (m, 24H); ^13C NMR (300 MHz, CDCl₃) δ (ppm) 69.2, 70.0, 71.0, 71.0, 71.1, 113.4, 123.3, 125.7, 125.8, 127.1, 139.2, 149.4

**1,4-Bis(thiophenyl)-7,10,13,16,19,26,29,32,35,38-decaoxa[13.13]paracyclophephane (15).**

To a 50ml Schlenk flask with magnetic stirring was added 6 (1.5g, 1.91 mmol) and PdCl₂(PPh₃)₂ (67 mg, 0.0955 mmol, 5 mol %) and was degassed/purged with argon 4x. 25ml of DMF was and 2-tributylstannylthiophene (3ml, 8.58 mmol, 4.5 equiv.) was then added. The reaction was then heated to 90°C for 14hrs. After this period the reaction was cooled and water was added to the reaction mixture. The aqueous phase was the extracted with methylene chloride (3x100ml) and was washed with aqueous KF solution. The organic phase was then dried with MgSO₄, filtered, and rotary evaporated. The gummy solid was dried under vacuum and recrystallized slowly from a solution of methylene chloride yielding yellow crystal plates (1.26g, 1.8 mmol, 95% yield): FABMS 701 (M+H)^+; ^1H NMR (300 MHz, CDCl₃) δ (ppm) 7.57-7.59 (dd, 2H, J = 2.7 Hz), 7.29-7.32 (dd, 2H, J = 4.2), 7.25 (s, 2H), 7.06-7.09 (dd, 2H, J = 1.2 Hz), 6.58 (s, 4H), 4.17-4.21 (m, 4H), 3.95-3.98 (m, 4H), 3.80-3.83 (m, 4H), 3.66-3.75 (m, 20H); ^13C NMR (300 MHz, CDCl₃) δ (ppm) 68.1, 69.3, 69.9, 70.0, 70.8, 71.0, 71.1, 71.2, 113.4, 115.5, 123.3, 125.8, 125.9, 127.2, 139.2, 149.5, 153.0

**1,4-Bis(bithiophenyl)-7,10,13,16,19,26,29,32,35,38-decaoxa[13.13]paracyclophane (17).** To a 50ml Schlenk flask was added 6 (0.504g, 0.641 mmol), and tributylstannylbithiophene (16) (1.17g, 2.56 mmol, 4 equiv.) in 25ml of DMF. The
solution was then stirred and purged with argon for 20 minutes whereupon PdCl₂(PPh₃)₂ (10mg, 0.0128 mmol, 2 mol %) was added. The reaction was then heated to 110°C for 14 hours. After this period, the solution was cooled and filtered through a plug of Celite. The DMF solvent was removed under high vacuum and the resulting oil was extracted with methylene chloride (3x50ml) and the organic phases were washed with a sat. KF solution. The organic phase was then dried with MgSO₄, filtered and rotary evaporated yielding a yellow-orange solid. The solid was recrystallized from a slowly evaporating methylene chloride solution yielding yellow crystals (0.471g, 0.58 mmol, 90% yield): FABMS 887 (M+Na)⁺; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.51-7.52 (d, 2H, J = 3.9 Hz), 7.23-7.24 (m, 2H), 7.23 (m, 2H), 7.22 (s, 2H), 7.16-7.18 (d, 2H, J = 3.9 Hz), 7.03-7.06 (dd, 2H, J = 4.2 Hz), 6.55 (s, 4H), 4.20-4.24 (m, 4H), 4.00-4.02 (m, 4H), 3.66-3.79 (m, 24H); ¹³C NMR (300 MHz, CDCl₃) δ (ppm) 68.1, 69.3, 69.9, 70.0, 70.8, 71.0, 71.0, 71.2, 112.5, 115.4, 123.0, 123.6, 124.0, 124.5, 126.6, 128.1, 137.5, 137.9, 138.1, 149.5, 153.0

1,4-Bis(trimethylsilylethynyl)-7,10,13,16,19,26,29,32,35,38-decaoxa[13.13]paracyclophane (18). To a 100ml Schlenk flask with magnetic stirring was added 8 (2.0g, 3.18 mmol), CuI (36mg, 0.19 mmol, 6 mol %), and PdCl₂(PPh₃)₂ (112mg, 0.159 mmol, 5 mol %). The solids were degassed/backfilled with argon thrice after which 50ml of dry degassed toluene was added. Diisopropylamine (2.5ml, 15.9 mmol, 5 equiv.) dry and degassed was then added followed by trimethylsilylacetylene (2.5ml, 15.9 mmol, 5 equiv.). The reaction was allowed to stir for 12hrs. at 60°C and a gradual increase in ammonium salt precipitate was evident. After 12 hours the solution was rotary evaporated yielding a black solid that was chromatographed with EtOAc. The product was eluted as the sole long-wave blue fluorescent spot yielding a off-white solid.
(1.2g, 1.3 mmol, 41% yield): FABMS 751 (M+Na)+; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 6.88 (s, 2H), 6.73 (s, 4H), 4.03-4.06 (m, 4H), 3.94-3.97 (m, 4H), 3.86-3.89 (m, 4H), 3.76-3.82 (m, 8H), 3.67-3.72 (m, 12H), 0.25-0.27 (m, 18H); \(^{13}\)C NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 0.16, 68.3, 69.2, 69.8, 69.9, 70.9, 71.0, 71.2, 71.3, 100.7, 101.1, 114.2, 115.6, 117.5, 153.1, 154.0

1,4-Bis(ethynyl)-7,10,13,16,19,26,29,32,35,38-decaoxa[13,13]paracyclophane (19). To a 50ml round bottom flask with magnetic stirring was added 33 (0.6g, 0.651 mmol) and was dissolved in 15ml of a 1:1 THF/MeOH solution. The heterogeneous solution was purged with argon for 20 minutes before K\(_2\)CO\(_3\) (0.9g, 6.51 mmol, 10 equiv.) was added. The mixture was allowed to stir for 14 hours, after which the solution was filtered and rotary evaporated. The resulting solid was recrystallized from EtOAc yielding a white solid (350mg, 0.599 mmol, 92% yield): FABMS 607 (M+Na)+; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 6.94 (s, 2H), 6.78 (s, 4H), 4.06-4.10 (m, 4H), 4.00-4.02 (m, 4H), 3.68-3.88 (m, 24H), 3.38 (s, 2H); \(^{13}\)C NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 68.2, 69.6, 69.7, 69.8, 70.9, 70.9, 70.9, 71.1, 79.6, 83.4, 113.6, 115.6, 118.2, 153.1, 154.1

1,4-Bis((3,9-hexyl)-bithiophenyl)-7,10,13,16,19,26,29,32,35,38-decaoxa[13,13]paracyclophane (21). A 250 mL Schlenk flask equipped with a stir bar was charged with (2.49g, 3.16 mmol,), (2-tributylstannyl-(3,6-hexyl))bithiophene (17) (8.0g, 12.8 mmol, 4.05 equiv) and DMF (60 mL). The flask was then capped with a septum and argon was bubbled through the solution for 15 minutes before the addition of PdCl\(_2\)(PPh\(_3\))\(_2\) (6.6mg, 0.0094 mmol, 3 mol %). The solution was heated to 100°C for 14 hours resulting in the precipitation of palladium black. The solution was cooled to room temperature and was rotary evaporated. The resulting yellow-black, blue fluorescent oil was subjected to high vacuum at 70°C. The resulting solid was then flash
chromatographed (85:15 hexanes/EtOAc) yielding a yellow solid (2.77 g, 2.3 mmol, 79% yield): FABMS 1224 (M+Na)⁺; 1H NMR (300 MHz, CDCl₃) δ (ppm) 7.45 (s, 2H), 7.29-7.31 (d, 2H, J = 5.4 Hz), 7.23 (s, 2H), 6.98-7.00 (d, 2H, J = 5.1 Hz), 6.58 (s, 4H), 4.18-4.21 (m, 4H), 3.96-3.98 (quartet, 4H), 3.63-3.79 (m, 24H), 2.49-2.59 (quintet, 8H), 1.54-1.59 (m, 8H), 1.25-1.34 (m, 24H), 0.82-0.89 (m, 12H); 13C NMR (300 MHz, CDCl₃) δ (ppm) 14.3, 14.3, 22.8, 22.8, 29.1, 29.2, 29.4, 29.5, 31.0, 31.1, 31.9, 31.9, 68.1, 69.3, 69.9, 70.0, 70.7, 71.0, 71.0, 71.2, 112.4, 115.4, 123.0, 125.4, 127.3, 128.8, 129.1, 129.4, 138.5, 142.3, 142.4, 149.5, 153.0

1,4-Bis((3,4-ethylenedioxy)thiophene)-7,10,13,16,19,26,29,32,35,38-decaoxa[13.13]

paraeryclophane (23). A 200 mL Schlenk flask equipped with a stir bar was charged with 8 (1.35 g, 1.71 mmol), (2-tributylstannyl-(3,4-ethylenedioxy))thiophene (19) (3.27 g, 7.58 mmol, 4.4 equiv), and DMF (50 mL). The flask was then capped with a septum and argon was bubbled through the solution for 30 min. before the addition of PdCl₂(PPh₃)₂ (6.6 mg, 0.0094 mmol, 5 mol %). The light-orange solution was then heated to 110°C for 1 hour resulting in the precipitation of palladium black. The reaction mixture was then cooled to room temperature, treated with sat. NaHCO₃ (50 mL) and extracted with CH₂Cl₂ (4 x 50 mL). The organic phases were collected, dried (Na₂SO₄), and filtered through a plug of Celite. The orange-fluorescent green solution was then concentrated in vacuo yielding an orange colored oil. The oil was then dissolved in CH₃CN and extracted with hexanes (10 x 100 mL) in order to remove tin-based impurities. The CH₃CN layer was decanted, rotary evaporated, and subjected to high vacuum yielding the title compound as an air-sensitive orange colored solid (1.3 g, 92%, mp 30-31°C): FABMS 816 (M)⁺; 1H NMR (500 MHz, CDCl₃) δ (ppm) 7.76 (s, 2H), 6.60 (s, 4H), 6.36 (s, 2H), 3.67-4.26 (m, 40H); 13C NMR (500 MHz, CDCl₃) δ (ppm) 64.4, 64.9, 68.0, 69.2, 69.8, 69.8, 70.7, 70.9, 70.9, 71.0, 99.8, 113.3, 113.3, 115.4, 121.0, 138.8, 141.3, 148.8, 152.9.
1,4-Bis((1',1''-ethynyl-4',4''-dodecyloxy)-benzene)-7,10,13,16,19,26,29,32,35,38-decaoxa[13.13]paracyclophane (25). To a 100ml Schlenk flask with magnetic stirring was added 8 (0.5g, 0.636 mmol), 1-dodecyloxy-4-ethynylbenzene (24) (0.191g, 0.666 mmol, 1.05 equiv.), CuI (39.1mg, 0.039 mmol, 6.1 mol %), and PdCl2(PPh3)2 (112mg, 0.0283 mol, 4 mol %) which was degassed/backfilled with argon 3x. To the solids was then added 15ml of degassed toluene and diisopropylamine (0.722g, 7.14 mmol, 11 equiv.) leading to a solution color change from light yellow to orange. After 14 hours the reaction was rotary evaporated, and the black solid was subjected to flash chromatography (60:40 EtOAc/hexane) affording the title compound as the fastest fluorescent spot as a white solid (0.1778, 0.159 mmol, 25% yield), and a more polar non-fluorescent spot as the mono-adduct, 1-iodo-4-((1'-ethynyl-4'-dodecyloxy)-benzene)-7,10,13,16,19,26,29,32,35,38-decaoxa[13.13]paracyclophane (26) (0.1842g, .195 mmol, 31% yield): FABMS 1123 (M+4H)⁺; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.44-7.47 (d, 4H, J = 8.4 Hz), 6.97 (s, 2H), 6.85-6.88 (d, 4H, J = 8.4 Hz), 6.70 (s, 4H), 4.11-4.12 (m, 4H), 3.90-3.99 (m, 12H), 3.74-3.77 (m, 4H), 3.66-3.74 (m, 12H), 1.79 (quintet, 4H), 1.27 (m, 40H), 0.86-0.91 (t, 6H); ¹³C NMR (300 MHz, CDCl₃) δ (ppm) 14.4, 22.9, 26.2, 29.4, 29.6, 29.6, 29.8, 29.8, 29.9, 29.9, 32.1, 54.0, 68.2, 68.3, 69.8, 69.9, 69.9, 70.9, 71.0, 71.1, 71.3, 84.7, 95.5, 114.2, 114.7, 115.4, 115.6, 117.0, 133.2, 153.1, 153.6, 159.5

1-Bromo-4-((1'-ethynyl-4'-dodecyloxy)-benzene)-7,10,13,16,19,26,29,32,35,38-decaoxa[13.13]paracyclophane (27). To a 100ml Schlenk flask with magnetic stirring was added 9 (0.234g, 0.317 mmol), 21 (92.6mg, 0.323 mmol, 1.01 equiv.), Pd(PPh₃)₄ (4mg, 0.0035 mmol, 1 mol %), and CuI (1.2mg, 0.0063 mmol, 1.8 mol %) in 20ml of toluene. Diisopropylamine (0.722g, 1ml, 7.14 mmol, 23 equiv.) was then added and the reaction was heated to 70°C. Within several minutes amine salts precipitated and the reaction was allowed to stir for 14 hours. After this period the reaction was cooled, the
solution was rotary evaporated, and the resulting solid was flash chromatographed with 60:40 EtOAc/hexane as the eluant. The yellow solid product was collected as the major fraction (200mg, 0.222 mmol, 70% yield): FABMS (M+Na)+; 1H NMR (300 MHz, CDCl3) δ (ppm) 7.43-7.46 (d, 2H, J = 8.7 Hz), 7.07 (s, 1H), 6.98 (s, 1H), 6.84-6.87 (d, 2H, J = 8.4 Hz), 6.72 (s, 4H), 4.05-4.11 (m, 4H), 3.90-3.96 (m, 8H), 3.77-3.83 (m, 8H), 3.66-3.72 (m, 12H), 1.79 (quintet, 4H), 1.27-1.46 (m, 40H), 0.86-0.90 (t, 6H); 13C NMR (300 MHz, CDCl3) δ (ppm) 14.3, 22.9, 26.2, 29.4, 29.5, 29.6, 29.7, 29.8, 29.8, 29.8, 32.1, 68.3, 69.7, 69.8, 69.9, 70.0, 70.9, 70.9, 71.0, 71.1, 71.2, 71.3, 84.0, 94.7, 112.8, 113.5, 114.7, 115.2, 115.6, 117.7, 118.5, 133.2, 149.7, 153.1, 153.1, 154.1, 159.5

