U.S.N.A—Trident Scholar project report; no. 322 (2004)

SYNTHESIS AND CHARACTERIZATION OF NOVEL ORGANIC CONDUCTING POLYMERS

by

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Report Documentation Page	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE **05 MAY 2004**	2. REPORT TYPE	3. DATES COVERED **-**

4. TITLE AND SUBTITLE **Synthesis and characterization of novel organic conducting polymers**	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) **Katharine Folz**	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **U. S. Naval Academy,Annapolis,MD,21402**	8. PERFORMING ORGANIZATION REPORT NUMBER **TRIDENT-2004-322**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR’S ACRONYM(S)
	11. SPONSOR/MONITOR’S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

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15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES **36**	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**			

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The last two years have seen an extraordinary growth of interest in photovoltaic (PV) cells made from organic conducting polymers. Such attention stems primarily from the prospect of using organic materials in manufacturing ultra thin, flexible devices. Polymeric photovoltaic cells also present a tantalizing possibility for producing coatings that function as sunlight-harvesting paints or even for developing fabrics to produce electricity from sunlight. The U.S. Navy developed an interest in electroactive polymeric research because of these specific potential applications for such devices and the materials from which they are based. The Office of Naval Research is currently probing new opportunities to convert energy into useful power sources, motivated by its interest in the development of an electric Navy for future years.

The technical objectives for this Trident Scholar project were the synthesis and characterization of high conductivity, high optical transparency conducting polymer films that incorporate 3,4-ethylenedixoythiophene (EDOT) monomers.

Initially, the EDOT derivative 2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl methanol was synthesized via a multi-step process starting from diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate. Triphenylamine and oligo(*p*-phenylene vinylene) units were also synthesized to be employed as light-harvesting groups.

Acknowledgements

While others have aided in the progression of this project, I would like to acknowledge those who have been particularly generous in their dedication of time, resources, and energies to contribute to this venture. I would first like to thank the Trident Scholar Committee and specifically Professor Shade for their consideration and the opportunity to undertake my research as well as their enduring support. I would also like to thank those who supported the continuation of my project following the damage resulting from Hurricane Isabel: Dean Miller, CAPT Pugh, and Professor Fitzgerald. Professor Copper allowed me to invade her lab space and Matt Schroeder helped retrieve and locate glassware and equipment with which to stock the lab. Dr. Brett Martin at Naval Research Laboratories (NRL) in Washington, D.C. also allowed me to share his lab space and provided instruction and direction for the post-synthetic component of my project. I extend my greatest thanks to Professor Whitaker, my Trident faculty advisor. Both before and after the hurricane, he spent countless hours working for and then defending the project and its efforts. He was irreplaceable in the rebuilding of the synthetic laboratory and the modification of the project approach. Thank you all for making the project and all its related experiences possible.

Very respectfully,

Katharine E Folz
MIDN USN

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1. Introduction and Background

Currently, the world relies heavily on its nonrenewable resources for its energy supplies. In addition to the concern of depletion of these resources, nonrenewable materials such as fossil fuels contribute to environmental problems like global warming because of carbon monoxide, carbon dioxide, and sulfur dioxide byproduct emissions. Sunlight provides a renewable energy alternative that limits negative environmental impact. Photovoltaics (PV), or solar cells, are one class of devices capable of converting light into electricity. Unlike wind, geothermal, or hydroelectric power sources, photovoltaic cells can be utilized to tap renewable energy over large ranges of locations.

In recent years, the stimulation of photovoltaic technologies has caused the expansion of the PV market to include organic electronic materials. Research has enhanced the understanding and increased the available suite of optoelectronic organic materials as well as developed confidence in their application.

Beyond research and development in the civilian sector, the Office of Naval Research (ONR) is also probing new opportunities to convert energy into useful power sources through the Direct Energy Conversion (DEC) component of its Engineering, Materials, and Physical Science Program. ONR is particularly motivated by its interest in the development of an electric Navy for future years. The Electric Warship vision will require numerous innovations. ONR is specifically emphasizing the design and synthesis of new conducting and semiconducting polymers for organic polymer PV devices during this stage of its research endeavor.

1.1. Traditional Photovoltaic Devices

Photovoltaic devices were first fabricated in the 1950s. These devices employ semiconductors to convert sunlight into electrical power by generating electric current. Early photovoltaics were made from crystalline silicon wafers and had quantum efficiencies of about 6 %.[1] Quantum efficiency is the measure of the effectiveness of a device to produce electronic charge from incident photons. As development continued, additional inorganic materials were investigated and quantum efficiencies were improved. Now, silicon solar cells have demonstrated efficiencies as high as 23 % and gallium arsenide cells up to 30 %.[2] Although commercial Si PV cells do not achieve such maximum efficiencies, they usually operate with efficiencies on the order of 10 %. Due to expenses of maintaining cleanroom facilities, device fabrication using these materials is costly compared to the use of nonrenewable energy sources. The resulting devices are also bulky and inflexible; thus they have limited terrestrial applications.

1.2. Organic Photovoltaic Devices

Organic conducting polymers provide a potential alternative to inorganic-based PV devices. Although not yet efficient enough to compete with inorganic solar cells, organic materials have many advantages over their inorganic counterparts: low-cost fabrication, less toxic manufacturing techniques, flexibility, and light weight.[3]

1.2.1. Device Operation

The operation of an organic photovoltaic device involves three consecutive fundamental steps: (1) absorption of light, (2) creation of separate charges at the donor-acceptor interfaces, and (3) selective transport of the charges through the bulk of the device to the appropriate collecting electrodes.[4] A prerequisite of high efficiency for the conversion of photons into electrical current is that the holes and electrons do not recombine before being swept out of the device to the external circuit. Creation of a charge-separated state and high charge carrier mobilities are important factors for organic photovoltaics. Once the charge-separated state is formed, the free charges are transported through the device via diffusion and drift processes because of the presence of an electric field.

The electric field over the active layer of the photovoltaic is induced by using top and bottom layer electrodes that have different work functions. The simplest organic photovoltaic device structure involves a layer of organic material sandwiched between two different conducting electrodes, typically indium tin oxide (ITO) and a low work function metal such as aluminum, calcium, or magnesium.[5] Within the active layer, holes are transported through the conjugated polymer matrix, and the electrons are transported by hopping between electron acceptors. A conjugated polymer is one that primarily has an alternating single- and double-bond structure. An electron acceptor is a material or, on the molecular level, a functional group that is electron deficient or has the potential for accepting electrons. Conversely, an electron donor has an excess of electron density.

1.2.2. Organic Semiconductors

Conjugated polymers are organic semiconductors, and as such, they possess electronic energy levels similar to those of inorganic semiconductors. Conjugated systems contain alternating single- and double-bonds and polymers include extended π-bonds. A π-bond is a molecular bond resulting from the overlap of atomic electron orbitals that are orthogonal to the direction of the bond. The area in which the π-bond electrons predominately reside is a π-orbital.

The extension of π-orbital overlap along a conjugated chain results in the merging of discrete sets of molecular electronic states to form bands. The highest occupied band originates from the highest occupied molecular orbital (HOMO) of a monomer unit and is called the valence band; the lowest unoccupied band originates from the lowest unoccupied molecular orbital (LUMO) of a monomer unit and is called the conduction band.[6] The difference in energy (E_g) between the levels is referred to as the band gap. The magnitude of E_g contributes to the electronic conduction properties of a given polymer.

