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April 08, 2017

Synthesis of Naphthalene Diimide-Based Polymers for High Charge Transport

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a thesis submitted to the Faculty of Emory College of Arts and Sciences
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Abstract

Synthesis of Core-Substituted Naphthalene Diimide-Based Polymers for High Charge Transport

By Shelly Saini

This thesis is primarily aimed at the development of synthetic strategies for *n*-type semiconducting polymers based on the two important building blocks, namely, naphthalenediimide as electron acceptor material, and BODIPY as an electron donor material. NDI-based monomers and BODIPY donor monomers have demonstrated large implications in the field of organic semiconductors. When polymerized, these monomers have the potential to absorb light in the visible range, unlike other organic semiconducting materials that absorb mostly in the UV range. By decreasing the amount of high energy light entering the system for excitation, there should be an increase in efficiency in exciting from the HOMO to LUMO energy levels. We were able to successfully synthesize both the NDI and BODIPY monomers, as well as measure their absorption and emission spectra. Two polymers were synthesized, one in which the NDI monomers were copolymerized with thiophene units, and the other in which NDI and BODIPY monomers were copolymerized. While pNDI-BODIPY formed successfully, pNDI-bithiophene only formed oligomers due to a short polymerization time and dilute solution. The pNDI-BODIPY showed a notable red shift in absorption from the individual monomers. The NDI monomer and BODIPY monomers originally absorbed in the 390nm and 540nm range, respectively. After polymerization, the absorption shifted to the 400-580nm range of visible light, eliminating the absorption of high-energy UV light, due to an increase in conjugation of the polymer versus the monomer alone. In addition to the polymerization, previously reported synthetic methods were evaluated and modified to produce higher synthetic yields. In many cases, the modified synthetic protocols were efficient in producing high monomer yields.

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1. Background

As society becomes more industrialized, there is an increase in energy demand. Traditional forms of nonrenewable energy, such as crude oil, not only harm the environment, but also are not sustainable energy sources. However, issues arise when trying to create an efficient, cost-effective alternative to nonrenewable energy sources. One such alternative is high-efficiency organic solar cells as a form of renewable energy.

Traditional inorganic solar cells are composed of donor and acceptor atoms. The donor atoms, or pentavalent impurities, have five valence electrons, allowing them to contribute extra electrons.¹⁰ Examples of such atoms include antimony, arsenic, and phosphorous. The acceptor atoms, or trivalent impurities, have three valence electrons, allowing them to accept extra electrons since they are electron deficient.¹⁰ Examples of such atoms include boron, aluminum, and gallium.

In *n*-type semiconductors, there is an excess of pentavalent impurities.^{9,10} These donor atoms have extra electron levels close to the conduction band.^{9,10} The electrons close to the conduction band act as free electrons, allowing them to be harnessed to produce current. In *p*-type semiconductors, however, there is an excess of trivalent impurities. These acceptor atoms have a deficiency in electrons, and have electron levels close to the valence band.^{9,10} The deficiency of valence electrons creates “holes” that allow for the production of current when electrons are transferred from one hole to the next (Figure 1).^{9,10}

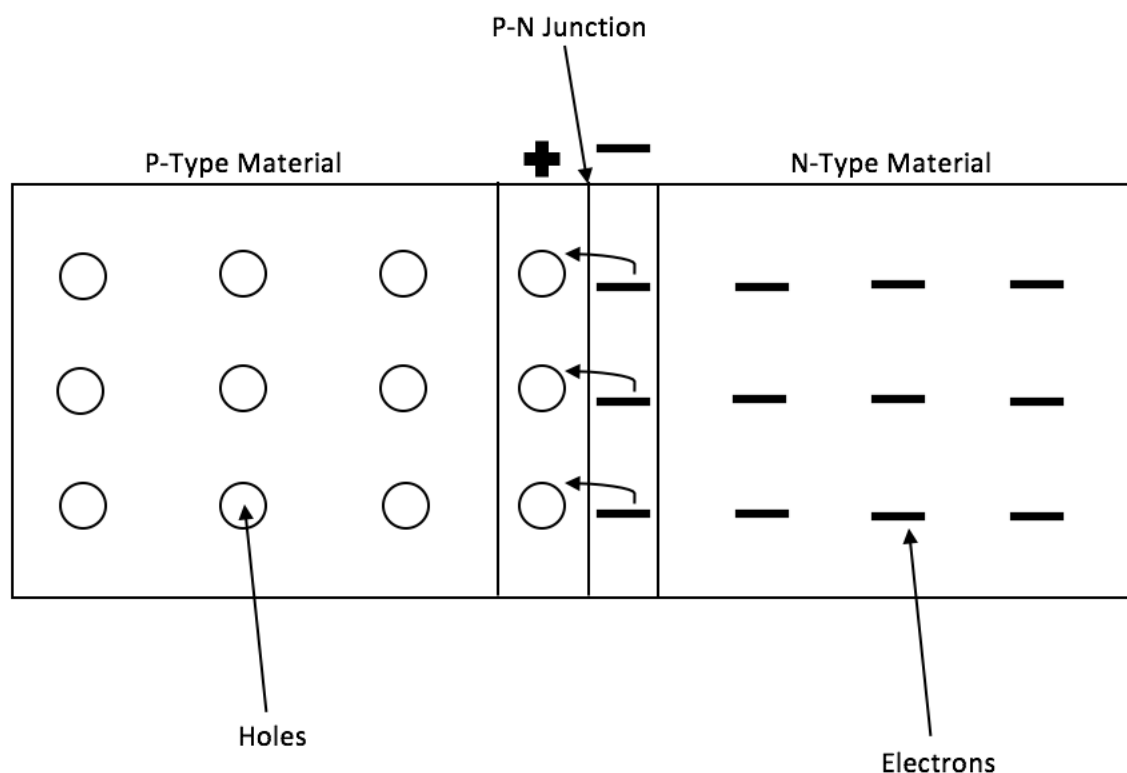


Figure 1 The diagram above shows the influence of the p-n junction on the production of current. The *n*-type material has an excess of electrons that try to fill the holes of the *p*-type material. This movement of charge generates current in semiconductors.

In a traditional solar cell, *n*-type and *p*-type semiconductors are silicon-based and are doped with various impurities.^{9,10} For *n*-type semiconductors, the silicon is doped with pentavalent phosphorous atoms. When energy in the form of light comes in, some of the electrons in the doped material are excited and become free electrons. On the other hand, for *p*-type semiconductors, the silicon is doped with trivalent boron atoms. When light strikes the *p*-type material, the electrons in the doped material are both excited into the conduction band as free electrons, and move to fill electron holes.^{9,10} Both processes can be successfully used to produce current. When we place the *n*-type and *p*-type materials together, the extra electrons in the pentavalent atom will fill the holes in the trivalent atom when photons are absorbed. This

action creates an electric field at the p-n junction since the *n*-type material is now positively charged while the *p*-type is negatively charged (Figure 1).¹⁰ The field created drives the movement of electrons across the semiconductor, producing current.

While inorganic solar cells have a high efficiency rate, reaching power conversion efficiencies up to 30%, they prove to be inflexible to change and quite costly.¹¹ To have highly efficient inorganic solar cells, they must be thoroughly purified. The purification process is quite costly and high in energy consumption, limiting their use as an eco-friendly energy source.¹¹ In addition, inorganic solar cells are inflexible. They are mostly found as thick, flat panels, limiting their applications in many electronic materials due to their bulky nature.¹¹ A possible solution to these issues lie in the generation and development of organic-based semiconducting materials instead of inorganic semiconducting materials.

Organic semiconductors, unlike inorganic ones, can be functionally modified by tuning the molecular structures, are less costly when it comes to manufacturing materials, and can be produced in large-scale.¹¹ Chemical modification of the materials allows chemists to choose well-defined nanomaterials that will absorb sunlight efficiently, and then incorporate those materials into polymer systems. The flexibility of these polymers also allows for the production of ultra-thin, flexible solar cells. The flexibility of the solar cells allows them to be easily incorporated into electrical devices. Currently, a major use of organic semiconductors is for OLED devices. These devices are used in things such as televisions, phones, and tablets to create digital displays.¹¹ The rise in demand of organic solar cells has led material chemists to synthesize polymers with higher charge-transport efficiencies, with current efficiencies near 5%.¹¹

A major difference between the inorganic and organic semiconductors is the energy band gap between the valence, LUMO, and conduction band, HOMO (Figure 2). The inorganic semiconductors have a much smaller band gap, allowing them to incorporate most of the visible light spectrum. On the other hand, organic semiconductors have a larger band gap, leading to the absorption of high energy light, such as UV. The smaller the band gap, the higher the efficiency in exciting electrons into the conduction band. In addition, the high-energy UV light can cause the polymers to degrade over time, leading to a low lifetime. Such obstacles must be overcome to produce more efficient organic semiconductors.

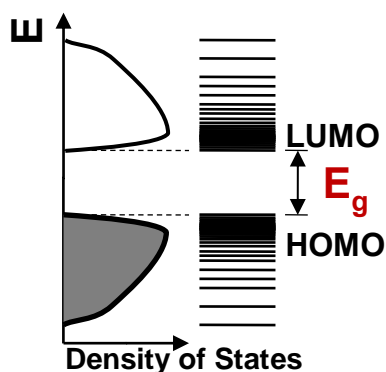


Figure 2 The diagram above represents the energy band gap (E_g) between the HOMO and LUMO of a polymer. Electrons must escape the HOMO and enter the LUMO to be harnessed for current.