1,4-Bis(ethynyl)-[(1',1''-ethynyl-4',4''-dodecyloxy)-benzene]-
7',7'',10',10'',13',13'',16',16'',19',19'',26',26'',29',29'',32',32'',35',35'',38',38''-
decaosa[13.13]paracyclophane] (29). To a 100ml Schlenk flask with magnetic stirring was added 23 (0.1842g, 0.1945 mmol), 1,4-diethynylbenzene (24) (12.3mg, 0.0949 mmol, 0.5 equiv.), Cul (1.7mg, 0.0089 mmol, 4.5 mol %), and Pd(PPh3)4 (2mg, 0.0102 mmol, 5 mol %). The solids were degassed/purged with argon 3x after which 10ml of air-free toluene was added. To this solution diisopropylamine (0.2024g, 0.3ml, 2 mmol, 10 equiv.) was added and within a few minutes after heating to 70°C amine salts began to precipitate and a fluorescent meniscus was evident. After heating for 14 hours the reaction was cooled and the solution was rotary evaporated. The resulting solid was flash chromatographed with 70:30 EtOAc/hexanes eluant yielding the product as an orange solid (41mg, 0.0233 mmol, 12% yield): FABMS 1782 (M+H3O)+, 899 (M+2H3O)2+; 1H NMR (300 MHz, CDCl3) δ (ppm) 7.51 (s, 4H), 7.45-7.48 (d, 4H, J = 8.7 Hz), 6.98 (s, 4H), 6.85-6.88 (d, 4H, J = 8.7 Hz), 4.12-4.13 (m, 8H), 3.90-3.97 (m, 16H), 3.76-3.77 (m, 8H), 3.60-3.70 (m, 32H), 0.83-1.90 (m, 50H); 13C NMR (300/400 MHz, CDCl3) δ (ppm)
14.4, 22.9, 25.8, 26.2, 29.4, 29.6, 29.8, 29.8, 29.9, 32.1, 44.7, 45.1, 52.1, 68.2, 68.3, 69.9, 69.9, 70.9, 71.0, 71.2, 71.3, 84.4, 84.5, 100.9, 104.36, 113.5, 114.5, 115.4, 117.0, 123.1, 128.0, 131.5, 133.1, 137.5, 138.1, 142.1, 152.9, 153.4, 165.4

1,4,21,24-Tetrakis(trimethylsilylthethyl)-7,10,13,16,19,26,29,32,35,38-decaoxa[13.13]paracyclophane (30). To a 100ml Schlenk flask with magnetic stirring was added 13 (0.373g, 0.358 mmol), CuI (16.8mg, 0.072 mmol, 25 mol %), and Pd(PPh₃)₄ (4.1mg, 0.0036mmol, 1 mol %). The solids were purged with argon and degassed under high vacuum thrice. Diisopropylamine (0.402g, 0.6ml, 2.87 mmol) and trimethylsilylacetylene (0.706g, 1.02ml, 7.2 mmol) were added and the solution was heated to 70°C for 14 hours. The solution was then cooled and rotary evaporated and TLC (95:5 CH₂Cl₂/EtOAc) indicated one fluorescent product. The crude solid was then dry loaded onto silica gel and flash chromatographed with a grade up to 80:20 CH₂Cl₂/EtOAc. Isolation of the fractions containing the white crystalline product yielded (0.2g, 0.22 mmol, 61% yield): FABMS 943 (M+Na)⁺; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 6.91 (s, 4H), 4.01-4.04 (m, 8H), 3.82-3.85 (m, 8H), 3.72-3.75 (m, 8H), 3.65-3.67 (m, 8H), 0.24 (s, 36H); ¹³C NMR (300 MHz, CDCl₃) δ (ppm) 0.21, 69.6, 69.9, 71.2, 71.3, 100.6, 101.2, 114.1, 117.6, 154.0

1,4,21,24-Tetrakis(ethynyl)-7,10,13,16,19,26,29,32,35,38-decaoxa[13.13]paracyclophane (31). To a 200ml round bottom flask with magnetic stirring was added 30 (0.176g, 0.191 mmol) and a 1:1 THF/MeOH solution. The solution was purged with argon for 30 minutes after which K₂CO₃ (0.527g, 3.81 mmol, 20equiv.). The reaction was allowed to stir for 16 hours whereupon TLC (5:95 MeOH/CH₂Cl₂) yielded one spot. The reaction solution was rotary evaporated yielding a solid that was neutralized with saturated NH₄⁺Cl. The mixture was then extracted with methylene chloride (4x50ml). The organic layers were dried with MgSO₄, filtered and rotary
evaporated. The solid was then recrystallized from acetone yielding a white insoluble solid that could not be characterized further. (0.1009g, 0.16 mmol, 83% yield)

**1,4,18,21-Tetrakis(thiophenyl)-7,10,13,16,23,26,29,32-octaoxa[10.10]paracyclophane (33).** FABMS 799 (M+Na)⁺; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.32-7.34 (dd, 4H, J = 2.7 Hz), 7.19-7.21 (dd, 4H, J = 4.2 Hz), 6.99 (s, 4H), 6.93-6.96 (dd, 4H, J = 1.5 Hz), 4.01-4.04 (m, 4H), 3.84-3.88 (m, 4H), 3.75 (s, 16H); ¹³C NMR (300 MHz, CDCl₃) δ (ppm) 68.9, 70.0, 71.4, 113.1, 123.0, 125.4, 125.5, 126.9, 139.2, 149.1

**1,4,21,24-Tetrakis(thiophenyl)-7,10,13,16,19,26,29,32,35,38-decaoxa[13.13]paracyclophane (33).** FABMS 887 (M+Na)⁺; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.43-7.44 (dd, 4H, J = 3.6 Hz), 7.23-7.25 (dd, 4H, J = 5.4 Hz), 7.01 (s, 4H), 6.99-7.01 (m, 8H), 3.97-4.00 (m, 4H), 3.85-3.88 (m, 4H), 3.69-3.73 (m, 24H); ¹³C NMR (300 MHz, CDCl₃) δ (ppm) 68.9, 70.0, 70.9, 71.4, 112.7, 122.9, 125.6, 125.7, 127.0, 139.3, 149.2

**[(Bis(ethyl-2,2'-ol))-bipyridinium]bis hexafluorophosphate (34).** To a 25 ml Schlenk flask equipped with magnetic stirrer was added 4,4'-bipyridyl (4.38g, 28 mmol). To this solid was added 1-iodo-ethan-2-ol (9.92g, 57.7 mmol, 4.5 ml, 2.06 equiv.) and was heated to 110°C. The solution was allowed to reflux for 5 minutes whereupon the formation of a highly viscous yellow slurry formed. The solid was collected and washed with ethanol and acetone until the effluent liquid was clear. The solid was then dissolved in water (2 ml H₂O/g of crude), filtered, and a saturated solution of NH₄⁺PF₆⁻ was added dropwise, leading to the formation of a white precipitate. The precipitate was then collected and washed with ethyl acetate. The solid was then recrystallized from a water/methanol solution yielding a white crystals (4.39g, 8.7 mmol, 36% yield).
FABMS 391 (M-HPF₆⁻); ¹H NMR (300 MHz, CD₂CN) δ (ppm) 8.90-8.92 (d, 4H, J = 7.2 Hz), 8.40-8.42 (d, 4H, J = 6.6 Hz), 4.68-4.72 (t, 4H), 3.87-4.00 (br t, 4H), 3.45 (br s, 2H); ¹³C NMR (300 MHz, CD₂CN) δ (ppm) 61.4, 65.1, 127.9, 147.1, 151.3

[(((S),(S)-2,2'-Dimethyl)-1,1’-propyl)-bipyridinium]bis hexafluorophosphate (35). To a 10 ml Schlenk flask under argon with magnetic stirring was added 4,4’-bipyridyl (0.519g, 3.32 mmol) and (S(+)-3-methyl-)butan-1-ol tosylate (2.012g, 8.3 mmol, 2.5 equiv.). The solution was heated to 130°C leading to the formation of a precipitate within 10 minutes. The reaction was allowed to cool, and the precipitate was then collected. The solid was dissolved in hot water, filtered and a saturated solution of NH₄⁺PF₆⁻ was added dropwise leading to the formation of a white precipitate. The solid is then dried, dissolved in acetonitrile and added dropwise to a solution of hot methylene chloride. The white opalescent solid was then collected and dried. (1.04g, 1.77 mmol, 53% yield): FABMS 443 (M-HPF₆⁻), 297 (M)²⁺; ¹H NMR (300 MHz, CD₂CN) δ (ppm) 8.85-8.88 (d, 4H, J = 7.2 Hz), 8.38-8.40 (d, 4H, J = 6.6 Hz), 4.60-4.62 (dd, 1H, J = 6.6 Hz), 4.56-4.58 (dd, 1H, J = 6.6 Hz), 4.41-4.43 (dd, 1H, J = 8.1 Hz), 4.36-4.39 (dd, 1H, J = 8.1 Hz), 1.92-2.13 (sextet, 2H, J = 3.6 Hz), 1.38-1.49 (dq, 2H), 1.26-1.38 (ttq, 2H), 0.95-1.00 (d, 6H, J = 15 Hz), 0.92-0.97 (t, 6H); ¹³C NMR (300 MHz, CD₂CN) δ (ppm) 11.3, 16.1, 26.9, 37.8, 68.2, 128.3, 146.8, 151.2

[1-Methylpyridinium-2-vinyl-(11-methylpyridinium)]bis hexafluorophosphate (36). To a 25ml Schlenk flask was added 2-vinylpyridine (0.824g, 7.82 mmol), 3-bromopyridine (1.26g, 7.98 mmol, 1.02 equiv.) in enough triethylamine to dissolve all components. The solution was degassed with argon for 20 minutes and PdCl₂(PPh₃)₂ (0.112g, 0.1597 mmol, 2 mol %) was then added. The solution was heated to 100°C for 14hrs. after which the reaction was cooled to room temperature, diluted with 6ml of
deionized water, and extracted with chloroform (3x50ml). The chloroform phase was collected, dried with MgSO₄, and rotary evaporated. The resulting oil was treated with hexanes whereupon it solidified into a non-fluorescent brown solid. The brown solid was continually washed with hexanes until no fluorescent effluent was observed. The fluorescent hexane phase was evaporated yielding a long-wave fluorescent blue oil. TLC of the oil in hexanes/THF (5:1) revealed one fluorescent blue spot running slower than the co-spotted starting materials. The oil was then dissolved in neat methyl iodide and within several hours a brown gummy precipitate formed. The solution was rotary evaporated and the solid was dissolved in hot water and filtered. To this solution was added a saturated solution of NH₄⁺PF₆⁻ resulting in the precipitation of an off-white solid. (1.12g, 2.23 mmol, 29% yield): FABMS 539 (M+2H₂O)⁺; ¹H NMR (300 MHz, CD₃CN) δ (ppm) 8.84 (s, 1H), 8.65-8.67 (d, 1H, J = 4.2), 8.64-8.65 (m, 1H), 7.95-8.00 (dd, 1H, J = 1.8), 7.81-7.87 (dd, 1H, J = 1.8), 7.71-7.76 (dd, 1H, J = 15.9 Hz), 7.53-7.58 (dd, 1H, J = 15.9 Hz), 7.54-7.57 (dd, 2H, J = 6.9 Hz), 7.33-7.37 (dd, 1H, J = 2.1 Hz), 4.30 (s, 6H); ¹³C NMR (300 MHz, CD₃CN) δ (ppm) 49.4, 125.0, 125.1, 125.3, 128.9, 136.3, 138.5, 138.6, 142.8, 144.5, 144.7, 151.0, 154.3

**Stability Constant Determinations by Spectrophotometric Titration Procedures.** The method employed for the evaluation of the stability constant described in this communication was based on the Stern-Volmer fluorescence quenching behavior of host and analyte. In the quenching study care was taken to avoid changing the concentrations of the emitting compounds. This was accomplished by preparing the quencher in the same solution as the emitting compound. All emitting sample solutions were optically dilute at a concentration between 1.0 x 10⁻⁶ M to 8.0 x 10⁻⁶ in CH₃CN. Paraquat solutions were prepared from a solution of emitter at a concentration of 1.0 x 10⁻² M in CH₃CN. The relative emission intensity for the Stern-Volmer analysis was recorded at the λ_max of
the emission spectra. The samples were manually shaken and equilibrated after each addition of paraquat for 5 min. prior to data collection. The average $K_a$ value was determined from three independent experiments within one standard deviation. UV-vis spectra were obtained on a Hewlett-Packard 8453 diode array spectrophotometer. Fluorescence studies were conducted with a SPEX Fluorolog-2 fluorometer (model FL112, 450 W xenon lamp) equipped with a model 1935B polarization kit. Solution spectra were recorded by right angle detection.
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![Chemical Structure](image)
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Chapter 3

Synthesis and Electrochemical Properties of Cyclophane and [2]-Catenane Polymers Based on 3,4-ethylenedioxythiophene
3.1. Introduction

Great interest has been devoted to the development of multicomponent arrays that undergo inter- and intramolecular electron-transfer via an exergonic gradient. Dyads, triads and higher order arrays have been synthesized in attempts to mimic and better understand the photosynthetic reaction center\(^1\) and toward the realization of molecular-based storage devices.\(^2\) Catenane and rotaxane architectures consisting of electron-rich and electron-poor aromatic units are ideal substrates for investigation because they exhibit charge-transfer interactions that facilitate electron migration.\(^3\) Recently, a transition metal based [2]-catenane has been reported that exhibits migration via an intramolecular gradient,\(^1a\) however, research into conductive poly([2]-catenanes) has gone undeveloped.\(^4\) Herein, the synthesis and electrochemical study of an electrically conducting poly([2]-catenane) and assess the efficacy of this architecture toward photoconduction.