In reality, many conjugated polymers do not conduct to the full potential that band theory might indicate. Two main factors limit the intramolecular conduction. First, alternation, which is an example of Jahn-Teller stabilization, tends to occur in long polymer chains. Instead of equal bond lengths between carbon atoms, alternating long and short bonds occur, which limits the delocalization of electrons.[7] Because of alternation, lengthening the polymer chain does not delocalize the π-electrons over a greater area. Secondly, rotation occurs about the bonds, which disrupts the conjugation because atomic p-orbitals cannot overlap properly. These two factors can be limited through design via the construction of linear polymers that are locked into the required configuration.[7]

The band gap of organic material can also be manipulated via polymeric design. To increase polymer conductivity, the desired E_g would be comparable to or less than those of inorganic semiconductors. The band gap energy is inversely related to the maximum absorption wavelength of a material and can be indirectly examined by investigating a substance's maximum absorption. The relationship is indicated by the following equation:

$$E = hc/\lambda$$

where h is Planck's constant (6.626×10^{-34} J s), c is the speed of light (2.9979×10^{8} m s^{-1}), E is energy, and λ denotes wavelength. In a conjugated system, the schematic display of a molecule indicates alternating single- and double-bonds, but in reality, the bonds share electron density and exhibit bond character between that of an isolated single-bond or an isolated double-bond. The extent to which a specific bond appears as a single-bond or a double-bond can vary. Reduction of bond-length alternation by increasing the double-bond character between repeating units of a conjugated polymer results in a decreased band gap. Such increased double-bond character may be generated through interaction between a strong electron donor and a strong electron acceptor. Therefore, the appropriate electron donor and acceptor subunits can yield a desired band gap.[6]

1.2.3. Photoconduction

Exposing semiconducting material to light or other electromagnetic radiation can result in a temporary increase of charge carriers. Under the influence of an electric field the current flow generated due to charge carrier movement is referred to as photoconduction. The charge carriers can be generated via a variety of interactions between the radiated photons and the semiconducting material.

In the simplest interaction, the absorption of a single photon promotes an electron directly from the valence band to the conduction band. The removal of an electron from the valence band creates an empty state in that energy band. This empty state is referred to as a hole and has an effective positive charge. The yielding an electron-hole pair inherently enhances the concentration of intrinsic charge carriers (Figure 1). Intrinsic carriers are the electrons and holes that are ‘native’ to the material, rather than charge carriers that result from dopant, or external additives.

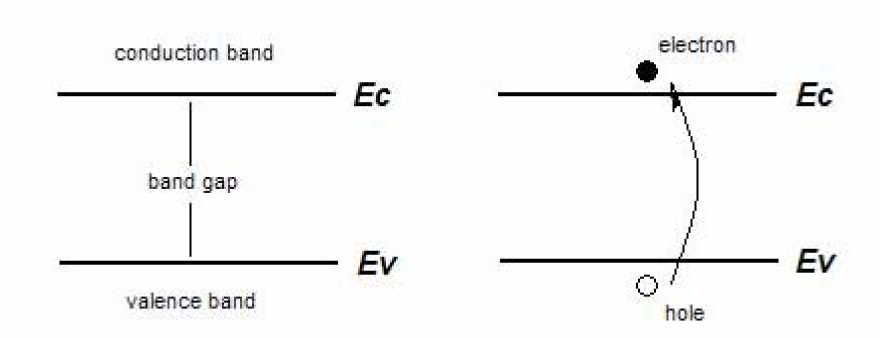

Figure 1. Band diagram; electron promotion from valence band to conduction band, yielding an electron-hole pair.

For the photoconduction process to be possible, the photon energy must exceed the energy of the band gap, which means that the photon must exceed a wavelength threshold. Photogeneration may also result from less direct means. The photon absorption may initially result in ‘exciton’ production. Excitons are localized, mobile, excited electronic states, which cannot transport charge by themselves; however, two excitons may collide to produce an electron-hole pair. Excitons may also migrate and then react with a surface state to generate a charge carrier.[7] While photoconduction is extremely difficult to detect in ordinary polymers like polyethylene, even when photon energies exceed the polymeric energy gaps, it can be seen in some conjugated polymers.

1.2.4. Organic Photovoltaic Progression

In recent years, two classes of conjugated polymers have attracted attention for use in organic photovoltaic devices.[8] Poly(*p*-phenylene vinylene)s (PPV) have had the most success in PV devices. The addition of cyano substituents to PPV derivatives formed a better electron acceptor, while underivatized PPV proved to be a good hole-transporting material. Polyanilines

(PA) were found to be perhaps the most versatile of the conducting polymers with respect to processing options. They were made using either chemical or electrochemical oxidation. The electrochemical method was used to produce thin films directly on conductive substrates such as ITO.

Conducting research independently on organic-based photovoltaics, Sariciftci *et al.* and Yoshino *et al.* reported on the photophysics of mixtures of conjugated polymers with fullerenes.[9,10] The experiments illustrated an ultrafast, reversible, metastable photoinduced electron transfer from conjugated polymers onto buckminsterfullerene (C_{60}) in solid films (Figure 2). Using this molecular effect at the interface of bilayers consisting of a semiconducting polymer and C_{60} films, a PV effect was created.[11] The power conversion efficiency of devices made from a bulk heterojunction of conjugated polymer-methanofullerene composites increased dramatically compared to single polymer devices.[12] A bulk heterojunction material is a composite which contains a mixture of electron acceptors and hole acceptors. At any point in the material the electron acceptors and hole acceptors are never more than a few nanometers apart. Rather than having a donor/acceptor active bilayer, the morphology of the donor-acceptor phase separation is controlled to yield an interpenetrating network in which a large interfacial area is achieved within bulk material.

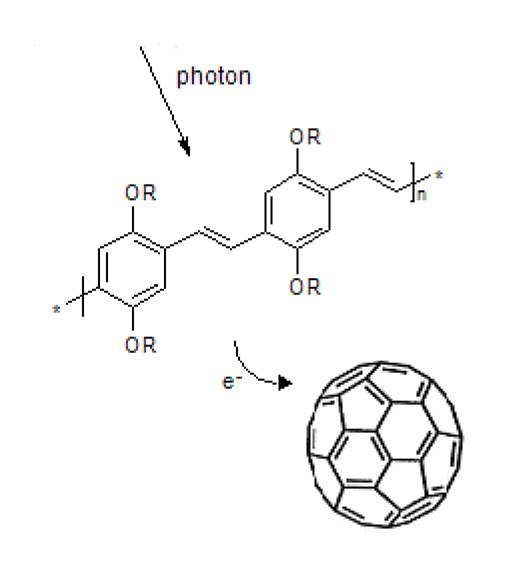

Figure 2. Conjugated polymers with fullerenes; N.S. Sariciftci, A.J. Heeger in *Handbook of Organic Conductive Molecules and Polymers*, Vol. 1, H.S. Nalwa (Ed.), John Wiley & Sons, New York 1997**.**

The groups of Heeger and Friend developed an alternate approach using acceptor-type conjugated polymers in an interpenetrating polymer-polymer composite with donor-type conjugated polymers, yielding polymeric PV devices with efficiencies comparable to the fullerene mixed devices.[13,14] Significant improvements in device performance have been demonstrated by mixing polymer donor and acceptor systems together and thereby creating a single-layer device with a phase-separated network structure (Figure 3). Phase-separated implies distinct donor and acceptor regions/clusters within the active layer. Through such integrated systems, donor/acceptor interfacial area is significantly increased while the interpenetrated network morphology still allows for the electrons and holes to be collected at their respective electrodes.

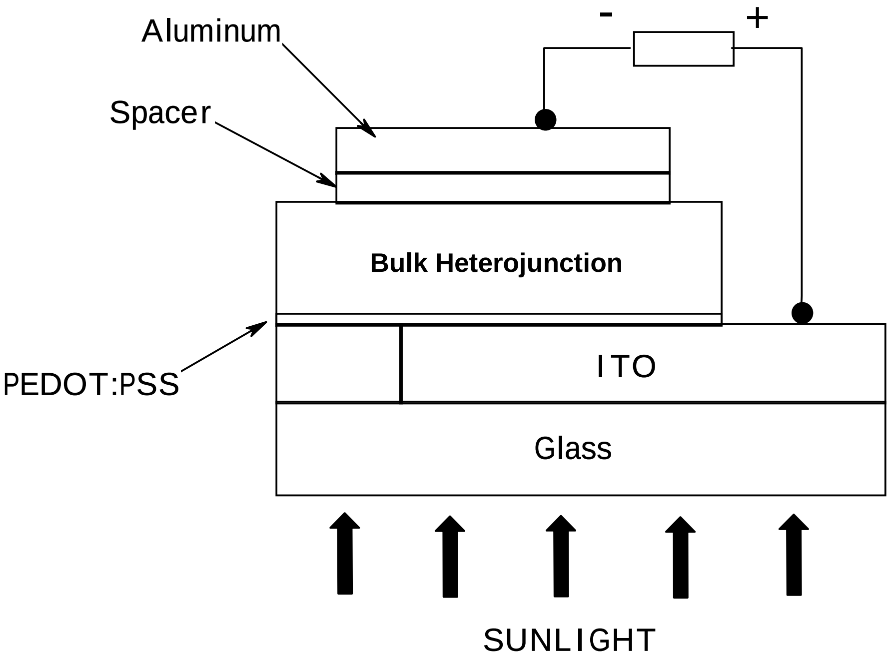

Figure 3. Single-layer organic-based photovoltaic device; Brabec *et al.*, 1518.