Naphthalenediimide (NDI) monomers are increasingly being studied for organic semiconducting polymers (Figure 3). NDI monomers are attractive for organic electronics due to their electron accepting ability, thermal, chemical, and photochemical stability, as well as their high electron affinities and charge-carrier mobility.³ Their molecular structure allows them to have such noteworthy properties. The imide substituents, for instance, have a strong electron-withdrawing tendency.² This allows the NDI monomers to act as acceptor materials. The naphthalene core of the NDI monomer decreases the HOMO-LUMO band gap due to its

conjugation. The higher the conjugation, the smaller the band gap, so NDI derivatives can be utilized in polymers to shift away from UV absorption for excitation and towards visible light absorption. The R-groups on the NDI are usually branched or unbranched alkyl chains. These alkyl chains do not directly influence the electronic and optical properties of the NDI, but rather are used to control solubility, aggregation, and intermolecular packing.³

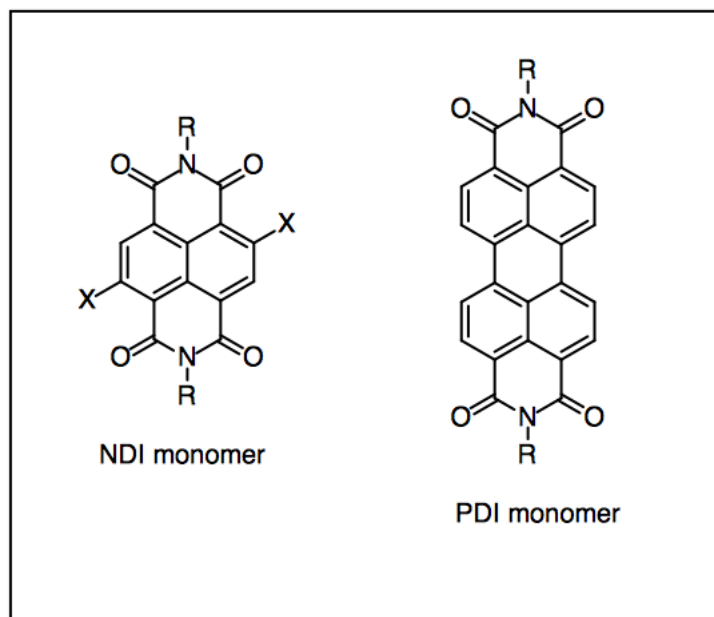


Figure 2 The figure above shows the structures of the NDI and PDI monomers. While PDI monomers are heavily used in organic semiconductors, NDI monomers have gained attention for their desirable electronic and synthetic properties.

Prior to the research of NDI monomers as possible monomers in organic semiconductors, PDI was more extensively studied and used (Figure 3).⁵ PDI derivatives were utilized in semiconductors because of their high photostability and electron mobility, ability to absorb in the visible spectrum, and low production cost.⁵ The issue with the PDI monomers is that they tend to aggregate into columnar superstructures, limiting charge transport ability, and are difficult to obtain in a regioisomerically pure form.^{2,5} NDI monomers, on the other hand, are readily

obtained in their dibrominated form. In addition, the NDI has a smaller naphthalene unit, so it will likely have greater solubility and lower chances of forming aggregates.²

Along with NDI acceptor monomers, 4,4-difluoro-4-borata-3a-azonia-4a-aza-s-indacene (BODIPY) donor monomers have also recently been researched for their applications in organic semiconductors. BODIPY dyes are promising monomers for organic semiconducting polymers because of their high absorption coefficients, fluorescence quantum yields, and photostability.^{1,8} Since BODIPY is a weak donor, however, bithiophene is highly utilized as a strong donor molecule, often alongside other donor molecules.^{2,7} The bridge created by the bithiophene also helps limit the steric interactions of monomers such as NDI and BODIPY when polymerized.¹

This research incorporates NDI and BODIPY into polymers for use in organic semiconductors. Two types of donor-acceptor polymers are synthesized for testing charge transport. The first polymer is a NDI-bithiophene copolymer in which the NDI acts as an acceptor while the bithiophene acts as a donor. The second polymer is a NDI-BODIPY copolymer where the NDI acts as an acceptor and the BODIPY acts as a weak donor. The BODIPY is modified from previous research by incorporating a new branched R group, bithiophene units, and a new polymerization method. Once the monomers and polymers were synthesized, their absorption and emission spectra were obtained. The resulting polymers will be used as organic *n*-type materials for semiconductors. The synthetic methods of these polymers were evaluated and modified to produce higher yields.

2. Synthesis and Characterization of NDI-thiophene Polymers

To assess the efficiency of organic semiconductors, first we started by synthesizing dibrominated naphthalene diimide monomers for Stille cross-coupling with 2,2'-bithiophene

monomers to produce a conjugated NDI-bithiophene polymer (Figure 4). Procedures for the synthesis of the di-brominated naphthalene diimide monomers were adopted from S.

Thayumanavan *et al.*, and were slightly modified to produce the products in high yields.¹

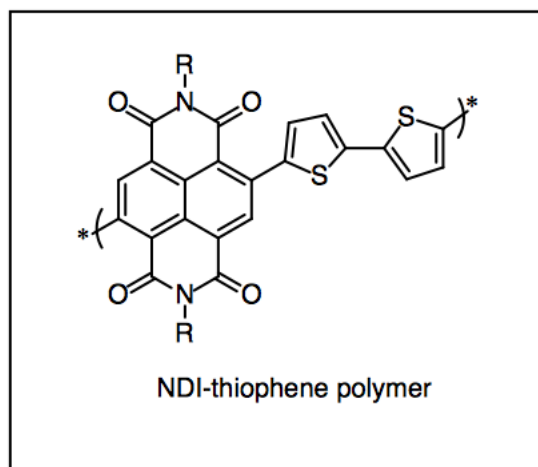
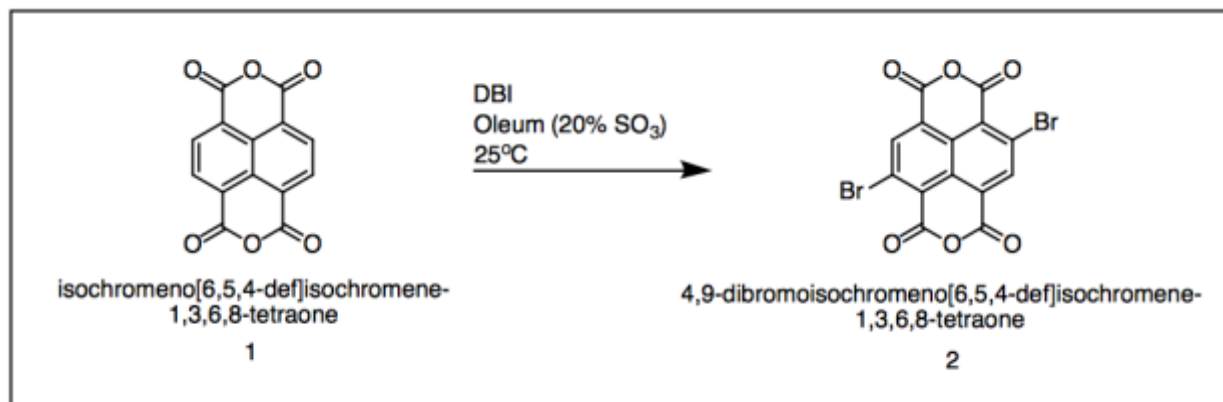


Figure 4 Proposed NDI-bithiophene polymer synthesized via Stille Coupling.

After di-brominated NDI monomer was synthesized, the NMR and LC-MS were used to determine product formation and possible byproducts in the reaction. Gas phase chromatography (GCP) was run on the polymer to see its molecular weight distribution and to determine whether a polymer or oligomer was synthesized.

i. Short-Chain NDI Monomer Synthesis

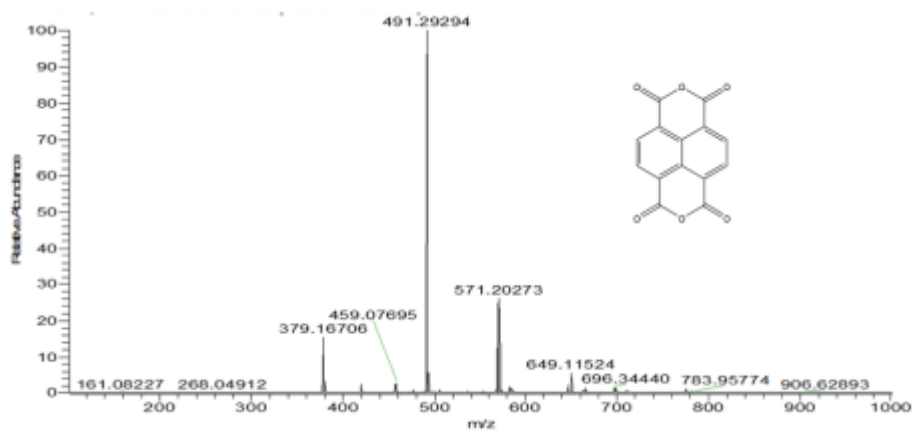
The first step for the synthesis of the NDI-bithiophene polymer shown in Figure 4 involved the bromination of naphthalenedianhydride (NDA) **1** to form di-brominated NDA **2** using dibromoisocyanuric acid as brominating reagent (Scheme 1).