3.2. Results and Discussion

3.2.1. Monomer and Polymer Synthesis

The investigation focused on macrocycle 23 and its [2]-catenane, Scheme 3.1. The choice of this system is largely based on previous work of Stoddart who showed the base BPP34C10 cyclophane unit (compound 23 without iodo groups) to bind dialkylated-4,4'-bipyridiniums producing rotaxanes and catenanes.\(^3b,5\) The self-assembly of [2]-catenane 38 follows from the association of macrocycle 23 with the trication derived from 37. Cyclization of the tricationic portion of the complex to the tetracation leads to the desired [2]-catenane geometry. As expected, the tetracationic cyclophane portion of 38 quenches
the fluorescence of the crown ether component. The deep-green [2]-catenane complex exhibits a charge-transfer absorption at $\lambda = 626$ nm ($\varepsilon = 1230$ M$^{-1}$cm$^{-1}$), which is red-shifted relative to the paraquat:23 complex indicating greater intimacy between donor and acceptor in the [2]-catenane. Transient absorption spectroscopic studies on 38 have determined that the lifetime of the charge-separated state induced upon irradiating the [2]-catenane charge-transfer band is $\leq 0.6$ nsec.

![Scheme 3.1. Synthesis and polymerization of [2]-catenane 38 and crown ether 23.](image)

The crystal structure obtained for 38, Scheme 3.1, supports an interlocked $\pi$-stacked geometry. The bipyridinium aromatic units are situated in electronically unique environments as illustrated by the inner bipyridinium aromatic positioned within the tetracationic cyclophane cavity and the outer bipyridinium aromatic on the outer
periphery of the cavity. The centroid-centroid distances between aromatic rings in the complex are ca. 3.4 Å, indicative of strong π-π stacking interactions between aromatic units. The [2]-catenane complex exhibits hydrogen bonding between the α- and β-bipyridinium aromatic protons and crown ether oxygen atoms as well as edge-to-face interactions between aromatic subunits. The distance between the central oxygen atom attached to the crown ether linkage and the α-bipyridinium protons is 2.51 Å. The edge-to-face distance between the inside hydroquinone ring protons and the p-xylyl spacers is 2.93 Å. The torsion angle between the thiophene-phenylene planes is 21.6°, orienting the thiophene ring 3,4-ethylenedioxy bridge within the receptor cavity. Surprisingly, the twist allows for a stabilizing interaction between the 3-position ether oxygen atom of the thiophene ring and β-bipyridinium protons, with a distance of 2.86 Å. Within the unit cell, complementary π-stacking between molecules persists with centroid-centroid distances of 3.47 Å, Figure 3.1.

Figure 3.1. Unit cell packing for [2]-catenane 38.
Scheme 3.2. Synthesis of diiodo-[2]-catenane 39.

[2]-catenane 38 was also synthesized with (R)-camphorsulfonic acid salt counter-ions in an attempt to synthesize single crystals with molecules that arrange with a helical bias in the unit cell. Multiple attempts at growing X-ray quality crystals, however, did not prove fruitful. The synthesis of diiodo-[2]-catenane 39 was undertaken in similar fashion as the synthesis of [2]-catenane 38, Scheme 3.2. The yield of 39 is diminished relative to the yield of 38, indicative of the poorer binding ability of 6 toward the tricationic intermediate of 37. The charge-transfer absorption band of 39 at 475 nm is blue-shifted in contrast to 38, indicative of weaker π-stacking interactions.

Aside from electrochemical polymerization of monomers 23 and 38 *vide infra*, synthesis of poly(23) and poly(38) were performed by chemical methods. The standard protocol for thiophene polymerization is either via FeCl₃ mediated oxidation⁷ or by the McCullough method.⁸ It has been well documented that Fe impurities in organic films for photovoltaic and electroluminescent devices detract from device efficiencies.⁹ With this in mind, an effort was made to avoid metal-based Lewis acids. The McCullough method requires that the terminal propagation positions of the thiophene groups require halide substituents. The halogenation of the thiophene termini of compound 23 is complicated
by functionalization of the more accessible electron-rich hydroquinol periphery. As an alternative, nitrosonium ion (NO⁺) was utilized as the oxidant, Scheme 3.3.

![Diagram of polymerization](image)

**Scheme 3.3.** Oxidative polymerization of compound 21.

NO⁺ has found widespread utility for the oxidative doping of conjugated polymers,¹⁰ however, little has been reported toward the polymerization of thiophene monomers.¹¹ In order to probe the efficacy of NO⁺ based polymerizations, compound 21 has been utilized for its highly organic soluble polymeric form. Initial attempts at Fe(III) based polymerizations gave at best oligomeric products as determined by GPC. Increasing the concentration of Fe(III) did not improve molecular weights but made the products intractable due to greater Fe(II) formation via coordination to sulfur atoms on the thiophene. The advantage of NO⁺ over Fe(III) is that the resulting reduced nitrosonium
ion is a gas, allowing for facile removal. If 21 is polymerized with 2.5 equivalents of nitrosonium, the resulting polymer has an $M_n$ of 44,000 with PDI's $>2$. If less 2.5 equivalents are used, more oligomeric products are formed. With 3.5 to 4 equivalents, a polymer gel forms within seconds of addition of NO$^+$ and can be attributed to extensive cross-linking with excess of oxidant. $^1$H NMR and elemental analyses indicate that nitrogen incorporation does not occur during polymerization for the 2.5 equivalents case. Based on these observations, NO$^+$ was determined to provide significant improvements over Fe(III) polymerization molecular weights and was used exclusively toward synthesizing poly(23) and poly(38) for photovoltaic device fabrication.

3.2.2. Electrochemical Polymerization

The electrochemical polymerization of macrocyclic monomer 23 and [2]-catenane 38 proceeds via two propagating sites centered at the 5-position of the 3,4-ethylenedioxythiophene functionality. As the voltage is cycled to a positive potential of 0.35V vs. Fc/Fc$^+$, the oxidation of monomer 23 ($E_{p,m}$) occurs (Figure 3.2A) indicating formation of radical-cationic species that can then propagate via radical combination forming dimers, trimers, etc. The chemical irreversibility of the process is exemplified in the smaller area under the reductive half-cycle relative to the oxidative half-cycle. Further oxidative cycling leads to polymer formation as evident by an oxidation peak growing in at a lower positive potential in Figure 3.2B.
Figure 3.2. A) Oxidative/reductive 1st cycle for monomer 23, B) Continued redox cycling of monomer 23 leading to the formation of poly(23). (0.1M TBAP/CH3CN, 100 mV/sec)

This lowering of the oxidative peak (E_{p,p}) for poly(23) versus monomer 23 indicates of the former's ability to stabilize cations via delocalization. The acyclic dimethoxyphenylene derivative of 23 has been synthesized by Reynolds, and exhibits a E_{p,m} = 0.46V. The lower E_{p,m} for 23 can be attributed to the stabilizing π-donation imparted by the neutral hydroquinone aromatic to the oxidized thiophene-phenylene-thiophene backbone.

The E_{p,m} of monomer 38 occurs at 0.43V vs. Fc/Fc⁺, indicating that it is slightly more difficult to oxidize than 23, Figure 3.3. This is expected due to the repulsive nature of the resulting radical-cation stacked above the inner-dicationic portion of the bipyridinium cyclophane. A mixed electrolyte solution of 7:3 tetrabutylammonium (ClO₄/PF₆) was required to deposit poly(38) as oxidized solution species freely diffused away from the electrode when pure hexafluorophosphate counterion was present.
Figure 3.3. Oxidation and polymerization of monomer 38. (0.1M (7:3 (TBACIO₄/ TBAP)), 100 mV/sec)

The $E_{p,p}$ for poly(38), 0.07V vs. Fc/Fc⁺, is also shifted to a less positive potential than its monomer. The similarity between $E_{p,p}$ for poly(38) and poly(23) is not surprising considering the small difference in oxidation potential of their respective monomers, Figure 3.4. The three-peak reduction potentials observed for the tetracationic cyclophane portion of poly(38) are identical to those for monomer 38. This behavior suggests that the neutral polymer backbone has the same electronic influence on the tetracation as the thiophene-phenylene-thiophene aromatic in 38.
Figure 3.4. Redox profiles and conductivity measurements for; A) poly(23) (0.1M TBAP) B) poly(38) (0.1M (7:3 (TBACIO₄/TBAP))). (100mV/sec film, 50mV/sec conductivity, 40 mV offset)

The multiple reduction peaks are indicative of the energetic inequality between the inner- and outer-bipyridinium aromatics. This non-equivalence has been observed by Stoddart and Kaifer with the BPP34C10 derived [2]-catenane.³ The first one-electron reduction of poly(38), $E_{p,1} = -0.77$V, occurs at the more electropositive outer-bipyridinium, followed by a one-electron reduction of the inner-bipyridinium at $E_{p,2} = -0.93$V. A final two-electron reduction, $E_{p,3} = -1.32$V, yields a neutral cyclophane. The greater electron affinity (first reduced) for the outer-bipyridinium than the inner-bipyridinium leads to the formation of an electrochemical energy gradient within the polymer repeat unit, Figure 3.5.
Figure 3.5. The three step, four electron reduction of the tetracationic cyclophane.

3.2.3. In-Situ Conductivity Measurements

The electropolymerizations are performed such that the resulting polymer is deposited on a 2μm interdigitated electrode,\textsuperscript{13} allowing in-situ conductivity measurements.\textsuperscript{14} The cyclic voltammogram and conductivity profile for poly(23) in Figure 3.4A displays a peak oxidation for the polymer, $E_{p,p} = 0\text{V}$ and a maximum conductivity of 11 S/cm at 0.2V vs. Fc/Fc$^+$.\textsuperscript{15} The conductivity profile for poly(38) rapidly leads to a maximum value of 0.2 S/cm at 0.12V vs. Fc/Fc$^+$, which decays quickly thereafter, Figure 3.4B. In contrast, the conductivity profile for poly(23) shows that the oxidation of the polymer backbone occurs over a broad range of potentials without decay. The sharp parabolic nature of the conductivity profile of poly(38), as well as the calculated +1 charge per repeat unit reflects a more localized electronic state with characteristics similar to a redox conductor, \textit{i.e.} each repeat unit acts as a discrete entity) but with a $\sigma_{\text{max}}$ much larger than
a typical redox conductor. The optimum rate of electron-transfer in the material is realized when the number of neutral and oxidized repeat units is one to one. The tetracationic portion of poly(38) does not show any detectable redox conductivity upon reduction of the bipyridinium units.

The conductivity of poly(23) was determined to be 50 times greater than that for poly(38). This finding can be rationalized on the basis of a decreased mobility of hole carriers in poly(38) due to greater electrostatic repulsion. From electrochemical measurements it has been determined that the average number of carriers per repeat for poly(38) is less than that for poly(23) as a result of the repulsion.
3.2.4. Spectroelectrochemistry

Spectroelectrochemical investigations of poly(23) and poly(38) films revealed similar absorption characteristics as a function of film oxidation, Figure 3.6.

![Graphs A, B, C, D](image)

**Figure 3.6.** A) Oxidation of poly(23), B) Spectral shift as a function of the degree of oxidation of poly(23), C) Oxidation of poly(38), D) Spectral shift as a function of the degree of oxidation of poly(38).

In their neutral (insulating) form, the $\lambda_{\text{max}}$ for poly(23) was 527nm (2.35eV) and poly(38) 542nm (2.29eV) (Figure 82). When oxidatively doped, (point 2 on the spectra), both displayed a longer wavelength band appearing between 767-796nm (1.62-1.56eV), indicative of new states formed within the band gap upon reaching a conductive state. Further lower energy absorptions occur at higher oxidation potentials, point 3 on the spectra, leading to an absorption at $>1100$nm ($<1.13$eV) owing to the formation of free carriers. The films differ in that poly(38) requires higher oxidation potentials to reach...
its conductive state than does poly(23). The three points in the absorption spectra correspond to a colorometric change of red to blue to translucent grey. This chameleon-like behavior has spurred considerable interest toward utilizing conductive polymer based electrochromic materials for IR-inactive/IR-active switchable coatings.\textsuperscript{18}

\textbf{Figure 3.7.} Spectral changes upon reducing the tetracationic cyclophane of poly(38).

The reduction of the tetracationic cyclophane of poly(38) (Figure 3.7), leads to a blue-shift in the polymer absorption. The shift indicates that a charge-transfer interaction exists when the polymer backbone is neutral. The interaction must be weak because it is only evident via the absorption spectra and does not manifest itself as change in polymer oxidation potential in comparing poly(38) and poly(23). The absorption intensity of the tetracationic cyclophane group increases upon stepwise reduction. This increase is
attributed to the increase in the molar extinction coefficient of the cyclophane upon becoming more electron-rich; ground-state absorption transitions become more probable.

3.2.5. Photovoltaic Studies

The photovoltaic behavior of poly(23) and poly(38) have been studied in an attempt to correlate molecular design to bulk device behavior. The photovoltaic device configuration chosen for study is represented in Figure 3.8. The device consists of an indium-tin oxide (ITO) electrode that is a high work function metal (anode, positive polarity in forward bias) and acts as a transparent window for irradiation. In order to facilitate hole transport, a ca. 0.1μm layer of poly(styrene sulfonate)/poly(3,4-ethylenedioxythiophene) (PSS/PEDOT) was spin cast from a commercially available (Baytron P®) aqueous solution and was baked onto the ITO with heating under vacuum. The polymer is then coated on the ITO/Baytron P® electrode via spin coating or drop casting, and a low work function metal (cathode, negative polarity in forward bias) is evaporated on top. In this work, a 0.9μm thick calcium layer is utilized as the low work function metal with a protective overlayer of 1μm thick aluminum.

![Figure 3.8. Device configuration for photovoltaic devices.](image-url)
Polymer film thicknesses varied relative to the method utilized in depositing the film. Poly(23) films were spin coated from o-dichlorobenzene with thicknesses of 0.08μm while poly(38) films required drop casting from sulfolane and gave films with thicknesses of 0.3μm. Solutions of poly(38) did not readily form films via spin-coating on the Baytron P® coated ITO glass and thus drop casting was the only option. The active device area for both polymer devices was 0.1cm².

The IV-characteristics for poly(23) and poly(38) both display a photoresponse upon irradiation with light at 500nm, Figure 3.9. The irradiated short-circuit current for poly(23) was found to be 3700x greater than that for the dark short-circuit current. This change indicates a substantial increase in current occurring upon irradiation of the film at the band-gap energy of the polymer. The short-circuit current and open circuit voltage were determined to be 0.35μA and 0.52V for this unoptimized device.