The PEDOT:PSS layer indicated in Figure 3 is an aqueous solution form of poly(3,4-ethylenedioxythiophene), PEDOT, dispersed with poly(styrene-sulfonate), PSS. PEDOT (Figure 4) is an electrically conducting polymer that is also inherently electrochromic which allows voltage application to affect the material's ability to transmit light, and PSS functions as a charge-compensating polyelectrolyte.[15] When placed between the active layer and the ITO electrode, it enhances the injection of holes into the conducting polymer. The PEDOT:PSS layer also improves the device because it is thin enough to remain transparent, and it provides a smoother interface than the rough ITO surface alone, serving as a buffering layer between the ITO and the bulk heterojunction.

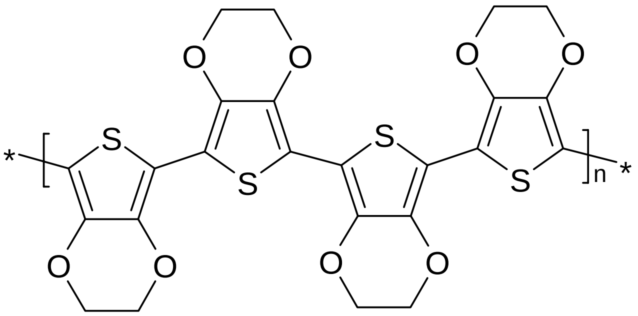

Figure 4. Poly(3,4-ethylenedioxythiophene), PEDOT.

2. Experimental

2.1. Instrumentation

Prior to Hurricane Isabel, a JEOL ECP 400 MHz spectrometer was used for the collection of nuclear magnetic resonance (NMR) spectra. After the hurricane, a Bruker 400 MHz spectrometer at NRL in Washington, D.C. was used for spectra collection. The ^1H NMR spectra in the appendix were obtained from this instrument, using deuterated chloroform as a solvent.

2.2. Materials

Reagent grade solvents were used in synthetic steps. Other reagents were purchased at the highest grade available from Aldrich Chemicals or Acros Chemicals and used without further purification.

2.3. Initial Synthesis

The product 2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl methanol (**7**), also known as methanol-EDOT, was synthesized via a six-step synthesis from the starting reactant thiodiglycolic acid (**1**) based on literature procedure (Figure 5).[16] Compound **7** was synthesized so that it could be functionalized through the hydroxy-group and used as the monomer unit in the polymer fabrication. Methanol-EDOT is a derivative of 3,4-ethylenedioxythiophene (EDOT), and as such, the polymer of this monomer is a high stability conducting polymer.[17] The high stability of poly(methanol-EDOT) is attributed to favorable ring geometry and the electron donating effect of the oxygen atoms at the 3,4-positions, which stabilize the positive charge in the polymer backbone.

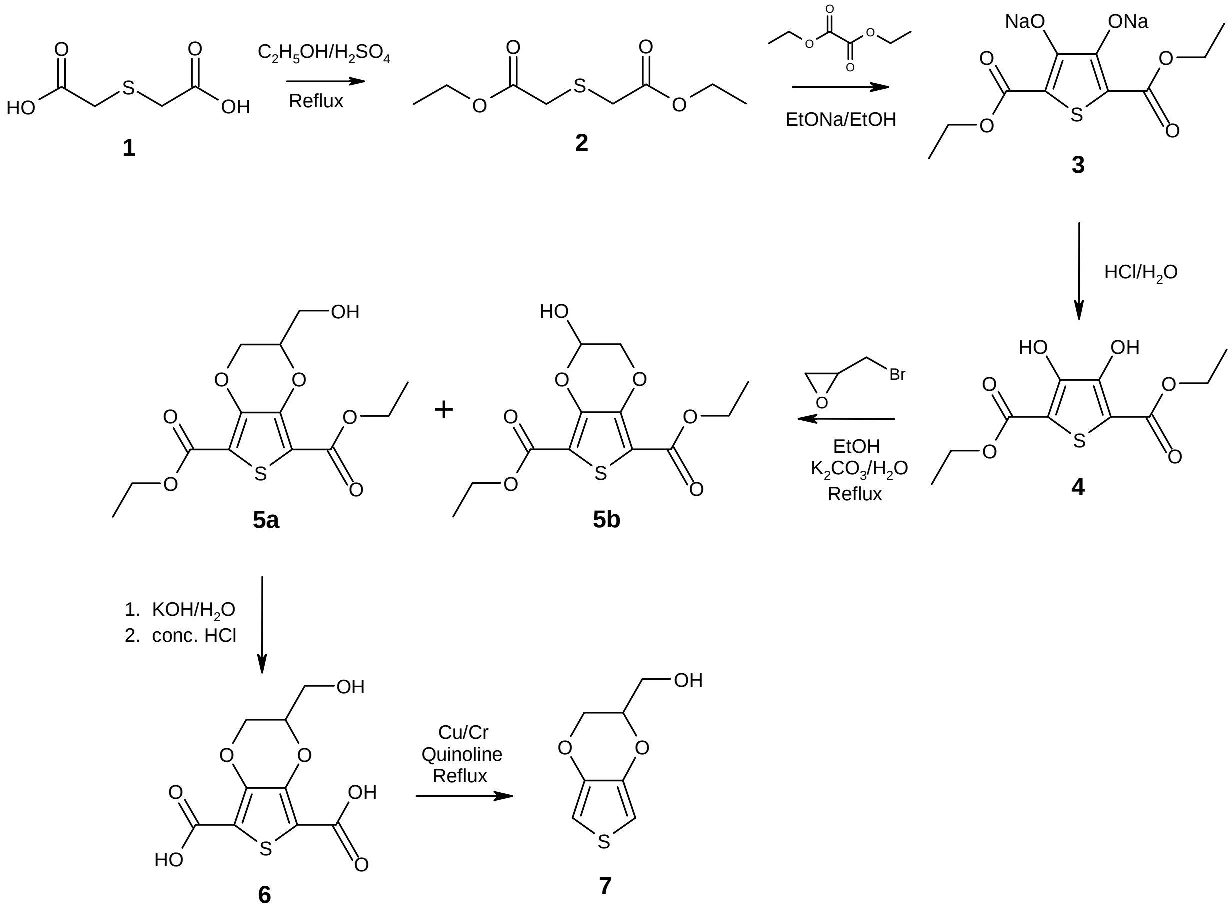

Figure 5. Synthesis of 2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl methanol.

*2.3.1. Diethyl thiodiglycolate (**2**)*

Thiodiglycolic acid (**1**) (50 g, 333 mmol) was dissolved in 250 mL of boiling ethanol in a 3-neck round bottom flask fitted with a reflux condenser. Concentrated sulfuric acid (20 mL) was added slowly while stirring continuously. The mixture was refluxed for 24 hours then cooled and poured into 300 mL of water. The water mixture was then extracted with diethyl ether. The organic layer was washed with saturated aqueous Na_2CO_3, dried over $MgSO_4$, and concentrated by rotatory evaporation. The reaction yielded 30. g (150 mmol, 45 % yield) of diethyl thiodiglycolate, which appeared as an orange oil. The purity was checked using ^1H NMR analysis, but the spectrum was lost due to Hurricane Isabel.

*2.3.2. Diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate disodium salt (**3**)*

Compound **2** (30. g, 0.20 mmol) and diethyl oxalate (45 mL) were combined in a dropping funnel. Absolute ethanol (210 mL) was cooled in an ice bath. Sodium ethoxide (40. g; 590 mmol) was then added to the cooled ethanol. The solution of **2** and diethyl oxalate was then added to the ethanol solution dropwise while swirling. After the diethyl thiodiglycolate/diethyl oxalate solution was added, the round bottom flask was removed from the ice bath and refluxed for one hour. A yellow precipitate was obtained, washed with ethanol, and dried under vacuum. The resulting yellow powder disodium salt (**3**) was used in the next synthesis step without purification.