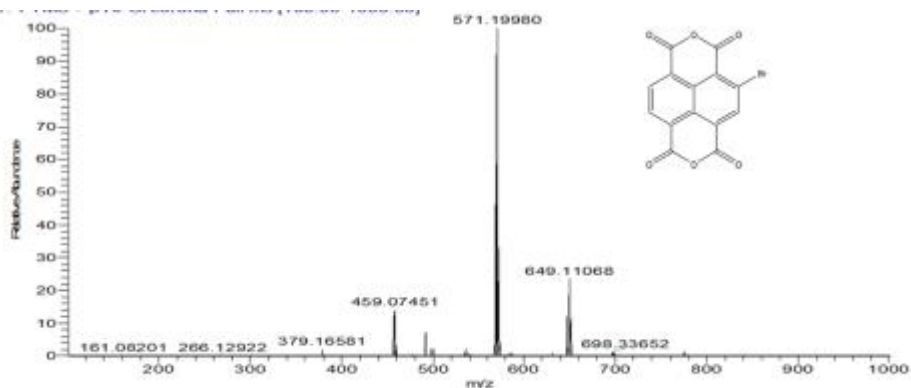
Scheme 1 Reaction scheme for the bromination of starting material NDA to obtain desired di-brominated naphthalene core

After completion of the reaction, as predicted, the crude product contained mono-, di-, and non-brominated NDA product, which was confirmed by mass spectroscopy (Figure 5). The products were not separated, so the non-, mono-, and di-brominated products were used for further reactions. The di-brominated product was used for the core of the polymer to promote the addition of bithiophene specifically at the 2,6-positions.

5a



5b



5c

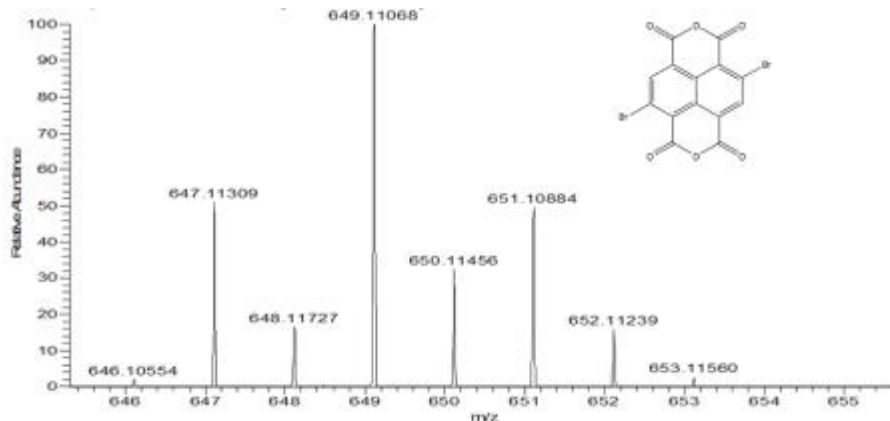
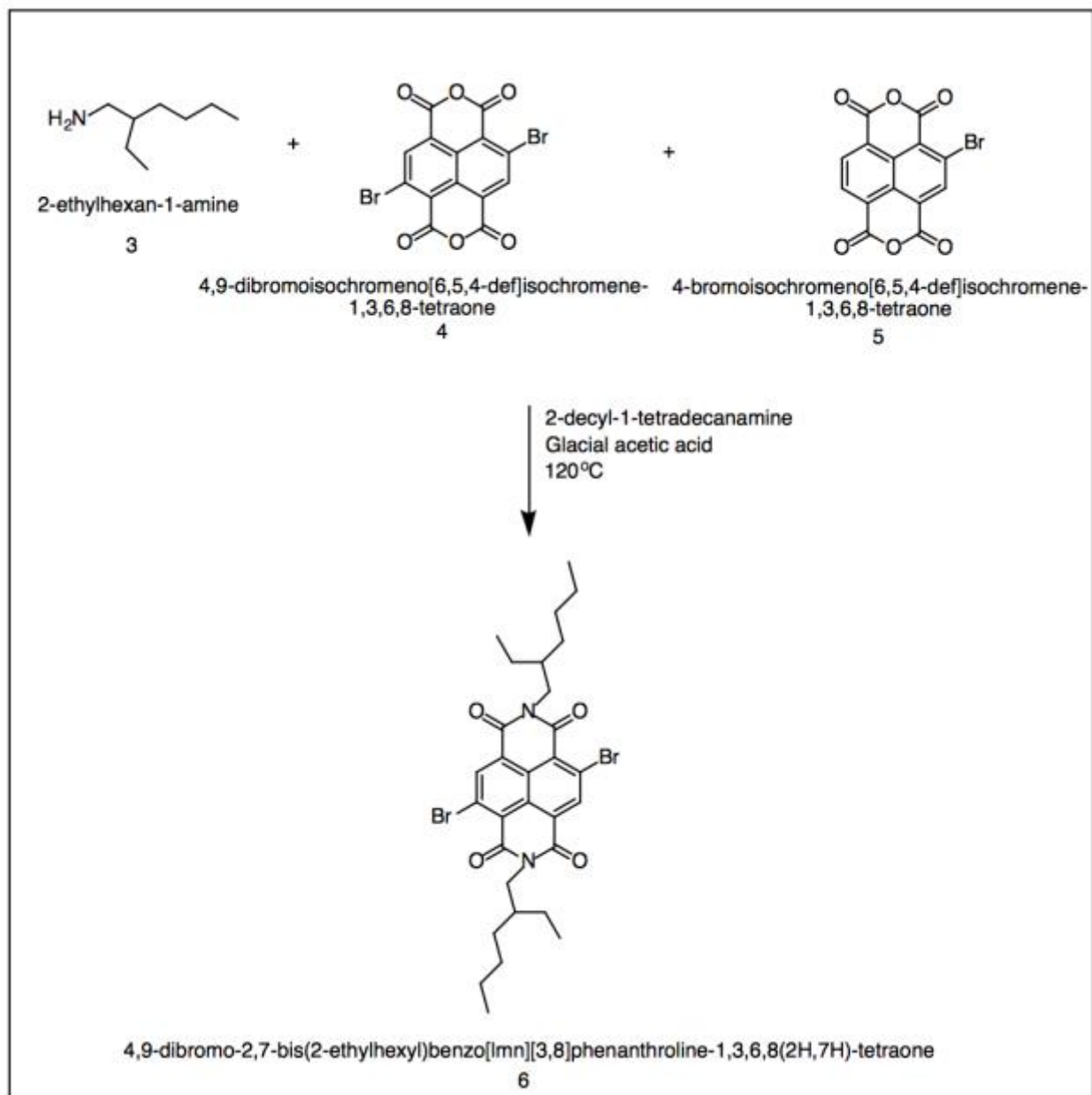


Figure 5 The products after the bromination reaction shown in Scheme 1 were analyzed using LC-MS and NMR spectroscopy. The mass spectroscopy results are shown above, and the highest fragment peak corresponds to the molecule displayed.

The next step of the polymer synthesis required di-brominated NDA monomer **4** to undergo a condensation reaction with 2-ethylhexan-1-amine **3** to form the final di-brominated NDI monomer **6** under high temperature (Scheme 2).



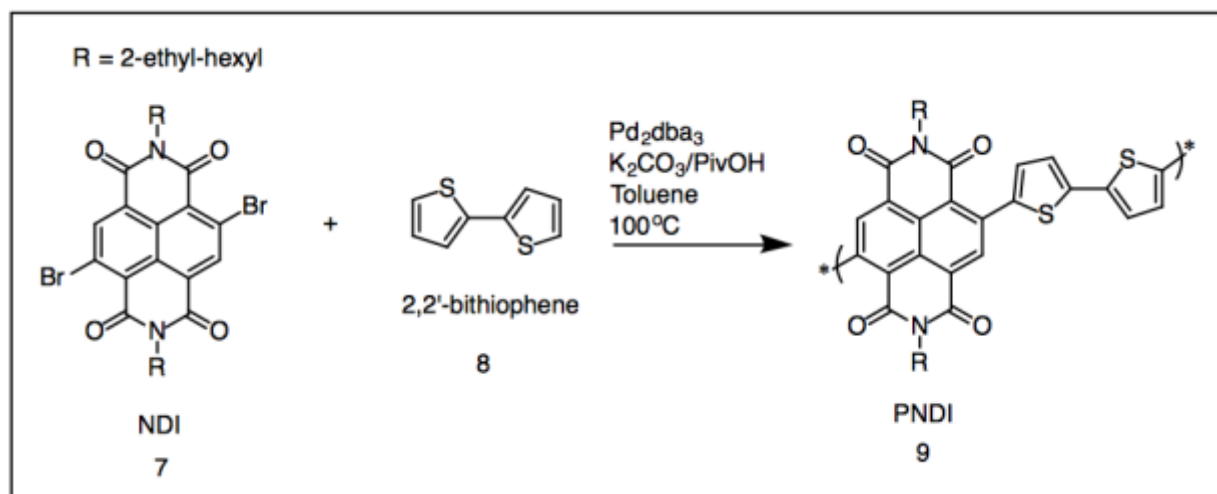
Scheme 1 Reaction scheme for the condensation reaction of 3, 4, and 5 to yield final monomer product 6.

Separation of the crude product revealed three monomers after column chromatography using DCM, confirmed by NMR, containing non-, mono-, and di-brominated NDI. The di-brominated product was isolated as an orange solid, and was used for further reaction with 2,2'-bithiophene. The percent yield, however, was originally only 22% for the di-brominated product

when following literature¹ procedures that used 2:1 naphthalene dianhydride/DBI. The mono-brominated and di-brominated NDI monomers had the highest percent yields, while the non-brominated product was minimal. In order to increase the bromination from mono- to di-brominated product, a 1:1 ratio of naphthalene dianhydride/DBI was used. After the modification, the percent yield increased from 22% to 40%. Further increase in the moles of DBI used, however, did not significantly increase the di-brominated product.

ii. NDI-Bithiophene Polymer Synthesis

The final step involved polymerization of the di-brominated NDI with 2,2'-bithiophene (Scheme 3). A C-H-type polymerization reaction was performed for the polymerization technique, and the reaction was left for one day to allow polymerization to occur.