**Figure 3.9.** Dark and light IV characteristics for: A) poly(23), B) poly(38) with the irradiation wavelength of λ=500nm.
The filling factor, FF, for the device can be determined from Eq. 26 (Chapter 1, sec 1.3.2.) and is described as the ratio of the peak power to the power calculated by the product of the open-circuit voltage and the short circuit current.\textsuperscript{9} The maximum attainable FF is 1 for a device that has a high resistance to current leakage ($R_{\text{shunt}}$) and a low resistance for the contact surfaces ($R_{\text{series}}$).

$$\text{FF} = \frac{V_{m}I_{m}}{V_{oc}I_{sc}} \quad (26)$$

The FF for poly(23) was determined to be 0.3 with an $I_{m} = 0.16\mu A$ and $V_{m} = 0.32V$. In contrast, commercial silicon photodiodes have FF's of 0.6 to 0.8. The irradiated short-circuit current for the poly(38) device is only a factor of 36x greater than that for the short-circuit dark current. The FF was determined to be 0.22 with an $I_{sc} = 9.5nA$, $V_{oc} = 5mV$, $V_{m} = 2mV$ and an $I_{m} = 7nA$. The low FF can be attributed to leakage current losses that can be circumvented with effective electrode edge blocking and CaO formation between the metal contact.\textsuperscript{19} The greater surface roughness for the poly(38) film could also be the cause of a low FF. The fill factors described for poly(23) and poly(38) devices are within the values reported for organic photovoltaic devices.\textsuperscript{9}

The two characteristics that can be scrutinized from IV plots are the change in $V_{oc}$ and current upon irradiation. For devices that obey a metal-insulator-metal model (MIM), $V_{oc}$ can be determined by the difference in work function of the metal contacts.\textsuperscript{9} For the devices under study, the PSS:PEDOT anode (5.0V) and Ca cathode (2.9V) have a work-function difference of 2.1V. Deviations upward of 2.1V indicate that the MIM model is not operative, while deviations below 2.1V arise from potential lowering carrier trapping
or donor/acceptor mismatching with the anode/cathode.\textsuperscript{9} The poly(23) device displays a $V_{oc} = 0.52V$; $\approx 1.6V$ less than the work function difference. This $V_{oc}$ lowering can also be attributed to impurity traps in the material and/or reaction of poly(23) with the Ca cathode leading to a 20 to 50Å layer of charged polymer.\textsuperscript{19} The $V_{oc}$ lowering for poly(38) is more substantial than poly(23) with an almost zero $V_{oc}$. In ITO/MEH-PPV/Ca devices, the $V_{oc}$ was found to be 1.6V, the work function difference between Ca and ITO.\textsuperscript{9} When a C$_{60}$ derived acceptor is blended into the MEH-PPV device, the $V_{oc}$ is effectively halved. The potential-loss was attributed to the LUMO of the C$_{60}$ derivative lying 0.8eV below the Fermi energy of the Ca electrode. The same effect is believed to be operative for the tetracationic cyclophane acceptor in poly(38) except to a more critical extent. The tetracationic cyclophane can also accommodate up to four electrons acting as a drain for electron charge carriers. It is known that poly(38) is a p-type polymer, therefore majority carriers are holes and minority carriers are electrons. Upon irradiation of the polymer, the increase in majority carriers is modest and the increase in minority carrier concentration at the ITO electrode can be substantial. This is the main reason why large photocurrents are detected in reverse bias; that is, the bias where minority carriers contribute to the current. This is observed in Figure 3.9A for poly(23) and to a poor extent for poly(38) in Figure 3.9B.

The weak photocurrent observed for poly(38) is therefore tied to the poor transfer of electrons from the tetracationic cyclophane to the Ca electrode. Trapping of electrons by the cyclophane without transfer to the Ca electrode will decrease the efficiency of the device. In order to better understand the nature of charged species in the device, capacitance-voltage measurements were undertaken, Figure 3.10.
Figure 3.10. Capacitance and $1/C^2$ vs. voltage bias plots for: A) poly(23) and B) poly(38) with 1kHz applied AC.

The $1/C^2$ vs V plot for poly(23) indicates that a deviation from linearity occurs at about 0V. This effect has been ascribed to larger doping concentrations in the polymer close to the metal/polymer interface than in the bulk\textsuperscript{20} and confirms that Ca or its oxide reacts with the polymer film, forming a charge-separated region. The $1/C^2$ vs V behavior for poly(38) also deviates from linearity at zero bias, and is reversible in forward bias, Figure 3.10B. The parabolic behavior arises from freely moving charges that migrate between the electrodes, and as the polarity of the device is reversed, the charge migration direction is reversed. This has been attributed to the migration of PF$_6^-$ counter-ions in the film and seems to override other capacitance-affecting phenomena such as the Ca/polymer interaction. The exact role of PF$_6^-$ ion in the device cannot be determined but may possibly interfere with the majority carrier in an attractive sense or repulse minority carrier electrons upon photogeneration. It is also possible that the tetracationic portion of poly(38) is reduced via contact with the Ca electrode, adding a further complicating mechanism.
Figure 3.11. Photoresponse and absorption spectra under short circuit conditions for: A) poly(23) and B) poly(38).

The photocurrent action spectrum for poly(23) and poly(38) indicate that they are in good coincidence with the absorption spectra of the films, that is, they are symbatic, Figure 3.11.\textsuperscript{21} It would be expected in the case of the thicker poly(38), that the reduced penetration depth for higher energy wavelengths would produce a high density of charge carriers or excitons with a narrow penetration depth. The carriers would undergo more rapid recombination, resulting in a reduced photocurrent yield. This scenario is thought to give rise to antibatic behavior; the photocurrent action spectra occurs for photon energies where the absorption is weakest. Antibatic behavior is not observed for poly(38), indicating that the poor photocurrent obtained upon irradiation is not a function of the device thickness but based on other microscopic phenomena such as trapping by ionic species or low-lying acceptor states. From the ratio of the products of the FF, $I_{sc}$, and $V_{oc}$, the power conversion efficiency was determined for poly(23) to be 5200x greater than for
poly(38). It was also found that the photon to converted electron efficiency for poly(23) was 40x greater than that for poly(38).

3.3. Conclusion

The synthesis of an electropolymerizable [2]-catenane 38 was undertaken in order to study the electronic properties of both monomer and corresponding polymer, poly(38). The electron-acceptor free poly(23) was also studied for purposes of comparison. Both monomer 23 and 38 electrochemically and chemically polymerize, allowing an assessment of the redox properties of their respective polymers as well as show promise as photovoltaic materials. The oxidative polymerization of monomer 21 by nitrosonium ion leads to poly(21) with improved molecular weight relative to Fe(III) based polymerization, and with minimal nitrogen impurities (actual source of nitrogen is most likely conversion of hydrazine to ammonium salts in the workup).

The conductivities of poly(23) and poly(38) films were determined to be 11 S/cm and 0.2 S/cm. The conductivity profile for poly(23) indicates that continuous oxidation up to 0.5V does not lead to an appreciable change in conduction. In contrast, continuous oxidation of poly(38) leads to a parabolic waveform indicating that oxidation is limited. The polymer backbone can support fewer hole carriers than poly(23). This behavior is consistent with the +1 average charge generated per repeat for poly(38). The limited number of carriers allowed by poly(38) is in keeping with electrostatic repulsion between the oxidized polymer backbone and the non-covalently bound tetracationic cyclophane. As a result, the conductivity for poly(23) films are 50x greater than that for poly(38).
Spectroelectrochemical studies on poly(23) and poly(38) revealed that oxidation of the polymer backbone leads to a shift in absorption from visible wavelengths to the infra-red. Reduction of the tetracationic cyclophane in poly(38) leads to a blue shift for the polymer absorption indicative of the loss of charge-transfer between the donor polymer and acceptor cyclophane. An increase in the molar absorption of the cyclophane upon reduction is evidenced in an increase in absorption at \( \lambda = 380 \text{nm} \).

Photovoltaic studies on poly(23) and poly(38) based devices indicate that poly(23) is 5200x more efficient as a photoconductor than poly(38). IV plots for poly(38) indicate that shifts in V_{oc} arise from possible mismatching of the acceptors energy level with the Fermi level of Ca as well as reaction with the Ca cathode. Capacitance-voltage plots indicate that charge-transport is occurring through the poly(38) film that is parabolic in nature and reversible from reverse to forward bias. This behavior is attributed to PF_{6}^{-} ion migration and the effect on device performance by this ubiquitous ion is unclear. Despite the greater film thickness for poly(38), absorption and photovoltaic action spectra indicate that syrbatic behavior exists. The source of the poor photovoltaic response for poly(38) other than energy-level mismatching is charge-trapping by the tetracationic cyclophane as it can accommodate up to four electrons per repeat unit. The trapping manifests itself in a 40x greater collection efficiency for poly(23) based devices over poly(38). Since minority carriers play a critical role in generating a photocurrent, low-energy trapping would create a considerable barrier to electron transport to the Ca electrode. Improvements in device performance may be possible by using a higher work-function and a lower reactivity cathode such as Al. Counter-ions are impossible to avoid
in any poly[2]-catenane), but a counter-ion that imparts greater organic solubility would aid in avoiding polar solvents such as sulfolane and allow for spin-coating.

3.4. Experimental

**General Methods.** Air- and moisture-sensitive reactions were carried out in oven-dried glassware using standard Schlenk line techniques under an inert atmosphere of dry argon. All chemicals used were of reagent grade or better and were purchased from Aldrich unless otherwise noted. Anhydrous DMF was used directly from Aldrich Sure-Seal bottles. Anhydrous CH$_3$CN was prepared by a literature procedure involving activated alumina and CaH$_2$.\textsuperscript{22} 1,4-bis(bromomethyl)benzene was obtained from Aldrich and purified according to a literature procedure.\textsuperscript{23} $N,N'$-Bis(4-bromomethylbenzyl)-4,4'-bipyridinium Bis(hexafluorophosphate)\textsuperscript{37}\textsuperscript{24} were prepared according to literature procedures. $^1$H NMR, and $^{13}$C NMR were acquired with a Varian INOVA 500 and Mercury 300 spectrometer and were taken in $d_6$-DMF, CDCl$_3$, and CD$_3$CN with $^1$H chemical shifts reported relative to internal tetramethylsilane (0.00 ppm) and $^{13}$C chemical shifts reported relative to CDCl$_3$ (77.23 ppm) and CD$_3$CN (1.39 ppm). Thin-layer chromatography (TLC) was performed on cut glass slides (2.5 x 5 cm) coated with Merck 5715 Kieselgel 60F. Developed plates were air-dried, scrutinized under a UV lamp and, if necessary, developed in an iodine tank. Baker 7024 (40µm mesh) silica gel was used to perform flash column chromatography. Fast atom: bombardment mass spectroscopy (FABMS), using a xenon primary atom beam in conjunction with a 3-nitrobenzyl alcohol matrix was preformed on a Finnigan MAT 8200. Melting points were determined using a Thomas Moore capillary melting point apparatus and are uncorrected.
(2)-[1,4-Bis((3,4-ethylenedioxy)thiophene)-7,10,13,16,19,26,29,32,35,38-decaoxa
(13.13)paracyclopahne][9,18,29,38-tetraazonia-[1.1.0.1.1.0]paracyclopahne]
catenane) Tetrakis(hexafluorophosphate) (38). A 200 mL Schlenk flask equipped with a
stir bar and a dropping funnel was charged with cyclophane (23) (1.3g, 1.58 mmol, 2.6
equiv) and CH$_2$CN (15 mL). A solution of (37) (0.43g, 0.609 mmol, 1 equiv) in CH$_3$CN
(15 mL) was added to the cyclophane 23 solution under an argon purge. A deep orange-
red color formed immediately, and a solution of 1,4-bis(bromomethyl)benzene (0.161g,
0.609 mmol, 1 equiv) in CH$_2$CN (15 mL) was added. Within 30 min. a precipitate
formed and the reaction was then allowed to stir at room temperature for 4 days. A green
precipitate was then filtered, washed with CHCl$_3$ (30 mL) and dissolved in deionized
water. The aqueous solution was then treated with NH$_4^+$PF$_6^-$ until no further precipitation
was evident. The green solid was then recrystallized from a CH$_2$CN/H$_2$O solution
yielding deep-green crystals (462mg, 40%, mp >250$^\circ$C): FABMS 1772 (M - PF$_6$)$^+$, 1627
(M - 2PF$_6$)$^+$, 1483 (M - 3PF$_6$)$^+$; $^1$H NMR (500 MHz, CD$_3$CN) $\delta$ (ppm) 8.79 (br s, 8H),
7.77 (s, 8H), 7.52 (br s, 8H), 7.07 (s, 2H), 6.54 (s, 2H), 5.66 (q, 8H, $J = 14.5$ Hz), 4.28-
4.55 (m, 12H), 3.56-4.00 (m, 8H), 3.46-3.49 (t, 4H, $J = 9.5$ Hz), 3.28-3.32 (t, 4H, $J = 9.5$
Hz); $^{13}$C NMR (500 MHz, CD$_3$CN) $\delta$ (ppm) 65.4, 65.6, 66.1, 67.6, 69.2, 69.8, 70.4, 70.9,
71.8, 72.0, 101.5, 111.9, 112.3, 113.7, 120.5, 126.1, 131.8, 137.7, 140.6, 142.7, 145.2,
147.8, 151.0

(2)-[1,4-diiodo-7,10,13,16,19,26,29,32,35,38-decaoxa[13.13]paracyclophane

(9,18,29,38-tetraazonia-[1.1.0.1.1.0]paracyclopahne]catenane)

Tetrakis(hexafluorophosphate) (39). To a 25 mL sealed tube equipped with a stir bar was
charged with cyclophane (6) (100 mg, 0.127 mmol, 1.5 equiv) and CH$_3$CN (5 mL). A
solution of (37) (60 mg, 0.0846 mmol, 1 equiv) in CH$_3$CN (5 mL) was added to the
cyclophane 6 solution under an argon purge. A deep orange-red color formed
immediately, and a solution of 1,4-bis(bromomethyl)benzene (22 mg, 0.0846 mmol, 1
equiv) in CH$_3$CN (5 mL) was added. Within 30 min, a precipitate formed and the
reaction was then allowed to stir at room temperature for 1 day. A red precipitate was
then filtered, washed with CH$_3$CN (10 mL) and dissolved in deionized water. The
aqueous solution was then treated with NH$_4^+$PF$_6^-$ until no further precipitation was
evident. The red solid was collected and recrystallized from a CH$_3$CN/H$_2$O solution
yielding deep-red crystals (16 mg, 5%, mp >250°C): FABMS 1744 (M - PF$_6$)$^+$, 1598 (M
- 2PF$_6$)$^+$, 1453 (M - 3PF$_6$)$^+$; $^1$H NMR (300 MHz, CD$_3$CN) $\delta$(ppm) 9.06 (br s, 8H), 7.92 (s,
8H), 7.80 (br s, 8H), 6.68 (s, 2H), 5.81 (qr, 8H, $J = 14.5$ Hz), 3.93-4.07 (m, 16H), 3.79
(m, 4H), 3.73 (m, 4H), 3.60 (m, 4H), 3.53 (m, 4H); $^{13}$C NMR (300 MHz, CD$_3$CN) $\delta$
(ppm) 65.7, 67.7, 70.3, 70.4, 70.8, 70.9, 71.4, 71.9, 72.0, 86.6, 113.8, 123.1, 126.2, 131.9,
137.7, 145.8, 146.5, 151.1, 152.7