*2.3.3. Diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate (**4**)*

Water (500 mL) was added to the disodium salt (**3**). Concentrated HCl was added to the solution dropwise until highly acidic as indicated by pH paper turning a deep red. The acidic mixture was filtered to obtain the precipitate that formed. Ethyl acetate (100 mL) and hexane (25 mL) were then added to the filtrate. The mixture was stirred until homogenous and then cooled. The solid precipitate was placed in a flask and 50 mL ethyl acetate and 12 mL hexane were added. The mixture was stirred until homogenous and was also cooled. After refrigerating overnight, both solutions were filtered to obtain the solid. The filtrate was then evaporated down to approximately 10 mL. Hexane was added to dilute the solutions while still allowing the precipitate to crash out of the solutions. The solutions were then refrigerated overnight. The reaction yielded 6.4 g (25 mmol, 13% yield) of **4** as a pale solid.

*2.3.4. Diethyl 2-(hydroxymethyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine-5,7-dicarboxylate (**5a**)*

The 6.4 g (25 mmol) of **4** was dissolved in 100 mL of boiling ethanol. Epibromohydrin (3.0 mL, 35 mmol) and 0.75 g (5.5 mmol) of potassium carbonate dissolved in 30 mL of water were then added. The mixture was refluxed for one hour. Additional amounts of K_2CO_3 (0.40 g, 3.0 mmol) and epibromohydrin (5.2 mL, 61 mmol) were added. The solution was then refluxed for 72 hours. The solution was allowed to cool and poured into 150 mL of acidified water (5 % HCl). The resulting solution was extracted twice with 100 mL chloroform. The organic layer was then washed with 100 mL aqueous 5 % solution KCl. The solution was dried over $MgSO_4$ and placed in the refrigerator. Then Hurricane Isabel intervened.

2.4. Modified Synthetic Approach

The hurricane drastically affected progression of the synthetic component of the project. With little time left in the academic year, reduced laboratory space, lack of characterization equipment, *et cetera*, the project was modified.

2.5. 2,3-Dihydrothieno[3,4-b][1,4]dioxin-2-yl methanol Synthesis

The product 2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl methanol (**7**) was synthesized via the same reaction steps as the initial synthesis; however, diethyl 3,4-dihydroxythiophene-2,5-dicarboxylate (**4**) was used as the starting reactant (Figure 5).

*2.5.1. Diethyl 2-(hydroxymethyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine-5,7-dicarboxylate (**5a**)*

Seven grams (27 mmol) of **4** was dissolved in 100 mL of boiling ethanol. Epibromohydrin (3.0 mL, 35 mmol) and 0.75 g (5.5 mmol) of potassium carbonate dissolved in 30 mL of water were then added. The mixture was heated at reflux for 1 hour. Additional amounts of K_2CO_3 (0.40 g, 3.0 mmol) and epibromohydrin (5.2 mL, 61 mmol) were added. After refluxing for 72 hours, the solution was allowed to cool and poured into 150 mL of acidified water (5 % HCl). The resulting solution was extracted twice with 100 mL of chloroform. The organic layer was then washed with an aqueous 5 % solution of potassium chloride. After drying over $MgSO_4$, the solvent was removed under vacuum by rotatory evaporation. A yellow solid was obtained which was recrystallized from 50 mL diethyl ether to give compounds **5** as a white crystalline powder after filtration (6.8 g, 21 mmol, 78 % yield).

*2.5.2. Diethyl 2-(hydroxymethyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine-5,7-dicarboxylic acid (**6**)*

Compound **5** (6.8 g, 21 mmol) was added to 150 mL aqueous potassium hydroxide (7.2 g; 130 mmol) in a round bottom flask fitted with a reflux condenser. The solution was heated at reflux for a total of 2 hours after complete solubilization of the reactants. The volume of the solution was then reduced to 60 mL by concentration under vacuum. Concentrated HCl (15 mL) was added dropwise to the cooled solution (ice bath) under continuous stirring. During addition of HCl, white precipitate formed then dissolved. As stirring continued, the solid formed again. After 2 hours of stirring over ice, the white solid formed was filtered and dried under vacuum at 80 °C. Compound **6** was obtained as a white powder (5.3 g, 20. mmol, 95 % yield).

*2.5.3. 2,3-Dihydrothieno[3,4-b][1,4]dioxin-2-yl methanol (**7**)*

Before beginning the reaction, quinoline was distilled. Quinoline was stirred over sodium sulfate overnight. Then the quinoline was filtered into a dry flask and zinc dust was added (5 g for 50 mL quinoline). About half of the volume was distilled directly into the reaction vessel.

A mass of 6.296 g (24.2 mmol) **6** was mixed with 0.68 g (2.2 mmol) of copper chromite catalyst. These two reactants and a stir bar were added to the reaction vessel containing distilled quinoline. A condenser with a 3-way stopcock with dry argon on one arm was attached. The flask was evacuated then backfilled with argon three times, being careful no to allow the air back into the flask while backfilling. During evacuation, the reaction mixture bubbled vigorously.

The flask was placed into a well-stirred, preheated 180 °C bath for 1-2 hours. During the reaction, carbon dioxide evolved. When the evolution ceased the reaction was completed. After cooling, the solution was gravity-filtered and washed with diethyl ether. The filter paper was then placed into a vessel containing diethyl ether and allowed to soak in order to ensure that all soluble product was removed. The diethyl ether was filtered and combined with the initial filtrate portion. The combined filtrate was washed repeatedly with 5 % HCl and twice with 5 % KCl. After drying over $MgSO_4$, the suspension was filtered and the ether reduced via rotatory evaporation. The residue was purified by column chromatography using silica gel and 95:5 (v/v) mixture diethyl ether and cyclohexane to obtain **7** as brown oil in 13 % yield (560. mg, 3.25 mmol). ^{1}H NMR ($CDCl_3$) δ 6.37 (m, 2H), 4.26 (m, 2H), 4.13 (m, 1H), 3.90 (m, 2H), 1.89 (t, 1H) (Appendix: Figure 10).

2.6. 4-Methyltriphenylamine Synthesis

4-Methyltriphenylamine was synthesized in order to covalently bond it to methanol-EDOT through the hydroxy- group. The triphenylamine derivative functions as a light-harvesting unit (LHU) and a hole-transporter. The incorporation of this LHU with the polymer of an organic photovoltaic active layer could potentially increase device quantum efficiency.

2.6.1. Aromatic Amination Using Diphenylamine and 4-Bromotoluene[18]

The synthesis of 4-methyltriphenylamine (**8**) was attempted using the following reaction scheme (Figure 6):

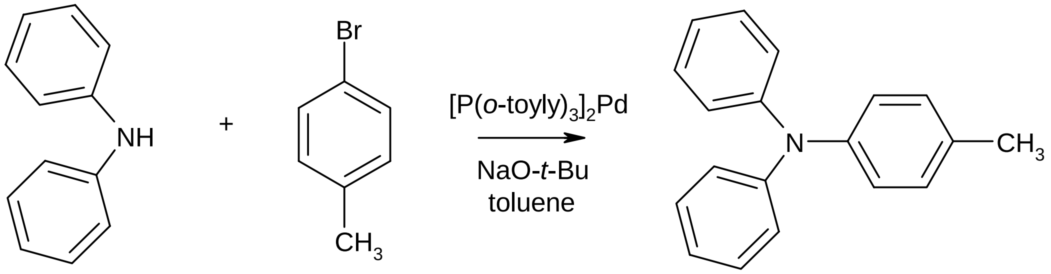

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Figure 6. Synthesis of 4-methyltriphenylamine by aromatic amination.