Scheme 2 Stille coupling reaction to obtain the polymerization of di-brominated NDI with 2,2'-bithiophene monomers.

The formation of polymer was confirmed by using gel permeation chromatography (GPC) (Figure 6). The largest molecular weight peak had an Mw value of 3664, and a PD value of 2.0356 (Table 1). This indicates that small oligomers were formed rather than the polymers. The formation of oligomers instead of polymers can be attributed to either the reaction mixture

being too dilute, or the reaction time being too short. In the future, both the reaction time and concentration of the solution can be tested to see whether a change in those factors leads to the formation of polymers.

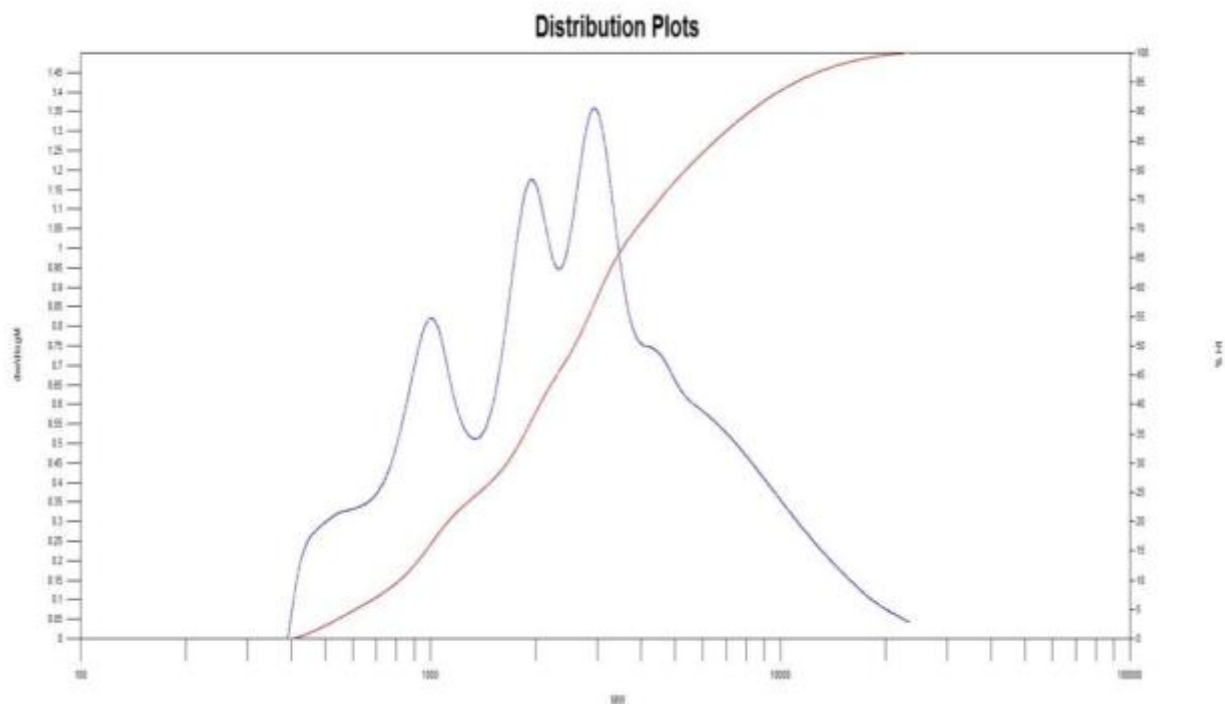


Figure 6 Shown above is the GPC measurement of the NDI-bithiophene polymer.

Peak No.	Peak Name	Start RT	Max. RT	End RT	Baseline Start RT	Baseline End RT	In FRM	Mp	Mn	Mw	Mz	PD	Peak Height [a.u.]	% Height	Peak Area [mV.e]	% Area
1		15.0055	18.3700	20.0049	15.5165	20.0049		2942	1000	3664	6967	2.0356	461017.295	21.8310	56362049.3	62.6962
2		20.9075	21.1788	21.8912	20.8897	21.8912		298	272	278	281	1.0147	1650742.58	78.1690	33502363.6	37.3438

Table 1 The largest molecular weight peak had a Mw value of 3664 and a PD value of 2.0356, indicating the formation of oligomers instead of polymers.

3. Synthesis and Characterization of NDI-BODIPY Polymers

In addition to NDI-bithiophene polymers, NDI-BODIPY polymers were synthesized to test whether BODIPY-thiophene donors increase charge transport compared to just using bithiophene (Figure 7). Procedures for the synthesis of the BODIPY monomers were obtained from S. Thayumanavan *et al.* and procedures for the synthesis of the di-brominated naphthalene

diimide monomers were obtained from Mark Watson *et al.*^{1,2} Both procedures were modified to produce higher yields of products.

Preparation of the NDI and BODIPY monomers were confirmed using NMR, and production of the NDI-BODIPY precursor was confirmed using GPC. The absorption and emission spectra of the monomers and polymers were obtained using UV-Vis and fluorescence spectroscopy.

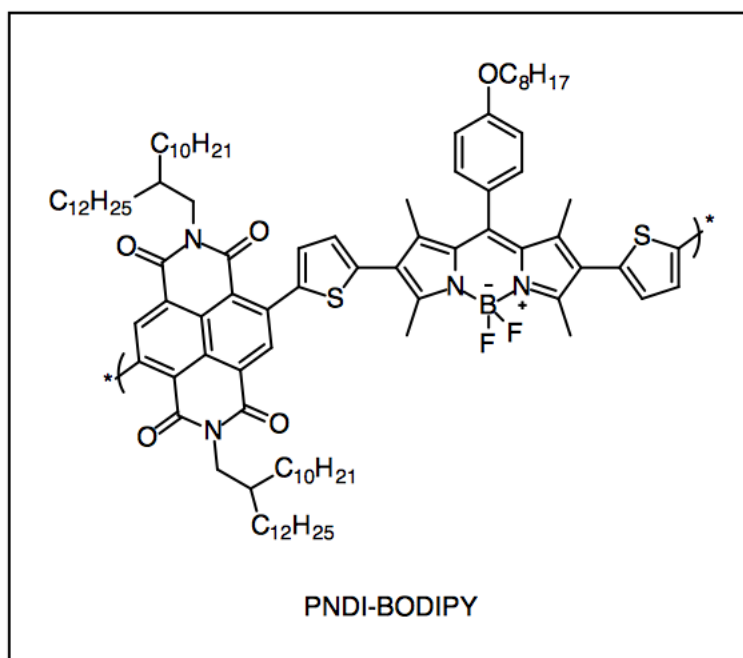
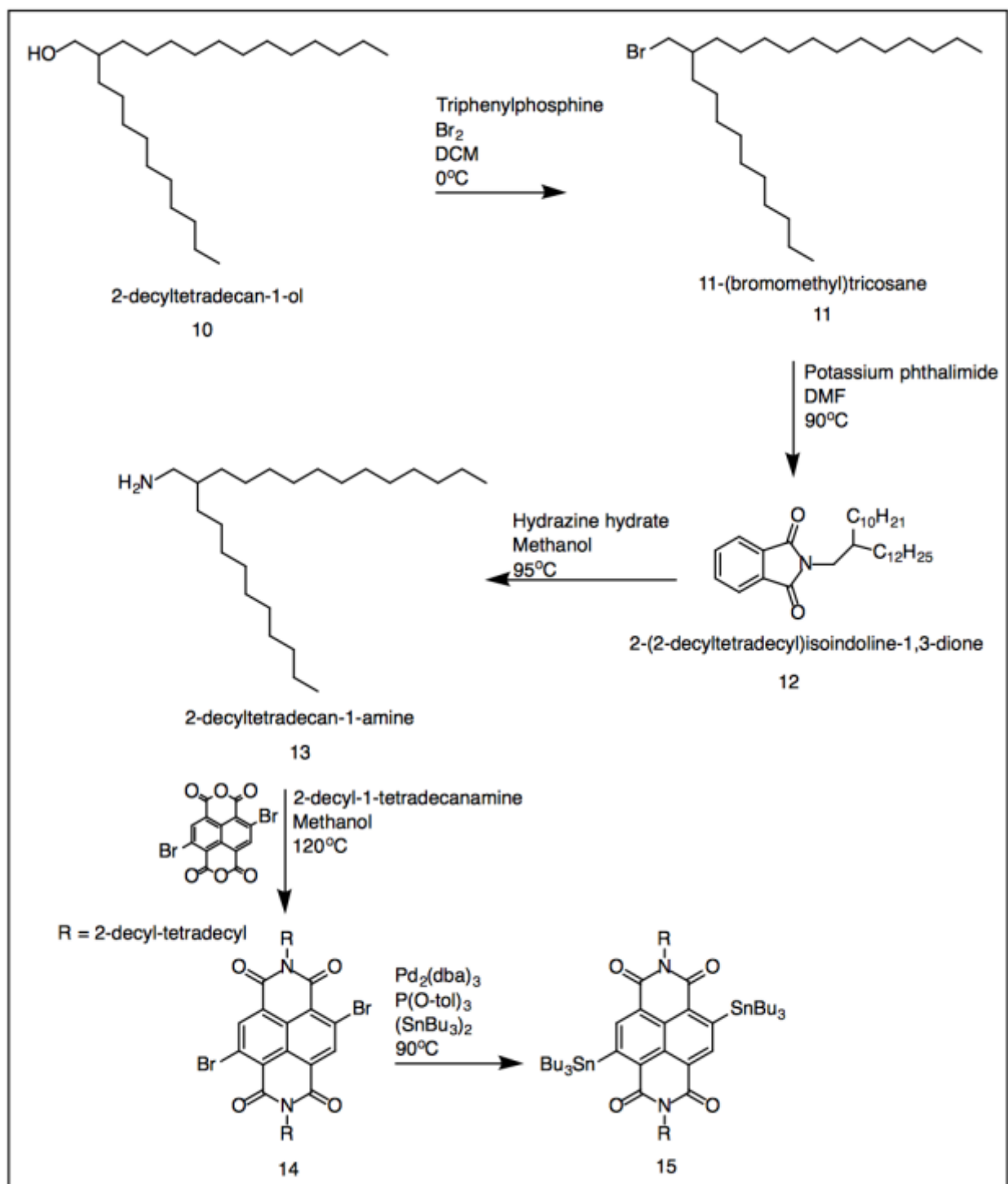