**Poly(21a).** In a glove box cyclophane (21) (148 mg, 0.1230 mmol, 1 equiv.) was
dissolved in 7 ml of dry chloroform. To this solution was added anhydrous FeCl$_3$ (80 mg,
0.5 mmol, 2.5 equiv.). The reaction was allowed to stir at room temperature for 24 hrs,
after which a 1.0 M solution of hydrazine in THF was added until conversion of the blue
solution color to red was achieved. The crude mixture was slowly added dropwise to a
solution of hot methanol. A precipitate formed which was collected and dried under
vacuum. The solid was then subjected to Soxhlet extraction for two days with methanol.
The resulting orange solid in the Soxhlet thimble was collected yielding (80 mg, 54%conversion). EA: theoretical C$_{68}$H$_{96}$O$_{10}$S$_4$, 67.96C, 8.05H, 13.31O, 10.67S; actual
67.93C, 7.88H, 0.22N, 13.26O, 10.10S; \(^1\)H NMR (300 MHz, CDCl\(_3\)) 7.46-7.48 (s), 7.30-7.32 (d, \(J = 6\) Hz), 7.24 (s), 7.07 (s), 6.99-7.00 (s), 6.60 (s), 4.19-4.22 (bt), 3.99 (bm), 3.65-3.84 (bm), 2.53-2.58 (bm), 1.58-1.60 (bm), 1.26-1.29 (bm), 0.85-0.86 (bm); \(^{13}\)C NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 14.3, 15.5, 22.8, 22.8, 29.1, 29.4, 29.5, 29.9, 30.9, 31.0, 31.1, 31.9, 66.1, 68.1, 69.3, 70.0, 70.7, 71.0, 71.1, 71.4, 115.4, 122.9, 123.1, 125.2, 125.4, 127.4, 128.1, 128.8, 129.0, 129.1, 129.4, 137.0, 138.5, 138.7, 142.3, 142.4, 142.6, 143.2, 149.5, 153.0; \(M_n\) = mixture of oligomers mostly pentamer

**Poly(21b).** To a vial with a magnetic stirrer was added cyclophane (21) (87.3 mg, 0.0725 mmol, 1equiv.) in 1.3 ml of 4:1 acetonitrile/chloroform solution. To the cyclophane solution was added a predissolved solution of nitrosonium hexafluoroantimonate (48 mg, 0.1813 mmol, 2.5 equiv.) in 0.8 ml of acetonitrile. Upon addition of a drop of the oxidant the reaction solution turns an intense blue color with solution species remaining soluble. After stirring for one day, the reaction was quenched with a 1.0M solution of hydrazine in THF. The solution becomes red from blue with the evolution of heat and a white gas. The resultant orange film was dried yielding (75 mg, 86% conversion). EA: theoretical

\(\text{C}_{68}\text{H}_{96}\text{O}_{10}\text{S}_4\), 67.96C, 8.05H, 13.31O, 10.67S; actual 67.91C, 7.86H, 0.36N, 13.49O, 10.41S; \(^1\)H NMR (300 MHz, CDCl\(_3\)) 7.48 (bs), 7.26 (bs), 7.08 (bs), 6.60 (bs), 4.22 (bm), 3.99 (bm), 3.66-3.76 (bm), 2.57 (bm), 1.61 (bm), 1.29 (bm), 0.86-0.88 (bm); \(^{13}\)C NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 13.1, 14.3, 21.6, 27.9, 28.2, 28.3, 28.7, 29.7, 29.7, 29.8, 30.7, 64.8, 66.9, 68.0, 68.7, 69.5, 69.8, 69.8, 69.9, 111.2, 114.2, 121.7, 121.7, 121.9, 124.0, 124.2, 126.2, 126.9, 127.6, 127.8, 127.9, 128.2, 135.8, 137.3, 137.5, 141.1, 141.2, 141.4, 142.0, 148.3, 151.8; \(M_n\) = 46,400, PDI>2
**Poly(23).** To a vial with a magnetic stirrer was added cyclophane (23) (96.5 mg, 0.1175 mmol, 1 equiv.) in 2.0 ml of 17:3 acetonitrile/chloroform solution. To the cyclophane solution was added a predissolved solution of nitrosonium hexafluoroantimonate (78 mg, 0.2939 mmol, 2.5 equiv.) in 0.9 ml of acetonitrile. Upon addition of a drop of the oxidant the reaction solution turns an intense blue color with solution species remaining soluble. After stirring for one day, the reaction was quenched with a 1.0 M solution of hydrazine in THF. The solution becomes red from blue with the evolution of heat and a white gas. The resultant orange film was dried yielding (90 mg, 93% conversion). EA: theoretical C_{46}H_{48}O_{10}S_{4}, 58.81C, 5.92H, 27.42O, 7.85S; actual 55.35C, 5.54H, 2.22N, 30.00O, 6.72S; \(^1\)H NMR (300 MHz, d$_6$-DMF); 6.68 (2H, brs, backbone aromatic protons), 6.22 (4H, brs, hydroquinol pendant), 4.55 (4H, brm, glycol protons), 4.29 (4H, brm, glycol protons), 3.5-4.1 (28H, brm, glycol protons).

**Poly(38).** To a vial with a magnetic stirrer was added [2]-catenane (38) (55.1 mg, 0.0287 mmol, 1 equiv.) in 0.6 ml of acetonitrile solution. To the cyclophane solution was added a predissolved solution of nitrosonium hexafluoroantimonate (16 mg, 0.0602 mmol, 2.09 equiv.) in 0.8 ml of acetonitrile. Upon addition of a drop of the oxidant the reaction solution turns an intense blue color with solution species remaining soluble. After stirring for one day, the reaction was quenched with a 1.0 M solution of hydrazine in THF. The solution becomes red from blue with the evolution of heat and a white gas. The crude product is then precipitated from hot methanol, and collected by filtration. The resultant orange film was dried yielding (50 mg, 91% conversion). EA: theoretical C$_{77}$H$_{84}$F$_{24}$N$_4$O$_{13}$S$_2$P$_4$, 48.23C, 4.42H, 23.78F, 10.85O, 3.34S, 6.46P; actual 46.00C, 4.60H, 3.67N,
13.49O, 2.69S; $^1$H NMR (300 MHz, d$_6$-DMF) 9.41 (8H; brs, α-pyridinium protons), 8.32 (8H, brs, β-pyridinium protons), 8.03 (8H, benzyl aromatic), 6.65 (2H, phenylene backbone protons), 5.98 (8H, brs, benzylic protons), 4.70 (4H, brm, glycol protons), 3.29-4.00 (28H, brm, glycol protons).

**Electrochemistry.** Electrochemical experiments were carried out at room temperature in a drybox with an Ecochemie Autolab PGSTAT10 multipurpose instrument interfaced to a personal computer. Interdigitated electrodes were fabricated with the following electrode dimensions: 2μm interdigit spacing, 99 interdigit gaps, 0.2005 cm electrode length and 0.04cm electrode width. The counter-electrode was a Pt wire, and the reference electrode was Ag wire/0.01M AgNO$_3$ in CH$_3$CN. All potentials are reported relative to an internal ferrocene standard. The concentration for the examined compounds was 5 mM in 0.1 M tetrabutylammonium perchlorate for 23 and 3 mM in 7:3 0.1M tetrabutylammonium perchlorate / 0.1 M tetrabutylammonium hexafluorophosphate for 38, in CH$_3$CN. Cyclic voltammograms and conductivity profiles were obtained at sweep rates of 50 mV/sec and 10 mV/sec respectively.

**Conductivity determination.** The conductivities of the polymer films were determined using the following equations:

\[
\sigma = \frac{i_d}{V_d} \cdot \frac{d}{N \cdot T \cdot L} \quad (1)
\]

\[
T = \frac{\Gamma M}{\rho} \quad (2)
\]

\[
\Gamma = \frac{Q_s}{n \cdot F \cdot A} \quad (3)
\]
σ: conductivity of the polymer film (S/cm = g cm² sec/ C²)

\( i_d \): measured drain current (A = C / sec)

\( V_d \): applied offset potential (0.04 V = g cm / C)

\( d \): interdigit spacing (2 x 10⁻⁴ cm)

\( N \): number of interdigit gaps (99)

\( T \): film thickness (cm)

\( L \): length of the electrode (0.2005 cm)

\( \Gamma \): surface coverage of the film (moles / cm²)

\( M \): molar mass of the polymer repeat unit (g / mol)

\( \rho \): density of the polymer film (g / cm³)

\( Q_+ \): charge deposited in the oxidative half-wave for the polymer film (C)

\( n \): number of electrons oxidized per polymer repeat unit

\( F \): Faraday's constant (96485.3 C / mol)

\( A \): area of the electrode (cm²)

The small interdigit gap did not allow for the direct measurement of polymer thickness \( T \). Therefore indirect calculations utilizing equations 2 and 3 were implemented. Starting from equation 3 with \( Q_+ = 4.291 \times 10^{-5} \) C and \( 8.884 \times 10^{-4} \) C with \( n = 1 \) and 2 for poly(38) and poly(23) respectively, \( \Gamma \) was calculated as \( 5.5 \times 10^{-8} \) and \( 5.7 \times 10^{-7} \) mol/cm².

The \( n \) value for poly(38) was obtained from the ratio of the integrated area for the polymer oxidation and the tetracation oxidation wave from the film cv. The \( n \) value was taken to be 2 for poly(23) which is reasonable for polythiophene based polymers.²⁵ Film thickness, \( T \), was calculated for poly(38) utilizing \( M = 1916 \) g/mol and a \( \rho = 1.44 \) g/cm³ obtained from the crystal structure giving \( 7.4 \times 10^{-5} \) cm. For poly(23) \( M = 816 \) g/mol and
\( \rho \) was estimated as 1.35 g/cm\(^3\) obtaining \( T = 3.5 \times 10^{-4} \) cm. The density for poly(23) was approximated from known values of Stoddarts\(^{3b}\) BPP34C10 macrocycle as 1.29 g/cm\(^3\), the corresponding [2]-catenane as 1.38 g/cm\(^3\) and the known density of [2]-catenane 38, assuming the polymer film obtains a similar crystalline packing arrangement. Applying equation 1 with \( i_d = 4.132 \times 10^{-6} \) and \( 1.784 \times 10^{-3} \) A obtained from conductivity profiles for poly(38) and poly(23), \( \sigma \) was determined as \( 1.42 \times 10^{-5} \) and \( 1.3 \times 10^{-3} \) S/cm respectively. In order to correct the conductivity to a known standard, poly(3-methylthiophene) films were grown on 2\( \mu \)m interdigitated electrodes. Furthermore, films were grown in both 0.1 M TBA ClO\(_4^\cdot\) and 7:3 (0.1 M TBA ClO\(_4^\cdot\) / 0.1 M TBA PF\(_6^\cdot\)) in order to normalize counter-ion effects. For the mixed electrolyte poly(3-methylthiophene) film \( Q_v = 1.056 \times 10^{-3} \) C with, \( \rho = 1.46 \) g/cm\(^3\), \( n \) taken as 2.25\(^{26}\) and \( M = 96 \) g/mol. From these values \( \Gamma \) was calculated as \( 6.1 \times 10^{-7} \) mol/cm\(^2\) and \( T = 4 \times 10^{-5} \) cm giving \( \sigma = 3.9 \times 10^{-3} \) S/cm from a measured \( i_d = 6.107 \times 10^{-4} \) A. For the TBA ClO\(_4^\cdot\) grown poly(3-methylthiophene) film \( Q_v = 1.798 \times 10^{-3} \) C, \( \Gamma = 1.0 \times 10^{-6} \) mol/cm\(^2\), \( T = 6.6 \times 10^{-5} \) cm, \( i_d = 1.87 \times 10^{-3} \) A, giving \( \sigma = 7.2 \times 10^{-3} \) S/cm. The relation used to correct the poly(38) and poly(23) conductivities follows as:

\[
\frac{\sigma_{\text{poly(23)}}}{\sigma_{\text{P3MT}}} \cdot 60 \text{ S/cm} = \sigma_{\text{poly(23)(corr.)}} \tag{37a}
\]

\[
\frac{\sigma_{\text{poly(38)}}}{\sigma_{\text{P3MT(mixed)}}} \cdot 60 \text{ S/cm} = \sigma_{\text{poly(38)(corr.)}} \tag{37b}
\]

were \( \sigma_{\text{P3MT}} \) and \( \sigma_{\text{P3MT(mixed)}} \) correspond to perchlorate and mixed counter-ion electrolyte conductivities. The value of 60 S/cm was obtained from the literature for poly(3-methyl thiophene) films grown in a manner similar to ours, with a single 20\( \mu \)m gap electrode.
insuring uniform film coverage.\textsuperscript{27} From the aforementioned values $\sigma_{\text{poly}(38)(\text{corr.})}$ and $\sigma_{\text{poly}(23)(\text{corr.})}$ can be calculated as ca. 0.2 and 11 S/cm respectively.

**Spectroelectrochemistry.** Spectroelectrochemical experiments were carried out in a cell consisting of quartz and an ITO glass (working electrode) window. The cell volume was 2 ml and supported a Pt wire counter and Ag wire reference electrode. The concentration for the examined compounds was 7 mM for 23 and 5 mM for 38 in 7:3 0.1M tetrabutylammonium perchlorate / 0.1 M tetrabutylammonium hexafluorophosphate in CH$_3$CN. The polymer films formed upon electropolymerization adhered to the ITO working electrode, which was rinsed three times with electrolyte solution, and then refilled with fresh electrolyte. Absorption spectra were obtained at 100 mV increments. UV-vis spectra were obtained on a Hewlett-Packard 8453 diode array spectrophotometer.