Diphenylamine (2.25 g, 13.3 mmol), 4-bromotoluene (2.06 g, 12.0 mmol), tetrakis(triphenyl-phosphine)palladium(0) (0.278 g, 0.241 mmol), sodium *tert*-butoxide (1.62 g, 16.9 mmol), and dry toluene (100 mL) were heated to 70 °C for 8 hours while stirring. Upon cooling to room temperature, the reaction mixture was filtered and concentrated by rotatory evaporation. Attempts to purify by column chromatography yielded a mixture of compounds. Numerous attempts were made to isolate **8**, but none were successful.

2.6.2. Reduction of a Carbonyl-Substituted Triphenylamine

Because the aromatic amination using diphenylamine and 4-bromotoluene was unsuccessful an alternate route was attempted via the reduction of carbonyl-substituted triphenylamine was attempted (Figure 7). The 4-formyltriphenylamine used in the reaction had been previously synthesized by Professor Whitaker.

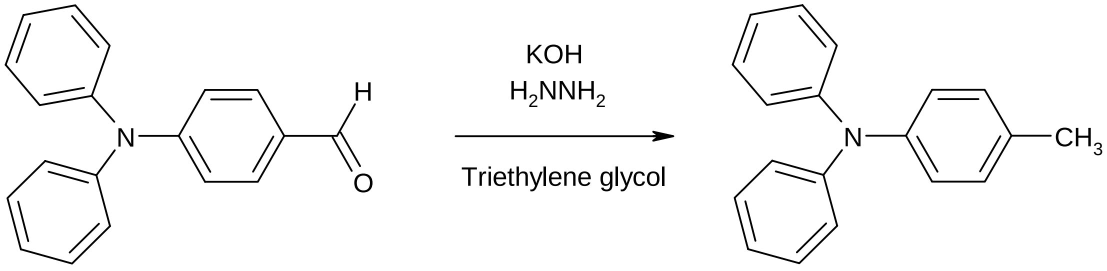

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Figure 7. Synthesis of 4-methyltriphenylamine by reduction of an aldehyde.

Carbonyl-substituted triphenylamine (0.491 g, 1.80 mmol), potassium hydroxide (0.34 g, 6.06 mmol), hydrazine (0.25 mL), and triethylene glycol (2.75 mL) were combined in a round bottom flask. The reactants were heated at reflux while stirring for 1.5 hours in order to allow the low-boiling components to evaporate. The reaction was then heated at 195 °C for 4 hours. The mixture turned bright yellow, then became colorless. The solution was allowed to cool to room temperature. The solution was diluted with 2.5 mL water and poured into 1.5 mL 6 N HCl. The resulting solid was vacuum filtered away from the remaining solution. The solid was then purified by column chromatography using 1:1 dichloromethane/n-pentane. The reaction yielded **8** as a white solid (0.467 g, 1.78 mmol, 99 % yield). ^{1}H NMR ($CDCl_3$) δ 7.26 (t, 2H), 7.09 (m, 12H), 2.36 (s, 3H) (Appendix: Figure 11).

2.7. Bromination of 4-Methyltriphenylamine

Multiple attempts were made to brominate the 4-methyltriphenylamine using *N*-bromosuccinimide (NBS), 2,2’-azobis(2-methylpropionitrile) (AIBN), carbon tetrachloride, and heat, but none of the reactions were successful. The desired product (Figure 8) could not be synthesized by this route. The intent was to brominate the methyl-substituted derivative and react it with 2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl methanol prior to polymerization in order to have a light-harvesting unit covalently bound to poly(methanol-EDOT).

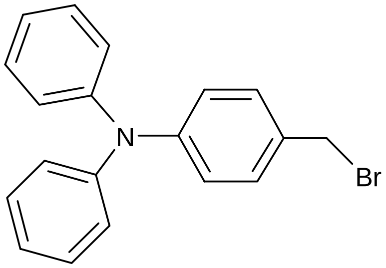

Figure 8. Brominated 4-methyltriphenylamine.

2.7.1. Initial Bromination Reaction

Carbon tetrachloride was dried over calcium chloride and filtered. The dry carbon tetrachloride was combined with 4-methyltriphenylamine (0.23 g, 0.88 mmol) and heated to 70 °C. Then NBS (0.16 g, 0.88 mmol) and AIBN (7.4 mg, 0.044 mmol) were added, and the reaction mixture was heated at reflux for approximately 2 hours. Upon adding the NBS and AIBN, the solution turned green, but upon heating, the solution turned brown. The product mixture was filtered, and the solvent was removed by rotatory evaporation. The products were isolated via column chromatography (silica gel, 1:1 dichloromethane/hexane by volume). ^{1}H NMR indicated that the triphenylamine derivate had not been successfully brominated.

2.7.2. Second Bromination Reaction

Carbon tetrachloride was dried over calcium chloride and filtered. The dry carbon tetrachloride was added to 4-methyltriphenylamine (0.23 g, 0.88 mmol) and heated to 70 °C. AIBN (0.059 g, 0.35 mmol) was then added to the reaction vessel. After allowing the mixture to heat for 5 minutes, NBS (0.189 g, 1.06 mmol) were added. The reaction was heated at reflux until all of the NBS rose to the surface of the mixture (approximately 1.5-2 hours). After cooling, the mixture was gravity-filtered, and the solvent was removed by rotatory evaporation. The product was dissolved in 1:1 dichloromethane/n-pentane by volume. Not all of the product would go into solution, but column chromatography was used to separate the soluble products (silica gel, 1:1 dichlomethane/n-pentane by volume). The triphenylamine was not successfully brominated as determined by ^{1}H NMR.

2.8. Oligo(p-phenylene vinylene) Synthesis

Oligo(p-phenylene vinylene)s (OPVs) were synthesized (Figure 9) with the intention to covalently bind them through the hydroxy- group of compound **7** prior to polymerization in order to have a light-harvesting unit covalently bound to poly(methanol-EDOT).[19] OPVs function as electron acceptors. The incorporation of this group to the polymer system used in the active layer of an organic-based photovoltaic could potentially increase device power conversion efficiency.