Figure 7 Proposed NDI-BODIPY polymer synthesized via Stille Coupling.

i. Long-Chain NDI Monomer Synthesis

The NDI core was synthesized using the reaction shown in Scheme 1. The R-group on the NDI was modified from 2-ethyl-hexyl to 2-decyl-tetradecyl (Scheme 4). To synthesize the R-group, 2-decyltetradecan-1-ol **10** underwent an Appel reaction to produce the brominated branched alkyl chain 2-decyl-1-tetradecylbromide **11**. The brominated product was converted into a branched amine 2-decyltetradecan-1-amine **13** using Gabriel synthesis. A condensation

reaction ensued, resulting in the branched, di-brominated NDI monomer **14**. The final stannylated product is formed through stannylation of monomer **14**. During the synthesis of the di-brominated NDI monomer **14**, three products formed according to TLC. Originally, the three spots were separated using column chromatography after the reaction. However, the spots were very close, and some product could not be fully separated, resulting in a lower percent yield. Previous research has shown that the stannylated NDI **15** has better separation than the non-, mono-, and di- brominated products since the spots are farther apart.⁴ Thus in future experiments, the separation method can be changed from running a separation technique on reaction **14** to reaction **15** to increase overall yields. The resulting stannylated NDI **15** was used for further polymerization.



Scheme 4 Reaction scheme for the synthesis of 2-decyl-tetradecyl NDI monomer.

The absorption and emission spectra of the branched NDI monomer **14** was obtained in chloroform (Figure 8 & 9). The maximum absorbance has a peak at ~390nm, while the maximum intensity emission has a peak at ~494nm. The maximum absorbance is between the UV and visible range, while the maximum emission is in the visible range. The polymer had high solubility in chloroform.

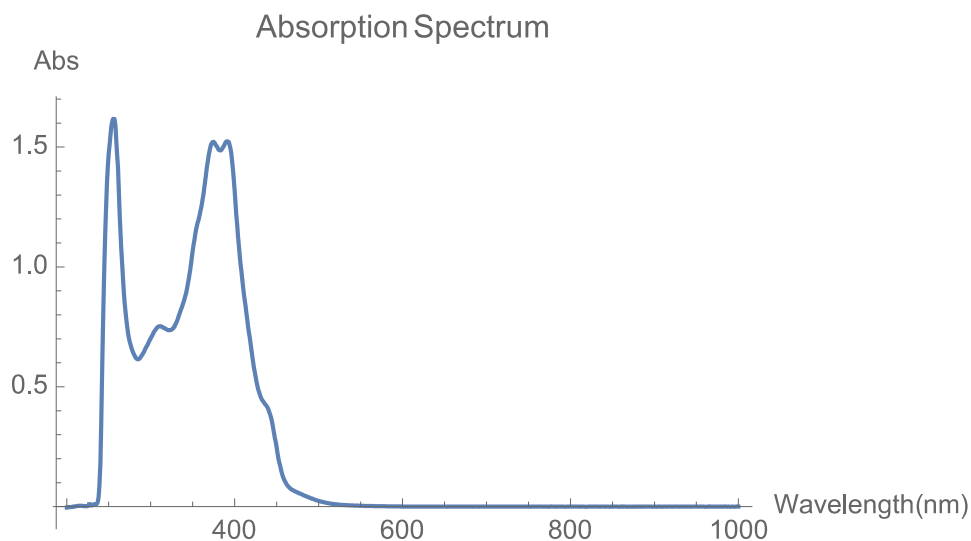


Figure 8 UV/Vis spectrum of branched NDI Monomer in chloroform. Maximum absorbance peak seen at 390nm.

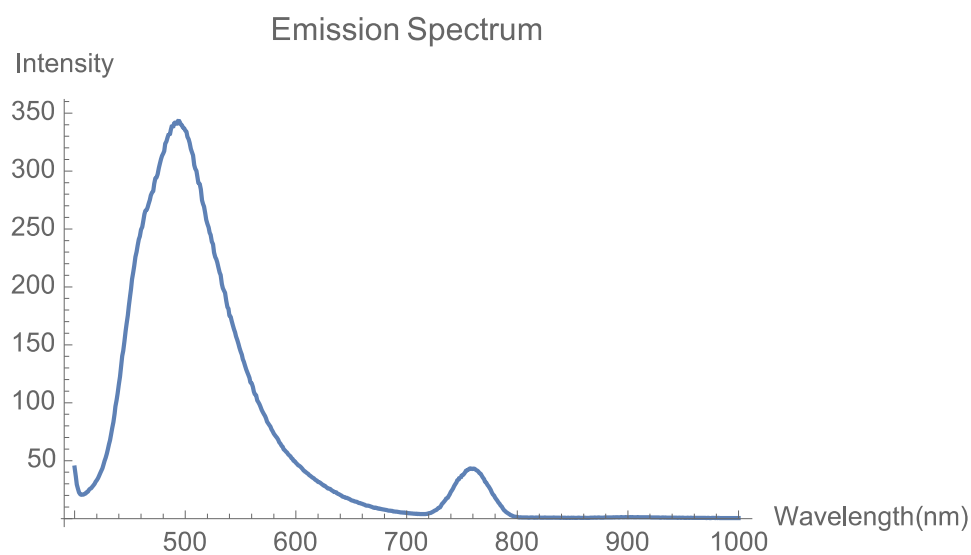


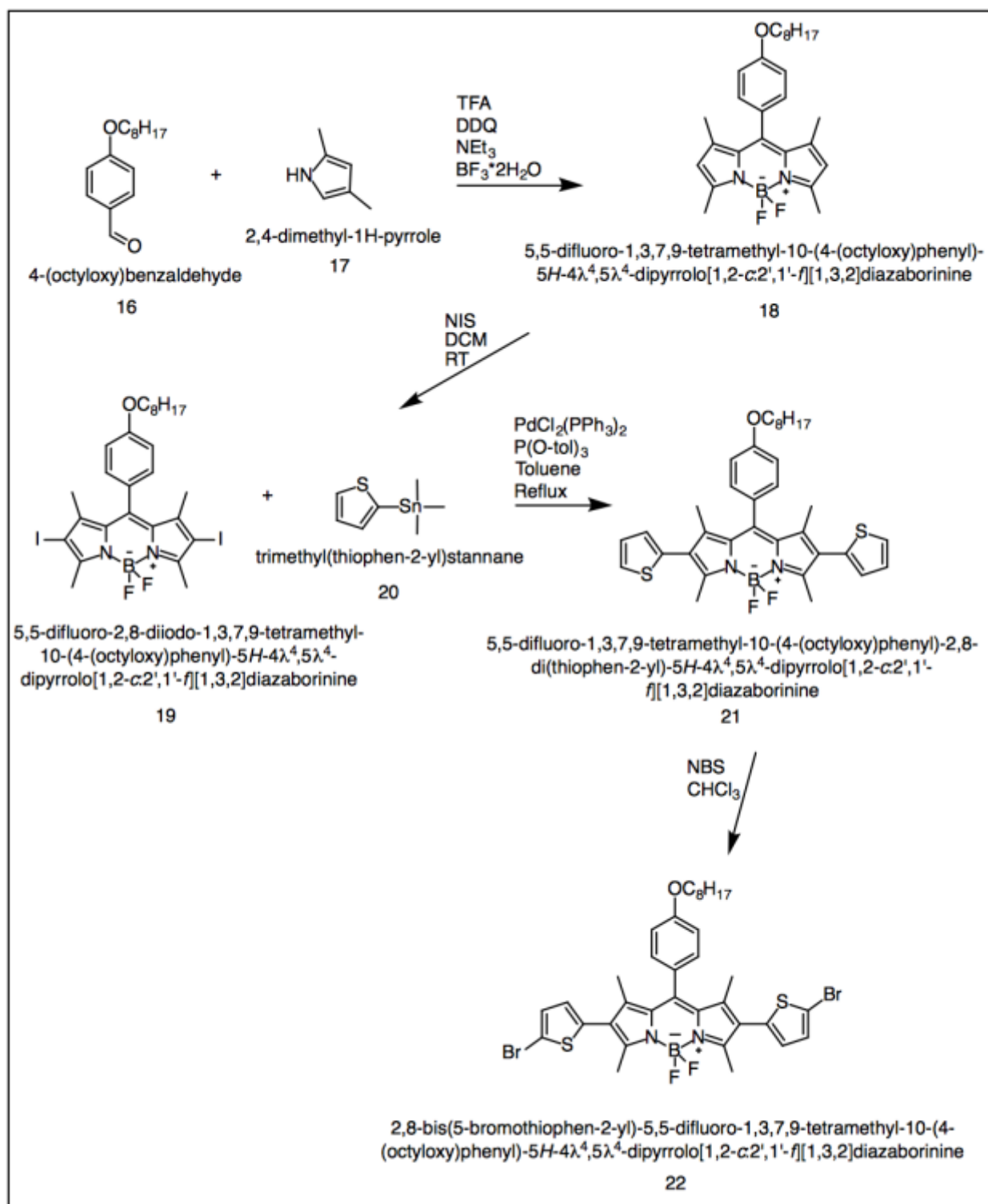
Figure 9 Emission spectrum of branched NDI monomer in chloroform. Maximum emission peak seen at 494nm.