**X-ray Crystallography.** X-ray crystals suitable for study were grown by vapor diffusion of CH$_2$Cl$_2$ into a solution of 38 in CH$_3$CN at 20$^\circ$C. Crystal data, data collection, and structure refinement for 38: empirical formula C$_{80}$H$_{90}$F$_{24}$N$_6$O$_{14}$P$_4$S$_2$, $M_r = 2003.58$, orthorhombic, space group Pccn, $a = 17.51110(10)$ Å, $b = 19.4321(2)$ Å, $c = 27.1684(5)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 9244.8(2)$ Å$^3$, $Z = 4$, $\rho_{\text{calc}} = 1.440$ Mg/m$^3$. Crystal of size 0.38 x 0.12 x 0.12 mm. Seimens SMART/ CCD diffractometer. Temperature 163(2) K, $\lambda$ = 0.71073 Å. Monochromator: graphite. $\theta$ range for data collection: 1.50 to 20.00°. The structure was solved by direct methods and refined by full-matrix least squares on $R^2$; 25221 reflections collected of which 4320 ($I > 2\sigma(I)$) were classified as observed. Programs used: SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997). Goodness-of-fit on $F^2$: 1.356. Final $R$ indices [$I > 2\sigma(I)$]: R1 = 0.1556, wR2 = 0.2861. R
indices (all data): $R_1 = 0.1659$, $wR_2 = 0.2919$. Largest difference peak and hole: 0.399 and $-0.384 \text{ eÅ}^{-3}$. 
3.5. References


(13) Electrodes were fabricated having the following dimensions: 2µm interdigit spacing, 99 gaps, 0.2005 cm electrode length and 0.04 cm electrode width.


(15) Non-uniform film coverage on the interdigitated electrodes required a correction factor in the form of a poly(3-methylthiophene) standard to be applied to the conductivity values calculated (see Kingsborough, R. P.; Swager, T. M. *Adv. Mater.* **1998**, *10*, 1100).


Appendix. NMR Spectra
Spectrum 3.2. $^{13}$C NMR of [2]catenane 38 in CD$_3$CN.
Spectrum 3.3. $^1$H NMR of [2]-catenane 39 in CD$_3$CN.
Spectrum 3.4. $^{13}$C NMR of [2]-catenane 39 in CD$_3$CN.
Spectrum 3.5. $^1$H NMR of poly(21a) in CDCl₃.
Spectrum 3.6. $^{13}$C NMR of poly(21a) in CDCl$_3$. 
Spectrum 3.7. $^1$H NMR of poly(21b) in CDCl$_3$. 
Spectrum 3.8. $^{13}$C NMR of poly(21b) in CDCl$_3$. 

Poly (21b)
Spectrum 3.9. $^1$H NMR of poly(23) in d$_6$-DMF.
Spectrum 3.10. $^1$H NMR of poly(38) in $d_6$-DMF.
Chapter 4

Strategies and Efforts Toward the Synthesis of Poly(Rotaxanes)
4.1 Introduction

In the previous chapters, the electronic properties of crown ethers, [2]-catenanes 38, 40, and poly(38) were probed in order to gain insight into the efficacy of charge transport in donor-acceptor based systems. The crown ether:paraquat complexes achieved a pseudorotaxane architecture consisting of a localized donor/localized acceptor relationship, allowing for the quantification of binding affinities. An extension of this base interaction was achieved in the synthesis of poly(38), consisting of a delocalized-donor polymer and a localized, non-covalently bound acceptor. The next generation of donor-acceptor assemblies was envisioned to arise from poly(rotaxane) architectures consisting of non-covalently bound strands of localized and delocalized polymers, Figure 4.1. As witnessed for [2]-catenanes, rotaxanes allow for unidirectional electron migration, an antenna effect, resulting in the transferal of electrons to a specific component within a molecule.¹

![Localized-Donor, Localized-Acceptor Model](image)

- Charge-transfer state involves intimately associated ion-pair.
- Model system for investigating charge-transfer mechanism, most simplistic.

![Delocalized-Donor, Localized-Acceptor Model](image)

- Charge-transfer state is intermediate between the two models.

![Delocalized-Donor, Localized or Delocalized-Acceptor](image)

- Charge-transfer state is localized or delocalized over diffuse polymer bands.

![Two Strand Delocalized-Donor, Localized or Delocalized-Acceptor](image)

- Charge-transfer state is localized or delocalized over diffuse polymer bands.

Figure 4.1. The donor-acceptor complex variants under investigation.
Each architecture will be expected to exhibit unique electronic properties dependent on the conjugation or lack of conjugation of the donor and acceptor components. The ability to chemically or electrochemically oxidize the donor constituent would allow for the assessment of macromolecular displacement via electrostatic repulsion, resulting in a change in volume. This reversible phenomena is expected to give rise to an effect analogous to muscle expansion and contraction. In the two-strand delocalized donor case, extraction of the acceptor polymer would give rise to an ion-channel type architecture.

4.1.1 Synthetic strategies

From previous studies it was found that crown ethers form complexes with electron-deficient aromatics such as paraquat and derivatives thereof. Qualitative tests indicate that increases in temperature lead to loss of the intense charge-transfer coloration characteristic of such complexes. This dethreading effect\(^2\) is also experienced when the crown ether is oxidized electrochemically, Figure 4.2.

![Graph and molecular structures](image)

**Figure 4.2.** Decomplexation of a 1:1 mixture of 23 and 35. (0.1M TBAP in CH\(_2\)CN, 50mV/sec)
A solution containing a 1:1 ratio of crown ether 23 and paraquat diol 35 was subjected to electrochemical oxidation/reduction, leading to the growth of pcy(23). The growth is accompanied by a shift in the reduction potentials of 35 toward its uncomplexed potentials, indicating it is becoming easier to reduce. The decrease in current for the reduction of 35 is attributed to its diffusion away from the electrode leading to the dominance of 23’s redox behavior. The synthesis of a localized-donor/localized-acceptor architecture cannot be realized via electrochemical or chemical polymerization means as the acceptor is ejected upon oxidation of 23 or reduction of 35. In order to maintain the integrity of the 1:1 nature of the complex, 35 was utilized in the synthesis of acceptor containing copolymers via condensation polymerization, Scheme 4.1.

Scheme 4.1. Polymerization of diol 35 forming electron-deficient polymers 40 and 41.

It was proposed that for polymeric acceptors chain entanglement might aid in keeping the crown ether receptor from being ejected into solution. The syntheses of 40 and 41 are straightforward, involving the addition of nucleophile 35 to either adipoyl chloride or 4,4'-methylenebis(phenyl isocyanate). Both polymers decompose upon injection onto a GPC column, however the broadness of the $^1$H NMR and virtual lack of end-groups
support a polymeric structure. A solution of an excess of polymer 40 and crown ether 15 was subjected to electrochemical redox cycling leading to a similar decomplexation effect found for 23-35, Figure 4.3. The decrease in the reduction potential and current for 40 is accompanied by a shift in oxidation potential of 15 to higher potentials. The slow shift in potential for the oxidized 15 (as well as oligomers of 15) with cycling indicates the decomplexation rate is slower for the polymeric acceptor than the molecular acceptor.

The lack of complete complexation of crown ether receptors with polycarbamate or polyester based acceptors, has been reported by Gibson and co-workers. The best crown ether loading ratios are obtained with either decomplexation blocking end-groups, or very large crown ethers such as 60Crown20. Stoichiometric complexation in Gibson’s acceptor polymeric systems was not obtained because of the limitations of the binding strength of the crown ether BPP34C10, 9. The synthesis of larger crown ethers in this work is out of the question because of the diminished binding constant and the reliance on statistical threading. Further attempts at synthesizing rotaxanes was then focused on incorporating dethreading hindering end-groups.

**Figure 4.3.** Decomplexation of 15 from polymer 40 upon oxidation of 15. (0.1M TBAP in CH₃CN, 50mV/sec)
The incorporation of localized acceptors into polymeric systems is straightforward as evidenced by the synthesis of polymers \( 40 \) and \( 41 \). Interest also focused on the synthesis of electron-deficient conjugated polymers such as poly(methylpyridine-vinylene) (PMePyV). Figure 4.4. The synthesis of the random, head-to-tail, and head-to-head regioisomers were synthesized by Fu, Marsella, and Swager. The reduction of the head-to-tail form of PMePyV leads to an open-shell, non-Kekule form, while the head-to-head version gives rise to an quinoid-type structure. Conductivity measurements supported a >100 fold increase in conductivity for the open-shell reduced head-to-tail PMePyV, and is an attractive target as a rotaxane acceptor thread.

![Poly(methylpyridine-vinylene) isomers and their reduced forms.](image)

**Figure 4.4.** Poly(methylpyridine-vinylene) isomers and their reduced forms.

The limited solubility of PPyV’s and PMePyV’s has limited attempts to purify and process these polymers. Efforts by the author of this thesis were devoted to enhancing the solubility of these polymers via monomer and polymer modifications, Scheme 4.2.

![Scheme 4.2. Further attempts at enhancing the solubility of poly(pyridine-vinylene)’s.](image)
The synthesis of head-to-tail PMePyV involves the selective Stille\textsuperscript{5} coupling of a vinyl group in the 2-position of \textbf{42} followed by a Heck\textsuperscript{6} reaction. Methylation is then undertaken via heating the polymer in neat methyl triflate at 40°C. The alkylation does not proceed to completion due to the limited solubility of the precursor PPyV. In order to enhance the solubility of PMePyV and ensure 100% alkylation pyridine derivative \textbf{42} was methylated and ion exchange was undertaken. Attempts at the selective coupling of a vinyl group in the 2-position gave only a complex mixture of products. This result is attributed to the highly electron-deficient nature of \textbf{43}, leading to the decomposition of any vinyl substituted product.

The methylation of random PPyV \textbf{44} (obtained from Dr. D.K. Fu), was attempted under the more forceful conditions at 100°C in a sealed vessel with neat methyl triflate. The \textsuperscript{1}H NMR of the purified and soluble fraction of polymer \textbf{45} is detailed in Figure 4.5 (center). The random nature of the polymer is evidenced by the distribution of aromatic absorptions between 7 and 9.5 ppm. The deshielded nature of the polymer is apparent by the downfield shift relative to neutral pyridine derivatives. The peaks at 4.5ppm correspond to differing methyl group environments in the polymer, most likely arising from end-groups. Upon addition of a pentaethylene glycol crown ether, the methyl absorption becomes shielded (<4.5ppm) and the glycol region for the receptor broadens. This broadening is attributed to the decreased conformational flexibility of the crown ether when complexed. The same broadening effect is witnessed for the crown ether aromatic region. From the \textsuperscript{1}H NMR analysis it can be concluded that large cavity crown ethers can thread through PMePyV polymers. The limited solubility of PMePyV and low
molecular weight however, limits its utility in the fabrication of rotaxanes with well defined structures.

![Diagram of molecular structure]

Figure 4.5. $^1$H NMR spectra of: thiophene derivatized crown ether, random PMePyV, and a mixture of both donor and acceptor.

In response to the solubility challenges for PMePyV, the synthesis of poly(1,4-pyridiniums) (PPy$^+$) was begun. The reduced form of PPy$^+$ gives rise to an open shell non-Kekule form similar to that found for head-to-tail PMePyV, Figure 4.6.

\[
\begin{align*}
\text{Non-Kekule} & \quad 2(n-1)\text{e}^- \\
\text{Non-Kekule} & \quad n-1
\end{align*}
\]

Figure 4.6. Reduction of poly(1,4-pyridinium) to its non-Kekule form.
The synthesis of PPy\textsuperscript{+} has been reported by a several research groups.\textsuperscript{7} Their attempts failed to obtain high polymers and only conceived a myriad of oligomeric and molecular products. The polymerization was first attempted under the standard conditions A in Scheme 4.3. The 4-bromopyridine hydrobromide salt is deprotonated with aqueous sodium carbonate (KOH is also utilized). The resulting 4-bromopyridine is stable for short periods of time in its solid form; above 9°C the melted solid spontaneously "polymerizes" giving a multi-colored solid substance. The melting was thwarted by extraction of the bromopyridine in a sub-zero environment followed by careful drying with sodium sulfate. The pure pyridine is then dissolved in acetonitrile and tetrabutylammonium hexafluorophosphate (TBAP), and warmed to room temperature.

\begin{center}
\begin{equation}
\text{Scheme 4.3. Synthesis of poly(1,4-pyrindinium)\textsubscript{s} via deprotonation.}
\end{equation}
\end{center}
Method A gave only low molecular weight product in accordance with literature reports. Efforts were then devoted to eliminating the need to deprotonate the bromopyridine salt with aqueous base, as traces of water can aid in monomer and polymer decomposition. Method B utilizing Hunig’s base (diisopropylethyl amine) did not improve the extent of polymerization as evidenced by complex $^1$H NMR spectra. The third method C involved the careful isolation of the intermediate bromopyridine and reaction in CH$_3$CN in an ion exchange medium, while method D incorporated small amounts of methyl iodide as an ‘initiator’. Both attempts however, did not improve upon the distribution of products found previously. In a final effort, method E, tetraphenylborate counter-ion was added to the reaction as an organic solubilizing agent. The polymerization proceeded with the formation of a blue product that was just as polydisperse as previous attempts. The blue color arose from a charge-transfer interaction between the pyridinium nitrogen and the tetraphenylborate counter-ion and was deemed potentially competitive if utilized to bind crown ethers.

\[
\begin{align*}
\text{Br-} & \text{N-O} \quad \xrightarrow{\text{Ph$_2$PCLI or PB$_3$}} \quad \text{Br-} \left[ \begin{array}{c}
\text{N}^+ \\
\text{nPF}_6
\end{array} \right] \\
\text{CH$_3$CN/TBAP} & \quad \Delta \\
\text{Br-} & \text{N-O} \quad \xrightarrow{\text{Ph$_2$PCLI or PB$_3$}} \quad \text{Br-} \left[ \begin{array}{c}
\text{N}^+ \\
\text{nB(Ph)$_4$}
\end{array} \right] \\
\text{THF/NaB(Ph)$_4$} & \quad \Delta
\end{align*}
\]

Scheme 4.4. Synthesis of poly(1,4-pyridinium) via deoxygenation.

The chloropyridine hydrochloride was also utilized as a monomer because of the improved displacement of chloride in aromatic substitution reactions. These polymerizations however, failed in producing high polymer let alone higher oligomers.
The commercially available N-oxide derivatives, Scheme 4.4, were then utilized as in-situ deoxygenation/polymerization monomers. Interestingly, the polymerization gave an improved yield of higher oligomer as determined by $^1$H NMR, though high polymer was never obtained. The improved yield can be attributed to the limited exposure of the intermediate to moisture and air. The oligomeric products do decompose upon standing in air as evidenced by color changes and increased complexity in the $^1$H NMR. The phosphorous based side products are difficult to remove, and careful workup is required so as not to decompose the oligomer.