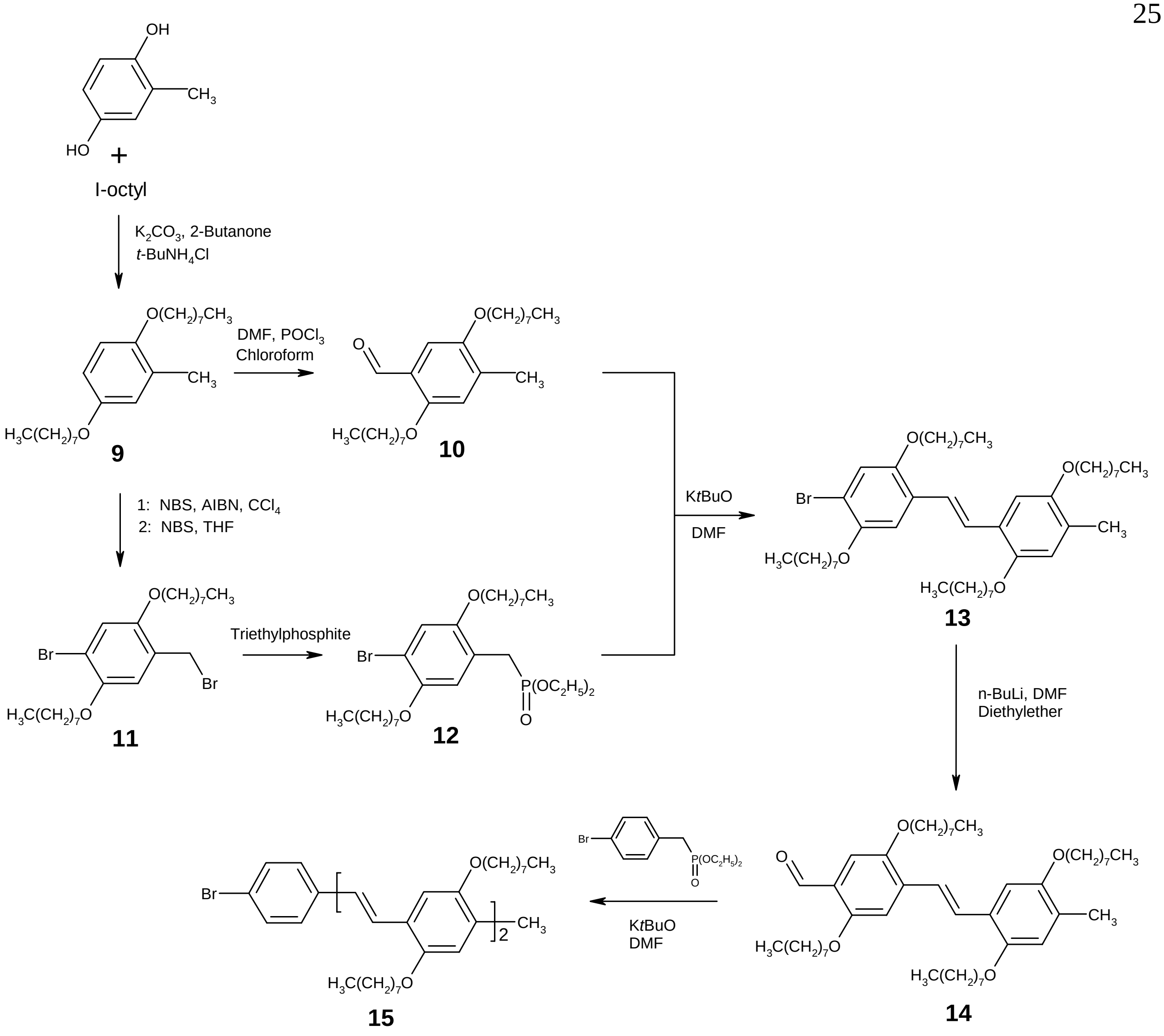

Figure 9. Synthesis of oligo(p-phenylene vinylene)s.

2.8.1. *1,4-Bis-oxyoctyl-2-methylbenzene (9)*

Methylhydroquinone (15.1 g, 0.122 mol), iodooctane (40.6 g, 0.169 mol), and tetrabutylammonium chloride (2.43 g, 8.73 mmol) were added to a suspension of potassium carbonate (72.0 g, 0.52 mol) in dry 2-butanone (150 mL) under an atmosphere of dry argon. The reaction mixture was stirred for 16 hours at reflux temperature. After the mixture was cooled to room temperature, the suspension was filtered and the solvent was removed by rotatory evaporation. The resulting crude product was purified by column chromatography (silica gel, 2:1 pentane/chloroform by volume). The reaction yielded 16.85 g (71.6 mmol, 84.7 %) of **9** as a colorless oil.

*2.8.2. 2,5-Bis-oxyoctyl-4-methylbenzaldehyde (**10**)*

Phosphorus oxychloride (9.8 mL, 0.107 mol) was added to a mixture of dry *N*,*N*-dimethlformamide (DMF) (6.94 ml, 89.9 mmol) and dry dichloromethane (15 mL) under an atmosphere of dry argon. After the mixture was stirred for 1 hour, **9** (6.47 g, 27.5 mmol) was added, and the reaction mixture was stirred for 48 hours at reflux temperature. The mixture was allowed to cool to room temperature and poured on ice water (150 mL). The mixture was then stirred for 1 hour and extracted with diethylether (50 mL). During the extraction, NaCl was added to promote phase separation. The organic layer was washed with 1 M HCl (3 x 30 mL), water (3 x 30 mL), and a saturated $NaHCO_3$ solution (30 mL). After the organic phase was dried over $MgSO_4$, filtered, and the solvent evaporated, the product was purified by column chromatography (silica gel, 2:1 pentane/chloroform by volume). The reaction yielded 3.36 g (12.8 mmol, 46.4 %) of **10** as white crystals. ^1H NMR ($CDCl_3$) δ 10.44 (s, 1H), 7.25 (s, 1H), 6.82 (s, 1H), 4.04 (t, 2H), 3.97 (t, 2H), 2.30 (s, 3H), 1.81 (m, 2H), 1.48 (m, 2H), 1.33 (m, 13H), 0.91 (m, 13H) (Appendix: Figure 12).

*2.8.3. 1-Bromo-2,5-bis-oxyoctyl-4-bromomethylbenzene (**11**)*

NBS (3.76 g, 21.1 mmol) and AIBN (1.06 g, 6.34 mmol) were added to a solution of **9** (4.14 g, 11.9 mmol) in dry CCl_4 (20 mL) under an atmosphere of dry argon. After the reaction mixture was stirred for 1 hour under reflux, it was subsequently allowed to cool to room temperature and filtered. After evaporation of the solvent, pentane (20 mL) was added to the residue, and the resulting suspension was filtered and evaporated to dryness. The remaining residue was dissolved in dry tetrahydrofuran (THF) (20 mL). NBS (2.41 g, 13.5 mmol) was added, and the reaction mixture was stirred at reflux temperature for 1 hour. After evaporation of the solvent, pentane (20 mL) was added. The solution was filtered, and the solvent was removed by rotatory evaporation. Crystallization of the residue from ethanol yielded 1.92 g (3.79 mmol, 31.8 %) of **11** as white crystalline powder.

*2.8.4. Diethyl{2,5-bis-oxyoctyl-4-bromo-benzyl}-phosphonate (**12**)*

Triethyl phosphite (0.240 g, 1.4 mmol) and **11** (0.507 g, 1.0 mmol) were stirred at 160 °C for 1.5 hours while the liberated ethyl bromide was distilled off. The reaction mixture was cooled to 75 °C, and the excess triethyl phosphate was removed under reduced pressure to leave **12** (0.54 g, 96 %) as a light yellow oil. The product was not isolated because the phosphonate rapidly decomposes. It was used immediately in the next step.

*2.8.5. (*E*)-4-{4-Methyl-2,5-bis-oxyoctylstyryl}-2,5-bis-oxyoctylbromobenzene (**13**)*

A solution of aldehyde **10** (0.329 g, 1.1 mmol) in dry DMF (2 mL) was added dropwise to a solution of **12** (0.54 g, 1.1 mmol) and potassium *tert*-butoxide (*t*-BuOK) (0.145 g, 1.3 mmol) in dry DMF (1.5 mL) under an atmosphere of dry argon. The aldehyde was not completely soluble in DMF. The resulting reaction mixture was stirred for 8 hours at room temperature and subsequently poured on crushed ice (6.5 g). Aqueous HCl (5 M, 4 mL) was added, and the aqueous phase was extracted with chloroform (3 x 2 mL). The combined organic layers were washed with 3 M HCl and dried over $MgSO_4$. The solvent was evaporated, and the product was purified by column chromatography (silica gel, 2:1 pentane/chloroform by volume). The reaction yielded 255 mg (0.325 mmol, 37 %) of **13** as a yellow solid.

*2.8.6. (*E*)-4-{4-Methyl-2,5-bis-oxyoctylstyryl}-2,5-bis-oxyoctylbenzaldehyde (**14**)*

Bromide **13** (255 mg, 0.412 mmol) was dissolved in dry diethyl ether (6 mL). The solution was cooled to -10 °C using and ice/salt bath, and 2.5 M *n*-butyllithium in hexane (0.330 mL, 2 molar eqv.) was added slowly. After the addition of n-butyllithium, the mixture was allowed to come to room temperature gradually. Reaction progression was indicated by a color change from yellow to dark brown. TLC verified reaction progression. After the ice melted completely, the cooling bath was removed. After stirring for 1.5 hours, dry DMF (0.128 mL, 4 molar eqv.) was added dropwise. The mixture was stirred for another hour at room temperature. After addition of 6 M HCl (1.2 mL), the organic layer was washed with water (2 x 3 mL), with a saturated $NaHCO_3$ solution (4 mL), and again with water (4 mL). The organic layer was dried over $MgSO_4$, and the solvent was evaporated. The product **14** was partially isolated via column chromatography (silica gel, dichloromethane) to yield a yellow solid. Due to time constraints, the yellow solid was used in the next synthesis step without being completely purified.

*2.8.7. (*E,E*)-4-{4-(4-Methyl-2,5-bis-oxyoctylstyryl)-2,5-bis-oxyoctylstyryl}-2,5-bis-bromobenzene (**15**)*

4-Bromo-α-bromotoluene was phosphonated via the procedure used above, *vide supra*, for compound **12** (Figure 10).