ii. *BODIPY Monomer Synthesis*

The BODIPY monomer was synthesized using the reactions shown in Scheme 5. The starting materials 4-(octyloxy)benzaldehyde **16** and 2,4-dimethyl-1H-pyrrole **17** underwent a condensation followed by a cyclization reaction to produce the BODIPY starting material **18**. A halogenation reaction on **18** yielded the iodo-BODIPY monomer **19**. The BODIPY starting material **18** had a very low yield of 20% when using a one-pot synthesis. However, an even lower yield was obtained when separating out the synthetic steps and purifying before subsequent reactions instead of using one-pot synthesis. The lower yields seen when separating synthetic steps may be due to small amounts of product being lost when running column chromatography, or reactions not being carried out over enough time to allow for the molecules to react. To analyze the effects of time in the one-pot synthesis, the reactions were allowed to react for longer periods of time before adding the next step. However, this solution had negligible effects on the yield. Thus, perhaps new synthetic routes need to be found for the formation of **18** to decrease the amount of wasted chemicals and increase yields.

The iodo-BODIPY monomer **19** was then converted into the BODIPY-thiophene monomer **21** through Stille cross-coupling reaction. The original reaction used 1:2 equivalents of BODIPY/thiophene, but this resulted in a yield of <30%. To increase the yield, the equivalents of thiophene were increased to 1:3.5 BODIPY/thiophene, resulting in a yield of 39%. Subsequent increase in the equivalents of thiophene had minimal effects on the yield. The BODIPY-thiophene monomer **21** was then brominated using NBS, resulting in the formation of **22**. Multiple products were found after running TLC because of varying amounts of bromination.

The products were extremely close on TLC, resulting in the need to use prep TLC to get pure compound instead of column chromatography.



Scheme 5 Reaction scheme for the synthesis of BODIPY monomer.

The absorption and emission spectra of the BODIPY monomer (**3**) was obtained in chloroform (Figure 10 & 11). The maximum absorbance has a peak at ~540nm, while the maximum intensity emission has a peak at ~614nm. The maximum absorbance and maximum emission are in the visible light range. The polymer had high solubility in chloroform.

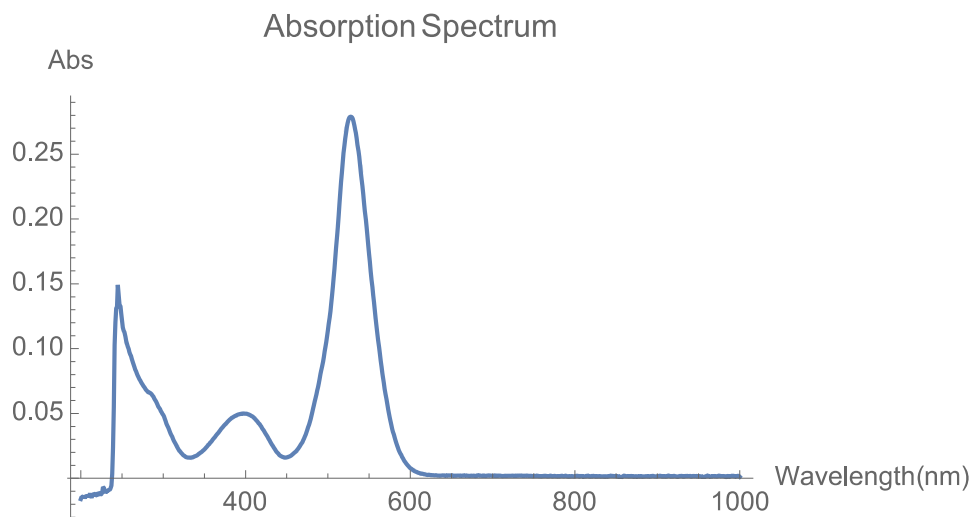


Figure 10 UV/Vis spectrum of BODIPY monomer in chloroform. Maximum absorbance peak seen at 540nm.

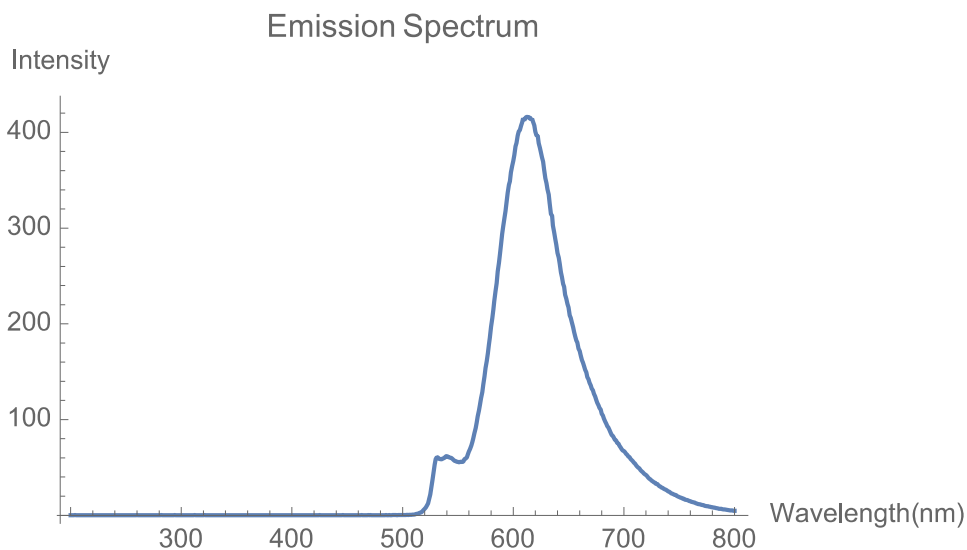
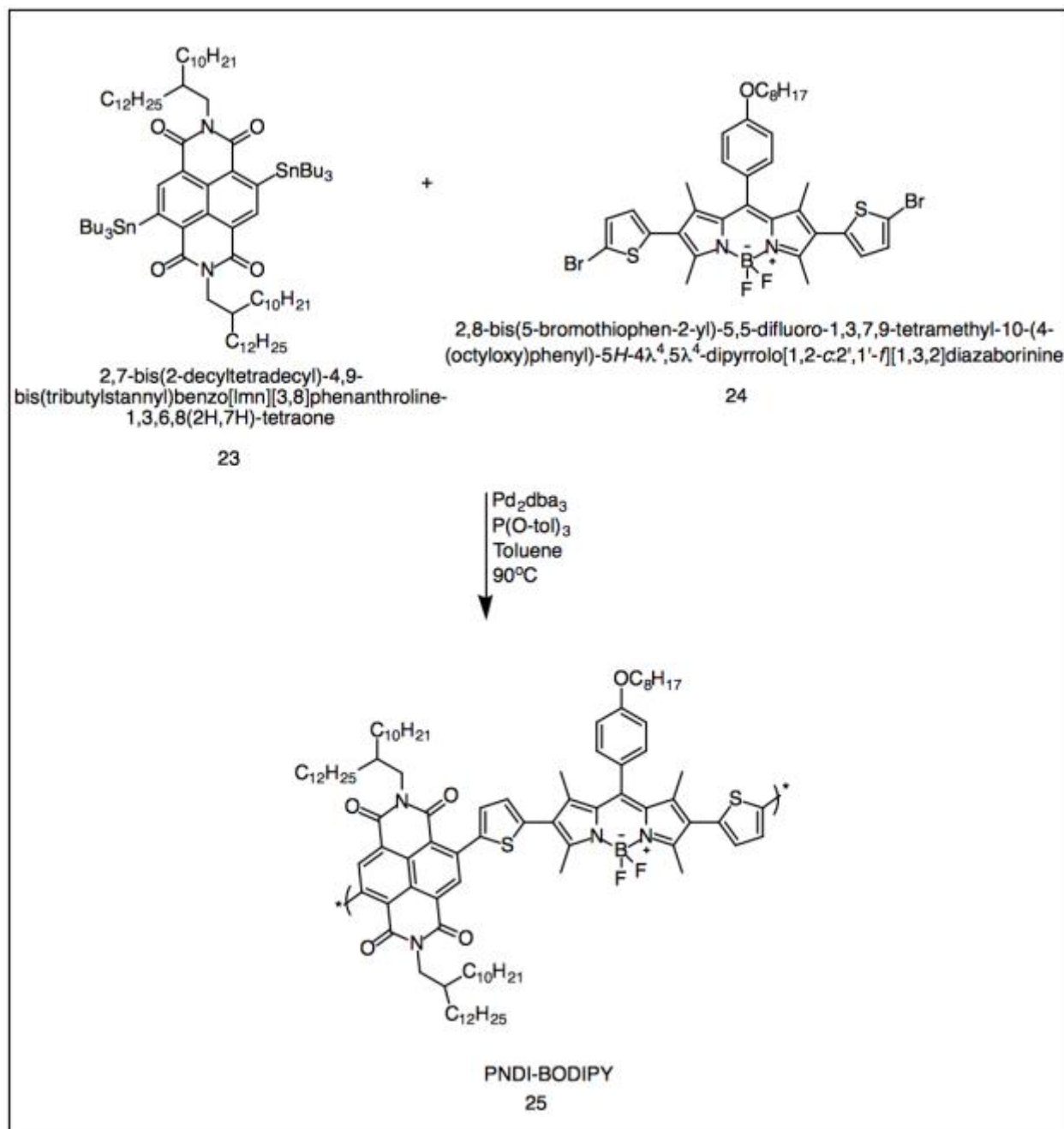


Figure 11 Emission spectrum of BODIPY monomer in chloroform. Maximum emission peak seen at 614nm.

iii. *NDI-BODIPY Polymer Synthesis*

Stille coupling was used for the polymerization technique, and the reaction was left for three days to allow successful polymerization to occur (Scheme 6).