Previous attempts at forming rotaxane architectures made clear that the linear portion of the rotaxane must be synthesized such that it can be well defined, support crown ethers in a 1:1 donor/acceptor ratio, and hinder any desire for crown ether decomplexation. The tetraphenylmethane end group introduced by Stoddart as an anti-dethreading agent provided part of the answer to this dilemma, Figure 4.7.  

![Figure 4.7. End-groups for hindering dethreading as studied by Stoddart.](image-url)
The end-group allows threading at 55°C to occur for R = H, methyl, or ethyl. Isopropyl and t-butyl groups hinder complexation even at elevated temperatures and will not thread unless subjected to ultra-high pressures of 12kbar. Once the crown ether complexed with the linear ‘axle’, dethreading occurs at 100°C in DMSO only for R=H, methyl or ethyl. Stoddart’s end-groups were then utilized in the synthesis of linear electron-deficient threads, and were subsequently tested with substituted crown ethers, Scheme 4.5.

Scheme 4.5. End-group synthesis and functionalization.

The synthesis of the ‘axle’ has been modified from Stoddart’s version and is one step shorter. The addition of 2equiv. of t-butylphenyl magnesium bromide to ester 46, yields the triphenyl carbinol 47. This end-group with R=H, will aid in determining whether the more sterically demanding substituted crown ethers can thread onto the end-group with the smallest energy barrier. Nucleophilic aromatic substitution on the carbocation derived from 47 with phenol, followed by KOH deprotonation gives the potassium salt 48.
Alkylation of 48 with chloroethoxyethoxyethanol yields the alcohol 49. The alcohol is then converted to the tosylate 50 for subsequent 4,4’ bipyridine alkylation, Scheme 4.6.

Scheme 4.6. One-pot synthesis of rotaxane 51.

The alkylation of 4,4’-bipyridine was accomplished in the presence of crown ether 23, giving rotaxane 51 in poor yields. The low yield is attributed to the difficulty in isolation via column chromatography. Stoddart’s conditions for eluting rotaxanes of this genre did not elute 51. The purple band consisting of 51 was scraped off the column, dissolved in methanol/water, ion-exchanged, filtered, and washed. The low yield could also arise from the more sterically encumbered 23 relative to 9. The 1H NMR for this compound is consistent with a 1:1 donor/acceptor binding ratio. A solution of 51 in CH3CN was heated in a sealed tube up to 80°C without the loss of the charge-transfer coloration, proving that dethreading upon heating does not occur readily.
Efforts were then focused on synthesizing the most sterically demanding end-group, in order to ascertain whether crown ether 23 could form a complex as with 51.

\[
\text{Scheme 4.7. Per t-butyl end group synthesis and functionalization via Stoddart's approach.}
\]

The conditions for the synthesis of the fully t-butylated end-group is identical to that for 50, Scheme 4.7. The inclusion of the extended aromatic alcohol in 57 is expected to enhance binding of crown ethers by creating a π-extended scaffold, Scheme 4.8. The rotaxane synthesis proceeds from 57 by conversion to the benzyl chloride 58.
Scheme 4.8. Further functionalization of per t-butyl end group.

The alkylation of chloride 58 with 4,4'-bipyridine yields 'axle' 59 in 5-10% yield, Scheme 4.9. Threading of 59 with crown ether 23 does not occur even upon heating, as expected for this large end-group. Scheme 4.10.

Scheme 4.9. Final step in the synthesis of Stoddart's rotaxane "axle".
Scheme 4.10. Attempt at forming a rotaxane with crown ether 23 and “axle” 60.

The high energy for threading required of the fully t-butyalted end-group, makes it the choice barrier for use in forming rotaxanes. The energy gain by complexing crown ether 23 coupled with the large barrier for dethreading, would likely thwart electrochemically motivated, oxidative decomplexation.

Scheme 4.11. Steps toward the synthesis of poly(pyridine-vinylene) end capped “axles”.

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To this end, the t-butyl end-group was envisioned to be incorporated into a conductive, electron-poor, PMePyV oligomer. The synthesis of a π-extended, head-to-head PMePyV repeat ‘axle’ via Heck coupling of 61 with pyridine 42, did not afford the coupled product, only starting materials were isolated, Scheme 4.11. A one pot synthesis of the head-to-head isomer was implemented via the phenyl bromide end-group 63, bis-stannyl ethylene, and head-to-head precursor 64. Thin layer chromatography of this reaction led to a myriad of products that overlapped considerably by chromatography, Scheme 4.12.

![Scheme 4.12. Random distribution synthesis of poly(pyridine-vinylene) with end-groups.](image)

A more methodical approach was undertaken via the synthesis of bromopyridine derivative 65, and coupling it to alcohol 55 under Mitsonobu\(^10\) conditions, Scheme 4.13.
Scheme 4.13. Improved synthesis of poly(pyridine-vinylene) "axle" 67.

The Stille coupling with 2.05 equiv. of 66 with bis-stannylenethylene and Pd$^0$ afforded the head-to-head axle repeat 67 in 35% yield. Methyl iodide was chosen as the alkylating agent for 67 because of the potentially sensitive ester linkages. The alkylation of 67 in neat CH$_3$I only converts one of the pyridine units to the pyridinium salt, Scheme 4.14. Furthermore, the semi-alkylated specie is blue-green in color indicating that it may exist in a quinoidal form. The electron-poor nature of the pyridine rings before alkylation may limit the extent of alkylation of this specie, and re-engineering of this linkage to a more electron-rich group may be necessary.
Scheme 4.14. Attempt at methylating 67 the pyridine-vinylene repeat "axle".

4.2 Conclusion

Electrochemical studies on donor-acceptor complexes indicate that decomplexation occurs readily upon oxidation of the donor or reduction of the acceptor. Higher-order architectures consisting of polymeric, localized-acceptors and complexed donor crown ethers also lose their integrity upon redox cycling. Studies by Gibson indicate that higher incorporation of crown ethers in electron-deficient polymers occur when large endgroups are used to semi-reversibly block crown ethers from dethreading.

Electron-deficient conjugated polymers such as poly(methylpyridine-vinylene)'s and poly(1,4-pyridinium)'s were found to be of limited use due to poor solubility, low degrees of polymerization, and high polydispersities. As an alternative, a molecule-up approach was proposed consisting of the synthesis of controlled and defined molecular-acceptor repeat architectures, utilizing large dethreading hindering end-groups.
The synthesis of rotaxane 51 proved that crown ether 15 can complex and hence form a rotaxane with thread 50. Heating of this rotaxane to 80°C does not lead to decomplexation attesting to the robust nature of the architecture. Attempts at threading crown ether 23 through axle 59 does not lead to the formation of rotaxane 60, because of the large barrier for threading associated with the end-groups in 59. The fully t-butyalted end-groups are expected to give rise to extremely robust rotaxanes capable of surviving electrochemical redox processes. In order to form a rotaxane with 59, high pressures of 12kbar are required.

In pursuit of conjugated electron-poor thread polymers, a number of syntheses were devoted to functionalizing the end-groups with halopyridines. The halopyridines would then be coupled via Stille or Heck reactions forming dimers, trimers, etc. An acryloyl based end-group was subjected to Heck conditions for selective coupling with pyridine 42. This reaction failed to give products and only the starting materials were isolated. The all or nothing approach in Scheme 4.12, yielded a veritable cocktail of products with a high degree of overlap as determined by thin layer chromatography. The most promising synthesis of a PMePyV based thread was outlined in Schemes 4.13 and 4.14. The thread 67 was produced in good yields, but failed to alkylate at both pyridines. In order to enhance the degree of alkylation, more electron-rich substituents should be incorporated in the pyridine linkage with the end-group.

4.3 Experimental

General Methods. Air- and moisture-sensitive reactions were carried out in oven-dried glassware using standard Schlenk line techniques under an inert atmosphere of dry argon.
All chemicals used were of reagent grade or better and were purchased from Aldrich unless otherwise noted. Anhydrous NMP was used directly from Aldrich Sure-Seal bottles. Anhydrous CH$_2$CN was prepared by a literature procedure involving activated alumina and CaH$_2$. Compounds 47, 48, 49, 50, 53, 54, 55, 56, 57, 58, 59, $^8$ 64 were prepared according to literature procedures. $^1$H NMR, and $^{13}$C NMR were acquired with a Mercury 300 spectrometer and were taken in CDCl$_3$, and CD$_3$CN with $^1$H chemical shifts reported relative to internal tetramethylsilane (0.00 ppm) and $^{13}$C chemical shifts reported relative to CDCl$_3$ (77.23 ppm) and CD$_3$CN (1.39 ppm). Thin-layer chromatography (TLC) was performed on cut glass slides (2.5 x 5 cm) coated with Merck 5715 Kieselgel 60F. Developed plates were air-dried, scrutinized under a UV lamp and, if necessary, developed in an iodine tank. Baker 7024 (40μm mesh) silica gel was used to perform flash column chromatography. Fast atom bombardment mass spectroscopy (FABMS), using a xenon primary atom beam in conjunction with a 3-nitrobenzyl alcohol matrix was preformed on a Finnigan MAT 8200. Melting points were determined using a Thomas Moore capillary melting point apparatus and are uncorrected.

**Polymer (40).** To a 10ml Schlenk tube was added 35 (1.01g, 1.88mmol) was dissolved in 7ml of dry acetonitrile. The solution was degassed and adipoyl chloride (0.223g, 1.92mmol) was added. Dry triethylamine (0.3ml, 4.3mmol) was added to promote acid scavenging. After overnight stirring the reaction solution was precipitated from MeOH. The off-white precipitated solid was then collected yielding 300mg of polymer. $^1$H NMR (300 MHz, CD$_3$CN) δ (ppm) 8.94-8.96 (d, J = 6Hz), 8.44-8.46 (d, J = 6Hz), 4.89 (s), 4.52(s), 2.32 (s), 1.51 (s); $^{13}$C NMR (300 MHz, CD$_3$CN) δ (ppm) 24.7, 33.9, 61.7, 63.1, 128.2, 147.3, 151.5, 173.7
**Polymer (41).** To a 25ml Schlenk flask with magnetic stirring under an atmosphere of argon was added 35 (1.00g, 1.87mmol) and 4,4'-methylenebis(phenylisocyanate) (0.5g, 2.00mmol) in 5ml of dry acetonitrile. The yellow solution was stirred and heated to 95°C for two days. After two days the yellow solution was precipitated into 400ml of MeOH. The solid precipitated can be characterized as a yellow fibrous solid. The solid was then redissolved in MeCN, and reprecipitated. The yellow fibers were then collected yielding 1.4g of polymer. $^1$H NMR (300 MHz, CD$_3$CN) δ (ppm) 8.94-8.95 (d, $J = 4.2$Hz), 8.39 (s), 7.85 (s), 7.25-7.28 (d, $J = 8.1$Hz), 7.08-7.10 (d, $J = 8.1$Hz), 4.91 (s), 4.58 (s), 3.81 (s), 3.67 (s); $^{13}$C NMR (300 MHz, CD$_3$CN) δ (ppm) 41.0, 62.0, 63.6, 119.9, 127.9, 128.1, 130.2, 137.2, 137.9, 147.4, 151.3, 153.6

**PMePyV (45).** PPyV (0.8121g) was obtained from Dr. D-K. Fu. The orange-brown solid was Soxhelet extracted for 3 days with chloroform. The solid was then further extracted with methanol for another three days. The resulting polymer (0.2554g) was dried under vacuum for two days. The solid was then added to methyltriflate (50g, 0.305mol) and was heated 70-80°C for three days in a sealed tube. After three days the excess triflate was distilled off yielding a fluorescent green solid that is soluble in MeCN (0.35g)$^1$H NMR (300 MHz, CD$_3$CN) δ (ppm) 8.2-9.3 (brm), 7.6-8.0 (brm), 4.55 (s), 4.45(s), 4.35(s)

**Poly(1,4-pyridinium) tetraphenylborate, Method D.** To a separatory funnel was added degassed water chilled to near freezing and bromopyridine hydrochloride (2.00g, 10.3mmol) was dissolved. To this solution was added chilled and degassed 2M KOH, and the free base was extracted with diethylether. The organic layers were separated and washed 2x with chilled H$_2$O and dried at -40°C with MgSO$_4$. The MgSO$_4$ was filtered off and the resulting solution was added to an oven-dried 200ml Schlenk flask with
molecular sieves. The solution was then subjected to vacuum at -78°C where the ether was allowed to evaporate over 24hrs. The sieves where then filtered off and the resulting liquid was distilled into another Schlenk flask equipped with stirring. The liquid was further subjected to vaccum until crystalline 4-bromopyridine was isolated. To this solid 40ml of dry THF and sodium tetraphenylborate was added. The reaction solution was heated to 65°C. Upon heating the solution color became yellow then orange and finally a dark green-blue color. The reaction was allowed to continue to stir at this temperature for two days. The reaction was then filtered, and the resulting solution was precipitated from petroleum ether. The solution was filtered and dried in a dessicator under high vacuum. After one day of drying the blue solid was reprecipitated from pet ether yielding a blue solid. The solid quickly changes color from blue to brown-red and even green if left in air. 80% yield with respect to NaBr isolated. (1.5g)\(^1\)H NMR (300 MHz, CD\(_3\)CN) \(\delta\) (ppm) 8.1-9.5 (brm), 7.8-8.0 (brm), 7.0-7.8 (brm), 6.7-6.8 (m), 4.8 (brs)