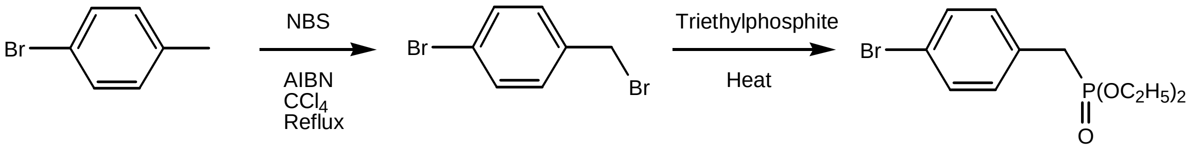

Figure 10. Phosphonation of 4-bromo-α-bromotoluene.

For the reaction, triethyl phosphate (0.088 g, 0.53 mmol) and 4-bromo-α-bromotoluene (0.110 g, 0.440 mmol) were stirred at 160 °C for 1.5 hours while the liberated ethyl bromide was distilled off. The reaction mixture was cooled to 75 °C, and the excess triethyl phosphate was removed under reduced pressure to leave diethyl(4-bromo-benzyl)-phosphonate as an oil.

A solution of aldehyde **14** (0.323 g, 0.440 mmol) in dry DMF (3 mL) was added dropwise to a solution of diethyl(4-bromo-benzyl)-phosphonate (0.0515 g, 0.440 mmol) and t-BuOK (0.059 g, 0.53 mmol) in dry DMF (1.5 mL) under an atmosphere of dry argon. The resulting reaction mixture was stirred at room temperature for 8 hours. The reaction was then poured on crushed ice (6 g). Aqueous HCl (5 M, 1.5 mL) was added, and the aqueous phase was extracted with $CHCl_3$ (3 x 5 mL). The combined organic layers were washed with 3 M HCl and then washed with water and dried over $MgSO_4$. After filtration, the solvent was evaporated. Column chromatography (silica gel, 1:1 dichloromethane/n-pentane by volume) was used to isolate **15** (110 mg, 0.13 mmol, 29 % yield) as a yellow solid.

3. Conclusion

The research conducted focused heavily on organic synthesis. The major molecules successfully synthesized were 2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl methanol (**7**), 4-methyltriphenylamine (**8**), and (*E*,*E*)-4-{4-(4-methyl-2,5-bis-oxyoctylstyryl)-2,5-bis-oxyoctylstyryl}-2,5-bis-bromobenzene (**15**). 2,3-Dihydrothieno[3,4-b][1,4]dioxin-2-yl methanol (**7**) was synthesized with an overall yield of 10. %. 4-Methyltriphenylamine (**8**) was synthesized with an overall yield of 99 %.

In the synthesis of (*E*,*E*)-4-{4-(4-methyl-2,5-bis-oxyoctylstyryl)-2,5-bis-oxyoctylstyryl}-2,5-bis-bromobenzene (**15**), 2,5-bis-oxyoctyl-4-methylbenzaldehyde (**10**) was synthesized with an overall yield of 39 % and diethyl{2,5-bis-oxyoctyl-4-bromo-benzyl}-phosphonate (**12**) was synthesized with an overall yield of 26 %.

The OPV-3 oligomer (**15**) was synthesized with an overall yield of 2.8 %. Compound **15** was a novel molecule synthesized for use as a light-harvesting unit, which had a maximum absorption wavelength in chloroform of 400 nm. When bonded covalently to a conducting polymer, this unit would increase the light-harvesting capability of the system. Such an increase would allow for the fabrication of more efficient photovoltaic devices.

The synthesis and purification of the final molecules were verified by ^{1}H NMR spectroscopy. The spectra peaks were assigned based on shielding, integration, and splitting. ^{1}H NMR was also used when possible during the intermediate synthetic steps. Unfortunately, due to the commute required to obtain spectra as well as the need to progress synthetically, spectra were not obtained for all intermediate compounds.

4. Continued Research

With the three molecules synthesized (**7**, **8**, and **15**), methanol-EDOT will be oxidatively polymerized in the presence of 4-methyltriphenylamine and in the presence of OPV-3. The resulting polymers will then be characterized with respect to molecular weight, conductivity, and optical transparency.

The two LHUs will be covalently bonded to the methanol-EDOT through the hydroxy-group. Once bonded, the functionalized methanol-EDOT will undergo oxidative polymerization. The resulting polymers will be characterized with respect to molecular weight, conductivity, and optical transparency.

The resulting data from the systems in which the LHUs were covalently bonded to methanol-EDOT will be compared to the data from the systems in which the LHUs were not covalently bonded to methanol-EDOT. The characterization data will also be used in optimizing the conductivity and optical transparency of the polymeric systems. Once optimized, the materials will ultimately be used in organic-based photovoltaic devices.

Appendix: ^{1}H NMR Spectra

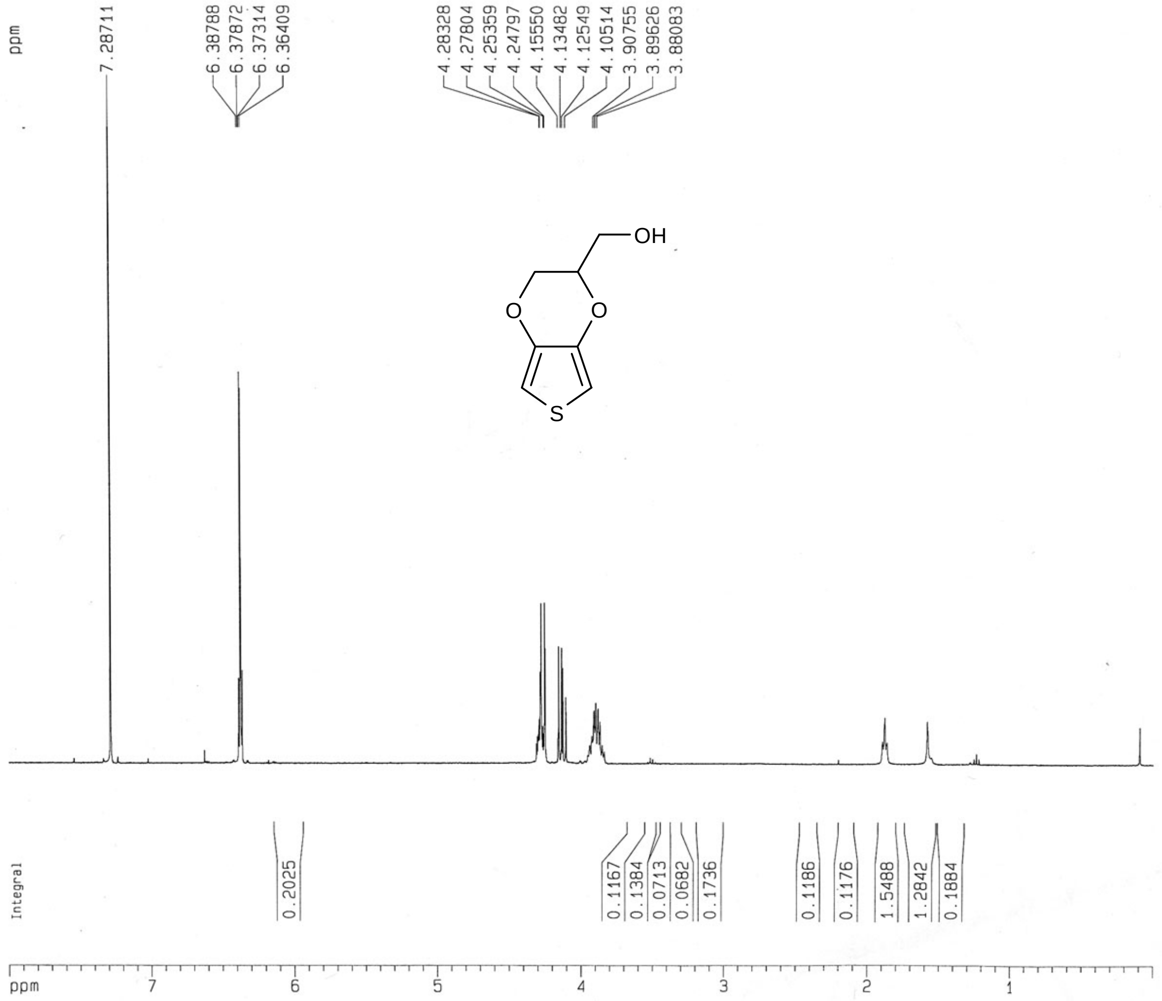

Figure 11. 2,3-Dihydrothieno[3,4-b][1,4]dioxin-2-yl methanol (7) ^{1}H NMR spectrum.