Scheme 6 Stille coupling reaction to obtain the polymerization of long-chain di-brominated NDI with BODIPY.

The formation of polymer was confirmed by gel permeation chromatography (GPC) (Figure 12). The largest molecular weight peak had an Mw value of 23228, and a PD value of 1.8. These values indicate that the polymerization reaction was successful, and the NDI-BODIPY polymer formed.

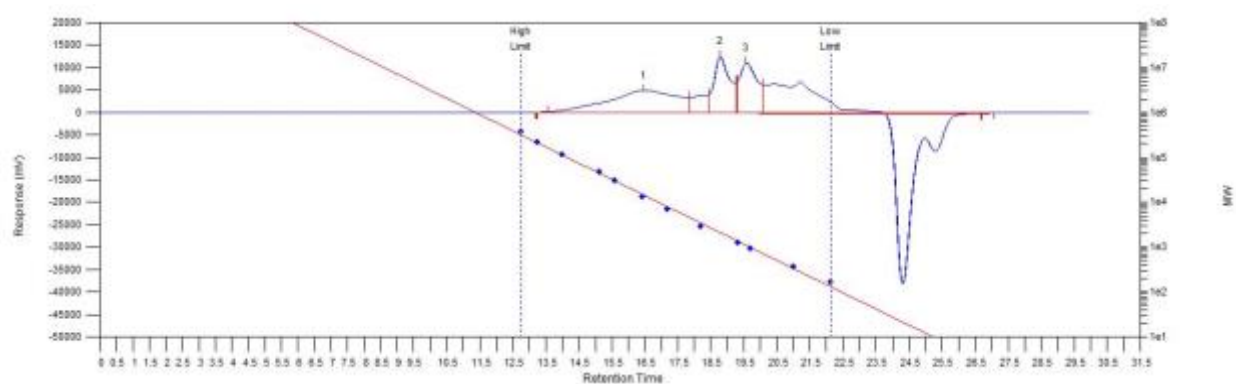


Figure 12 Shown above is the GPC measurement of the NDI-bithiophene polymer.

Peak	Peak Name	Start RT	Max. RT	End RT	Baseline St	Baseline En	Is FRI	Mp	Mn	Mw	Mz	PD	Peak Height	% Height	Peak Area	% Area
1	Unknown	13.5880	16.4891	17.8508	13.2210	26.6729		14412	12726	23228	44726	1.8252	4967.4152	17.2696	728848.738	46.4761
2	Unknown	18.4279	18.7722	19.2663	13.2426	26.7017		2118	1957	2620	2081	1.0322	12575.1919	43.7992	430031.164	27.4216
3		19.2960	19.5701	20.6768	13.1918	27.0491		1092	997	1627	1058	1.0301	11178.4082	38.9342	409343.930	26.1023

Table 2 The largest molecular weight peak had a Mw value of 23228 and a PD value of 1.8252, indicating the formation of polymers.

The absorption and emission spectra of NDI-BODIPY polymer (**5**) was obtained (Figure 13 & 14). The two absorbance peaks have maximums at ~400nm and 580nm, while the maximum intensity emission has a peak at ~678nm. Both the maximum absorbance and maximum emission values are in the visible light range. The maximum emission intensity is nearing the infrared region of light.

After polymerization, there is a shift in the absorption of the NDI and BODIPY monomers. The NDI monomer before polymerization had an absorption value of 390nm, while after polymerization it has an absorption value of 400nm. Similarly, the BODIPY monomer before polymerization had an absorption value of 540nm, while after polymerization it had an

absorption value of 580nm. The increase in the wavelength of the absorbed light indicates that the band gap between the HOMO-LUMO levels has decreased after polymerization, most likely resulting from the increased conjugation of the polymer versus just the monomers alone. In addition, the emission intensity has shifted to a higher wavelength for the polymer than both the BODIPY and NDI monomers alone.

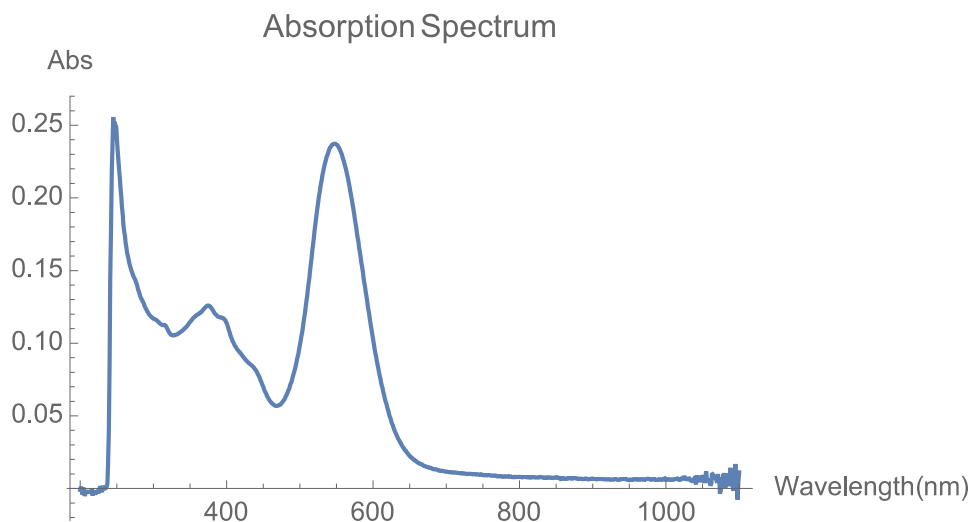


Figure 13 UV/Vis spectrum of NDI-BODIPY polymer in chloroform. Maximum absorbance peaks seen at 400nm and 580nm.

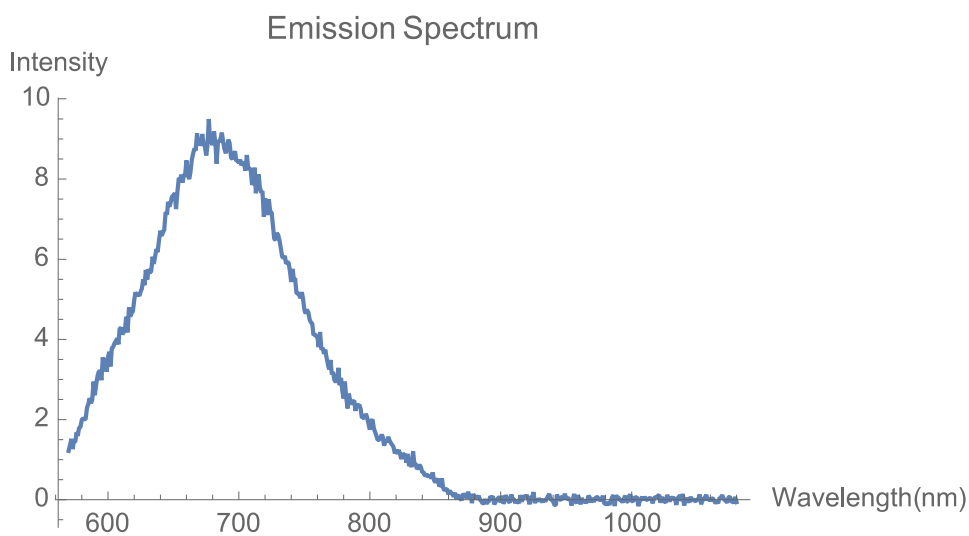


Figure 14 Emission spectrum of NDI-BODIPY polymer in chloroform. Maximum emission peak seen at 678nm.

4. Conclusion

The polymerization of just the short-chained NDI monomers failed to yield any polymers, but rather just oligomers. In the future, we will optimize the polymerization time and concentration to obtain polymers, and then take UV-Vis and fluorescence measurements, as well as test the polymer's charge transport properties. On the other hand, the polymerization of the long-chained NDI and BODIPY monomers was successful. Copolymerization of the NDI and BODIPY monomers gave a noticeable red shift in the absorbance wavelengths of the polymer compared to the individual monomers due to the increased conjugation of the polymer. While we were unable to test the charge transport, the polymer shows promise as a possible candidate for *n*-type organic semiconductors. Its shift away from absorption in the UV range, common of many organic semiconductors, and towards the visible range may indicate that the polymer will have a higher efficiency in successfully exciting electrons into the conduction band. In future experiments, we will test this theory by measuring the polymer's charge transport.