**Poly(1,4-pyridinium) hexafluorophosphate, N-oxide method.** To a 10ml Schlenk flask with magnetic stirring and \(N_2\) purge was added 4ml of dry MeCN, bromopyridine N-oxide (0.4003g, 2.3mmol), and sodium hexafluorophosphate (0.3879g, 2.31mmol). The solution was cooled to 0°C and phosphorous tribromide (219\(\mu\)l, 2.3\(\mu\)mol). The solution became yellow upon addition of the PBr\(_3\) and a fine white precipitate formed. The solution was then heated to 50°C. After three days of heating the reaction was cooled and filtered under \(N_2\). The solvent was removed in-vacuo and after two days a light orange solid was isolated (0.38g) \(^1\)H NMR (300 MHz, CD\(_3\)CN) \(\delta\) (ppm) 13.9 (brs), 9.4(brs), 8.5(brd), 8.2(brd); \(^{13}\)C NMR (300 MHz, CD\(_3\)CN) \(\delta\) (ppm) 123.0, 127.0, 137.0; \(M_n=\) 2500 by isolated NaBr.
**Rotaxane (51).** To a 5ml solution in a 20ml Schlenk flask was added 56 (0.2g, 0.272mmol), 4,4'-bipyridine (21mg, 0.1327mmol), and crown ether 23 (1.1g, 1.327mmol). This solution was refluxed and over time became progressively darker in color indicating that complexation occurred. After two days the reaction solution was rotary evaporated yielding a crude mixture of solids. The solids were subjected to silica gel chromatography (MeOH/2N aq. NH₄⁺Cl/MeNO₂ (7:2:1)). This cocktail of solvents removed impurities but failed to remove the product. The dark band on the column was then scraped off, dissolved in MeOH/sat aq. NH₄⁺Cl. The solution was rotary evaporated yielding a dark solid that was collected by filtration. (16mg, 5% yield) FABMS 2390 [M]+; 1H NMR (300 MHz, CD₃CN) δ (ppm) 8.6-8.65 (d, J = 12.5Hz, 4H), 7.65-7.70 (d, J = 12.5 Hz, 4H) 7.1-7.4 (m, 32H), 6.7-6.8 (d, J = 9Hz, 4H), 6.45 (s, 2H), 6.05 (s, 4H), 3.5-4.5 (m, 56H), 1.2-1.4 (s, 36H)

**Acryloyl end-group (61) To a 25ml pear-shaped flask with magnetic stirring was added 55 (1.5346g, 2.4094mmol), 15ml of methylene chloride, and Hunig’s base (0.63ml, 0.467mol). The reaction was stirred for 5min. whereupon acryloy chloride (0.294ml, 3.6mmol) was added leading to exothermic reaction. To the reaction solution was added a sodium bicarbonate solution in order to neutralize and hydrolyze any remaining acid chloride and acid. The biphasic mixture was extracted with sodium bicarbonate (2x20ml), followed by extraction with a saturated NaCl solution. The organic phase was dried with sodium sulfate, filtered and rotary evaporated yielding a brown white solid. The solid was recrystallized from hexanes yielding a white solid. (1.1041g, 66%yield). FABMS 713 [M+Na]+; 1H NMR (300 MHz, CDCl₃) δ (ppm) 7.21-7.24 (m, 6H), 7.05-7.09 (m, 6H), 6.76-6.79 (d, J = 9Hz), 6.447-6.451 (dd, J = 1.2Hz), 6.389-6.393 (dd, J = 1.2Hz), 6.16-
6.19 (dd, J = 10.2Hz), 6.10-6.13 (dd, J = 10.2Hz), 5.82-5.83 (dd, J = 1.8Hz), 5.787-5.792 (dd, J = 1.5Hz), 4.30-4.33 (m, 2H), 4.09-4.12 (t, 2H), 3.83-3.86 (t, 2H), 3.68-3.77 (m, 6H), 1.30 (s, 27H); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ (ppm) 31.6, 34.5, 63.2, 63.9, 67.4, 69.4, 70.0, 70.9, 71.0, 113.2, 124.3, 128.5, 130.9, 131.3, 132.4, 140.0, 144.3, 148.5, 156.7, 166.4

**Phenyl bromide end-group (63)** To a solution of refluxing 4-bromophenol (0.2430g, 1.404mmol), potassium carbonate (0.399g, 2.528mmol), and 25ml of dry DMF was added 56 (1.00g, 1.264mmol). The reaction was allowed to stir at reflux for 2 days. After two days water was added to the cooled reaction and the precipitated was collected. The white solid was washed with water and dried under vacuum. The solid was then recrystallized from hot hexanes yielding a white solid (1.00g, 99%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ (ppm) 7.30-7.33 (dd, J = 8.7Hz, 2H), 7.20-7.23 (d, J = 8.4Hz, 6H), 7.06-7.09 (d, J = 8.4Hz, 8H), 6.75-6.78 (d, J = 8.7Hz, 4H), 4.04-4.08 (m, 4H), 3.82-3.85 (m, 4H), 3.73 (s, 27H); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$ (ppm) 31.6, 34.5, 63.2, 67.3, 67.8, 69.9, 70.0, 71.0, 71.1, 113.2, 113.2, 116.6, 124.2, 130.9, 132.4, 132.4, 139.9, 144.3, 148.4, 156.7, 158.0

**Bis (tributylstanny)ethylene.** Procedure taken from J. Chem. Soc. Perkin Trans. I, 1993, 1657. Purification undertaken as per JOC 56, 16, 1991, 4985.FABMS 626 (M+Na)$^+$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ (ppm) 6.92 (s, 2H), 1.49-1.59 (m, 8H), 1.28-1.40 (m, 8H), 0.89-1.28 (m, 10H); $^{13}$C NMR (300 MHz, CDCl$_3$) $\delta$(ppm) 9.9, 14.0, 27.6, 27.8, 29.5, 31.0, 153.2
Bromopyridine ester end-group (66) To 20ml Schlenk flask with magnetic stirring was added 55 (2.5g, 3.925mmol) and triphenylphosphine (1.05g, 4mmol) to a CH₂Cl₂/Et₂O solution. To this solution was added a solution of DEAD (0.6836g, 3.925mmol) and pyridine 65 (1.5858g, 7.85mmol). The reaction was allowed to stir for three days whereupon the reaction was rotary evaporated yielding a crude white solid. The solid was subjected to silica gel chromatography (15% acetone/85% hexanes) gave the product as a white solid. (1.4g, 45% yield). ¹H NMR (300 MHz, CDCl₃) δ (ppm) 8.98 (s, 1H), 8.06-8.09 (d, J = 8.1Hz, 1H), 7.43-7.46 (d, J = 8.4Hz, 1H), 7.19-7.22 (d, J = 7.8Hz, 6H), 7.07-7.1 (d, J = 8.1Hz, 8H), 6.71-6.74 (d, J = 8.4Hz, 2H); ¹³C NMR (300 MHz, CDCl₃) δ (ppm) 31.5, 34.3, 63.1, 64.7, 67.2, 69.0, 69.8, 70.7, 70.8, 113.1, 124.1, 125.3, 128.1, 130.8, 132.3, 139.3, 139.8, 144.2, 146.9, 148.2, 151.5, 156.5, 164.5

Head-to-Head PPyV axle (67) To a sealed tube with magnetic stirring was added 66 (0.994g, 1.19mmol) and bis-tributylstannylethylene (0.3512g, 0.5794mmol) in 7ml of dry NMP. The mixture was evacuated and purged with argon before it was transferred to a glove box and Pd[Ph₃P]₄ (7mg, 0.005938mmol, 1 mol%) was added. The reaction was stirred overnight at 110°C. After 16hrs. water was added to the reaction and the solid was dissolved in methylene chloride. The methylene chloride layer was extracted with sat. KF solution, was collected, dried with MgSO₄ and filtered. The organic phase was evaporated yielding a solid that was subjected to silica gel chromatography (20% acetone, 80% hexanes) yielding 200mg of a yellow solid (35% yield). ¹H NMR (300 MHz, CDCl₃) δ (ppm) 9.25 (s, 1H), 8.25-8.27 (d, J = 7.8Hz, 2H), 7.83 (s, 2H), 7.38-7.41 (d, J = 8.1Hz, 2H), 7.19-7.22 (d, J = 8.4Hz, 12H), 7.07-7.09 (d, J = 8.7Hz, 16H), 6.73-6.76 (d, J = 9Hz, 4H), 4.51 (brs, 4H), 4.07 (brs, 4H), 3.84-3.85 (brs, 8H), 3.73 (brs, 8H), 218
1.28 (s, 54H); $^{13}$C NMR (300 MHz, CDCl$_3$) δ (ppm) 31.4, 34.2, 49.3, 63.0, 64.4, 67.1, 69.1, 69.8, 70.7, 70.8, 113.0, 124.0, 130.7, 132.2, 133.2, 137.9, 139.7, 144.1, 148.1, 151.1, 156.5, 158.0, 165.0, 174.9

**Monoiodo-Head-to-Head PPyV axile (68)** To a vial was added 67 (135mg, 0.09mmol) in neat methyl iodide with magnetic stirring. The reaction was allowed to stir overnight where it became a green-blue color that progressed in intensity over time. After several days the solution was rotary evaporated yielding a green solid. (150mg) FABMS 1663 [M$^+$]; $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 9.17-9.18 (d, $J = 2.1$Hz, 1H), 8.90-8.91 (d, $J = 2.4$Hz, 1H), 8.23-8.24 (d, $J = 2.4$Hz, 1H), 8.03-8.07 (d, $J = 10.8$Hz, 1H), 7.77 (s, 2H), 7.45-7.47 (d, $J = 8.1$Hz, 1H), 7.36-7.39 (d, $J = 8.1$Hz, 1H), 7.14-7.20 (m, 12H), 6.98-7.03 (m, 16H), 6.68-6.72 (d, $J = 11.7$Hz, 4H), 6.68-6.72 (m, 4H), 4.42-4.46 (m, 4H), 3.76-3.81 (m, 8H), 3.67 (s, 3H), 3.64-3.65 (m, 8H), 1.23 (s, 54H); $^{13}$C NMR (300 MHz, CDCl$_3$) δ (ppm) 31.6, 34.5, 63.2, 64.9, 67.3, 69.2, 70.0, 70.9, 71.0, 113.2, 124.2, 124.3, 125.0, 125.5, 128.2, 130.9, 132.4, 133.4, 138.2, 139.5, 140.0, 144.3, 147.1, 148.5, 151.4, 151.7, 156.7, 158.2, 164.7, 165.3
4.4 References


Appendix. NMR Spectra
Spectrum 4.1. $^1$H NMR for poly(40) in CD$_3$CN.
Spectrum 4.2. $^{13}$C NMR for poly(40) in CD$_2$CN.
Spectrum 4.3. $^1$H NMR for poly(41) in CD$_3$CN.
Spectrum 4.4. $^{13}$C NMR for poly(41) in CD$_3$CN.
Spectrum 4.6. $^1$H NMR for poly(1,4-pyridinium) tetrafluoroborate in CD$_3$CN.
Spectrum 4.7. $^1$H NMR for poly(1,4-pyridinium) hexafluorophosphate in CD$_3$CN.
Spectrum 4.8. $^{13}$C NMR for poly(1,4-pyridinium) hexafluorophosphate in CD$_3$CN.
Spectrum 4.9. $^1\text{H}$ NMR for rotaxane 51 in $d_6$-acetone.
Spectrum 4.10. $^1$H NMR for 61 in CDC$_3$. 
Spectrum 4.11. $^{13}$C NMR for 61 in CDCl$_3$. 
Spectrum 4.12: $^1$H NMR for 63 in CDCl$_3$. 

Br

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Br
Spectrum 4.13. $^{13}$C NMR for 63 in CDCl$_3$. 
Spectrum 4.14. $^1$H NMR for bis-tributylstannylethylene in CDCl$_3$. 
Spectrum 4.15. $^{13}$C NMR for bis-tributylstannylethylene in CDCl$_3$. 
Spectrum 4.16. $^1$H NMR for 66 in CDCl$_3$. 
Spectrum 4.17. $^{13}$C NMR for 66 in CDCl$_3$. 
Spectrum 4.21. $^{13}$C NMR for 68 in CDCl$_3$. 
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Education
Ph.D. in Chemistry (September 1996-expected June 2001) Cambridge, MA
Massachusetts Institute of Technology, Department of Chemistry
Advisor: Prof. Timothy M. Swager
Dissertation: Research interests focus on the synthesis of conducting polymers and their application as photoconductors, chemosensors, and artificial muscles.
University of Pennsylvania (September 1995-August 1996)
Philadelphia, PA Completed the first-year of graduate coursework prior to transferring to MIT.

B.S. in Chemistry (cum laude, GPA: 3.5/4.0, June 1995)
Brooklyn, NY
Polytechnic University, Department of Chemistry
Major: Chemistry; Minor: English Literature
Advisor: Prof. Yoshiyuki Okamoto

Experience
Massachusetts Institute of Technology, Department of Chemistry
Graduate Research Assistant (September 1996-present)
- Synthesized crown ether containing conjugated polymers for use as conductometric and fluorometric sensors
- Optimized the synthesis of an integral cyclophane monomer building block (yield increased from 14% to 50%)
- Applied chemical and electrochemical methods toward the polymerization of thiophene based monomers
- Utilized microelectrode technology and electrochemical methods in assessing polymer conductivity
- Fabricated devices for the elucidation of the photoconductive properties of donor-acceptor polymer architectures
- Collaboration in progress with the University of Groningen in studying the transient photoconductive properties of synthesized polymers
- Familiar with cyclic voltammetry, amperometry, coulometry, profilometry, and anaerobic techniques

Chemistry Outreach Program (January 1998-May 1998)
- Increased awareness of chemical concepts via interactive media to New England region grade school students
- Organized presentations in a format allowing for the easy understanding of chemical principles

Teaching Assistant (September 1997-May 1998)
- Managed tutorial sessions for the undergraduate organic chemistry course, and graded problem sets and exams
- Explained organic chemical concepts to student groups composed of multidisciplinary fields

Polytechnic University
Undergraduate Research (September 1991-June 1995)
- Collaborated with the Medical College of Wisconsin in designing and studying oxygen sensing polymers
- Fabricated non-linear optical chromophores through multistep organic synthetic sequences
- Synthesized organic ligands and their corresponding europium and terbium complexes
• Characterized products using $^1$H NMR, UV-visible, FTIR, and fluorescence spectroscopies as well as TGA, DSC, and viscometry.

**Undergraduate Teaching Experience (September 1994-January 1995)**
• Conducted the undergraduate advanced organic chemistry laboratory
• Planned laboratory experiments, led tutorial sessions, and graded lab reports

**Honors**
Gordon Research Conference, Polymers (East), Poster Award Winner (June 2000)
Roland Ward Prize for Best Undergraduate Thesis in Chemistry (June 1995)
Edward R. Russell Award for Outstanding Academic and Athletic Achievement (June 1995)
Julian R. Reasenberg Memorial Prize for Outstanding Original Research (September 1993-June 1995)
Captain of the Polytechnic University Varsity Baseball Team (September 1994-June 1995)
Tau Beta Pi Honor Society, Recognition for Academic Achievement (Spring 1995)
Dean's List Scholar (Fall 1992, Spring 1994, Spring 1995)
Cum Laude in Chemistry (June 1995)

**Affiliations**
American Chemical Society (ACS)
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