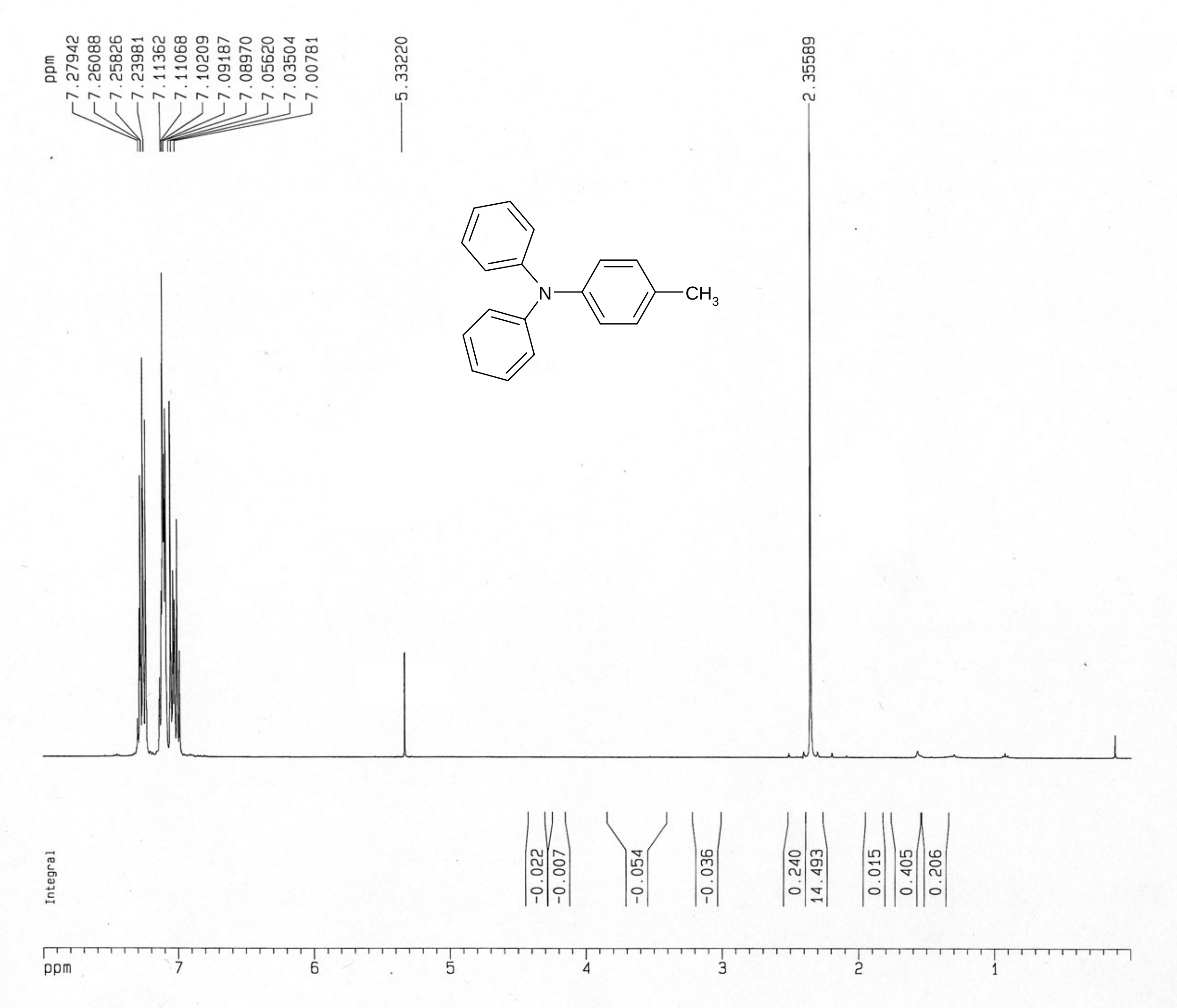

Figure 12. 4-Methyltriphenylamine (8) ^{1}H NMR spectrum.

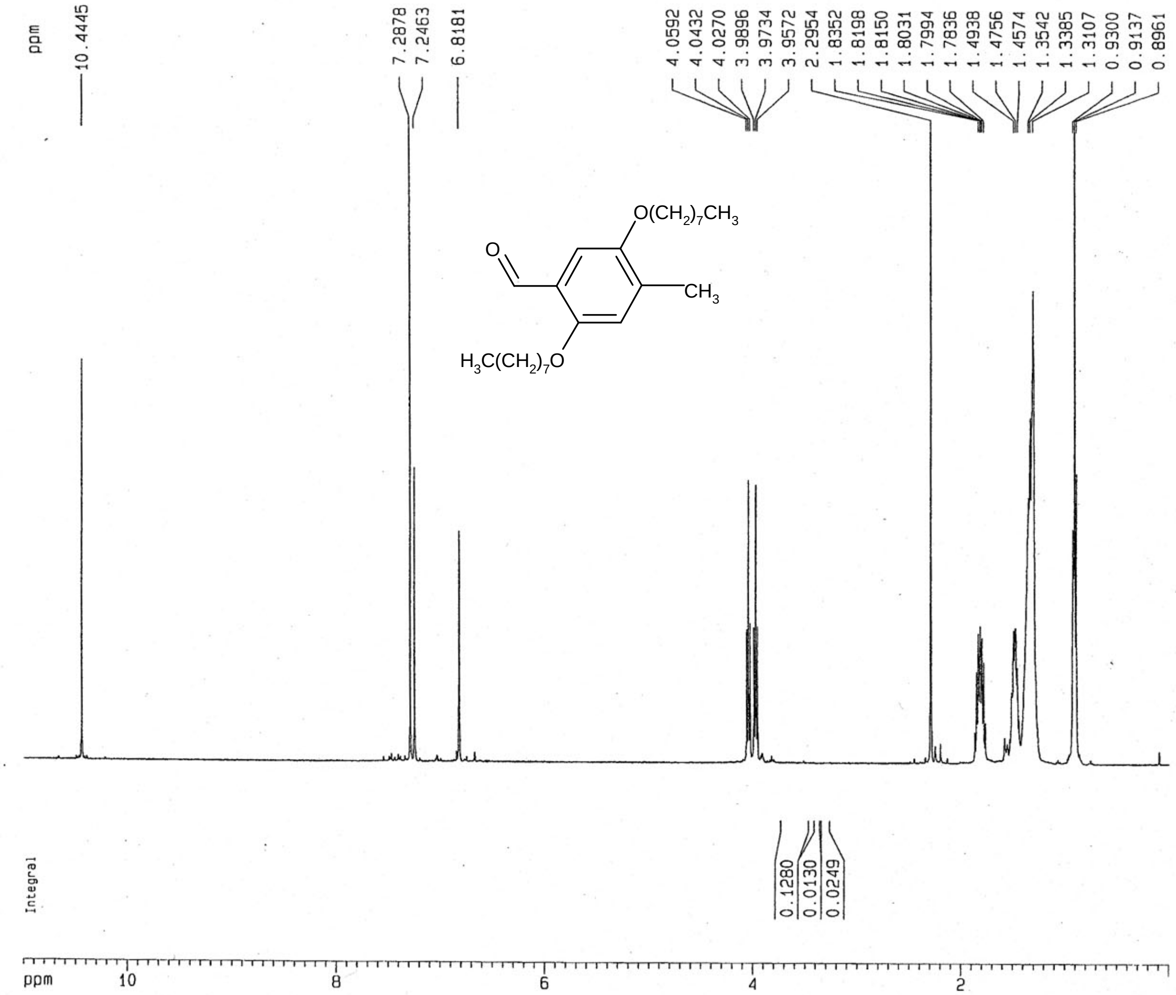

Figure 13. 2,5-Bis-oxyoctyl-4-methylbenzaldehyde (10) ^{1}H NMR spectrum.

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