5. Experimental Methods

5.1 Synthesis of 4,9-bromoisochromeno[6,5,4-def]isochromene-1,3,6,8-tetraone (2)

Commercially available isochromeno[6,5,4-def]isochromene-1,3,6,8-tetraone (10mmol, 2.86g) was dissolved in 100mL of oleum (20% SO₃). In a separate solution, dibromoisocyanuric acid (10mmol) was dissolved in 50mL of oleum (20% SO₃). The second solution was added into the first solution dropwise over 4 hours at 0°C over an ice bath. After 4 hours, the solution was left to stir for an additional 1 hour at room temperature, and then poured onto 500g of ice. The mixture was left for 3 hours, and then the yellow-green precipitate was collected using vacuum

filtration. The solid was washed with dilute HCl and dried without further purification to afford **2,3** as a brown-green solid (3.41g, 80%). ¹H NMR was confirmed by literature.⁴

5.2 Synthesis of 4,9-dibromo-2,7-bis(2-ethylhexyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (6)

2 (3g, 7.04mmol), 2-ethyl-hexylamine (3.64g, 28.16mmol), and 80mL of glacial acetic acid were stirred under argon at 120°C overnight. The concentrate was added to 200mL methanol, and the resulting precipitate was collected by filtration, washed with methanol and dried under reduced pressure. The product was purified using a silica gel column run in 100% DCM, followed by recrystallization from hexanes to afford **4** as a red solid (1.83g, 40%). ¹H NMR was confirmed by literature.¹

5.3 Synthesis of PNDIT₂ (9)

Commercially available 2,2'-bithiophene (6.73mg, 0.0405mmol), **6** (28mg, 0.0432mmol), potassium carbonate (59.94mg, 0.4337mmol), and pivalic acid (4.41mg, 0.032mmol) were weighed into a dry vial with stir bar added. 0.203mL of degassed dry toluene was added under argon, and the solution was stirred for 5min at room temperature to dissolve monomers. Commercially available Pd₂dba₃ (1.324mg, 0.001446mmol) was added under argon to the solution. The vial was heated to 100°C and stirred for 14 hours in an oil bath. The solution was cooled to room temperature, and then dissolved in 6.77mL of chloroform. The polymer was precipitated into 70mL of methanol, filtered, and purified using Soxhlet extraction with acetone, ethyl acetate, and hexanes. The resulting product was collected using chloroform, and filtered

through a silica gel plug. Gas phase chromatography was used to confirm the formation of polymer (Figure 3).

5.4 Synthesis of 2-decyl-1-tetradecylbromide (11)

Triphenylphosphine (18.7g, 0.0712mol) was sparged in 115mL of DCM with argon at 0°C for 15 minutes. 3.66mL of bromine was added dropwise into the solution. Commercially available 2-decyltetradecan-1-ol (30mL, 0.0712mol) was then added dropwise via addition funnel over 30 minutes. The reaction was stirred overnight under argon at room temperature. The DCM was evaporated and then resulting concentrate was filtered with pentane wash to yield a crude yellow oil. The resulting crude product was purified using a silica gel column run in 4:1 hexane/DCM to yield **2** as a yellow oil (16.946g, 57%). ¹H NMR was confirmed by literature.²

5.5 Synthesis of 2-(2-decyltetradecyl)isoinodoline-1,3-dione (12)

Potassium phthalimide (7.5g, 0.0404mol) was added to a solution of 2-decyl-1-tetradecylbromide (15.7g, 0.0376mol) in 45mL of dry DMF. The reaction was stirred overnight at 90°C and then cooled to room temperature. The reaction was poured into 150mL of water and extracted with DCM. The combined organic layers were washed with 200mL of 0.2M KOH, water, saturated ammonium chloride, and then dried over Na₂SO₄. Concentration yielded a crude yellow oil, which was purified using a silica gel column run in 100% DCM to yield **3** as a clear oil (15.8g, 87%). ¹H NMR was confirmed by literature.²

5.5 Synthesis of 2-decyltetradecan-1-amine (13)

N-(2-decyltetradecyl) phthalimide (10g, 0.021mol), 4mL of hydrazine hydrate (0.021mol), and 100mL of methanol were stirred at 95°C and monitored by TLC for completion. Once the starting imide disappeared, the methanol was evaporated and the residue was diluted with 100mL of DCM and washed with 10% KOH solution. The aqueous layers were combined and extracted with DCM. The resulting organic layers were washed with brine and dried with Na₂SO₄. The DCM was evaporated, yielding a yellow oil without further purification (5.346g, 73%). ¹H NMR was confirmed by literature.²

5.6 Synthesis of 4,9-dibromo-2,7-bis(2-decyltetradecyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (14)

Di-brominated naphthalene dianhydride (0.20g, 0.469mmol), 2-decyl-tetradecylamine (0.24g, 0.678mmol), and 6mL of glacial acetic acid were stirred under argon at 120°C. The acetic acid was evaporated once all the solids were dissolved, and the concentrate was added to 15mL of methanol. The resulting red solid was collected by filtration, washed with methanol, and dried. The solid was not purified further to yield **5** as an orange solid mixture (0.213g, 41%). ¹H NMR was confirmed by literature.²

5.7 Synthesis of 2,7-bis(2-decyltetradecyl)-4,9-bis(tributylstannyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (15)

Di-brominated NDI mixture **14** (300mg, 0.295mmol), commercially available tributyltin (344mg, 0.59mmol), tri(*o*-tolyl)phosphine (18mg, 0.059mmol), and tris(dibenzylideneacetone)dipalladium(0) (13.5mg, 0.01475mmol) were added to 4mL of dry toluene and refluxed overnight at 90°C under argon. The reaction was precipitated in methanol

and the solid was filtered using vacuum filtration. The crude orange product was purified using a silica gel column run in 100% DCM to yield **6** as an orange-yellow solid (203mg, 56%). ¹H NMR was confirmed by literature.¹²

5.8 Synthesis of 5,5-difluoro-2,8-diiodo-1,3,7,9-tetramethyl-10-(4-(octyloxy)phenyl)-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (**18**)

Commercially available 4-octyloxybenzaldehyde (0.75mL, 3.137mmol) and 2,4-dimethyl-1H-pyrrole (0.738g, 7.84mmol) were added into 80mL of dry DCM in a flask. A solution of trifluoroacetic acid (53.65mg, 0.47mmol) in 3.5mL of dry DCM was slowly added into the flask at room temperature. After 3 hours, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.712g-3.137mol) was added to the solution under an ice bath and stirred for 20 minutes. The resulting solution was left at room temperature and stirred for another 1 hour. Triethylamine (4.57g, 45.17mmol) was then added, followed by the slow addition of boron trifluoride diethyl etherate (7.57g, 53.33mmol). The reaction was left to stir overnight, and then washed with saturated sodium carbonate and dried with sodium sulfate. The solution was concentrated under reduced pressure, and the concentrate was dissolved in hexane. The product was purified using a silica gel column in 5:1 hexane/DCM, resulting in a red/green product with green fluorescence (284mg, 20%). ¹H NMR was confirmed by literature.¹

5.9 Synthesis of 5,5-difluoro-2,8-diiodo-1,3,7,9-tetramethyl-10-(4-(octyloxy)phenyl)-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (**19**)

Commercially available N-iodosuccinimide (601.7mg, 2.67mmol) and previously synthesized **1** (550mg, 1.21mmol) were added to 25mL of DCM. The solution was stirred at room temperature

overnight under argon and then washed with sodium thiosulfate. The product was carried to the next step without further purification (528mg, 62%). ¹H NMR was confirmed by literature.¹

5.10 Synthesis of 5,5-difluoro-1,3,7,9-tetramethyl-10-(4-(octyloxy)phenyl)-2,8-di(thiophen-2-yl)-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (21)

Previously synthesized **19** (50mg, 0.071mmol), commercially available 2-(tributylstannyl)thiophene (92.7mg, 0.249mmol), tris(dibenzylideneacetone)diipalladium(0) (6.5mg, 0.0071mmol), and tri(o-tolyl)phosphine (8.6mg, 0.0284mmol) were refluxed overnight in 5mL of toluene at 90°C under argon. The resulting crude product was purified using a silica gel column run in 1:4 DCM/hexane to yield (**21**) as a red-colored, fluorescent-pink molecule (17mg, 39%). ¹H NMR was confirmed by literature.¹

5.11 Synthesis of 2,8-bis(5-bromothiophen-2-yl)-5,5-difluoro-1,3,7,9-tetramethyl-10-(4-(octyloxy)phenyl)-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (22)

Previously synthesized **21** (17mg, 0.029mmol) and commercially available N-bromosuccinimide (15.5mg, 0.087mmol) were added into 1mL of chloroform. The reaction was covered with foil and run under argon at room temperature overnight. The resulting crude product was purified using prep TLC run in 1:4 DCM/hexane to yield (**4**) as a red solid (14.21mg, 73%). ¹H NMR was confirmed by literature.¹

5.12 Synthesis of NDI-BODIPY Polymer (25)

A mixture of previously synthesized tributyltin NDI monomer **14** (9.8mg, 0.00646mmol) and dibrominated BODIPY monomer **22** (5mg, 0.00646mmol),

tris(dibenzylideneacetone)diipalladium(0) (1mg, 0.0011mmol), and tri(o-tolyl)phosphine (1mg, 0.0033mmol) was degassed using a dry ice and acetone bath. After degassing, 0.1mL of toluene was added to the reaction mixture and refluxed at 90°C under argon for 3 days. The polymer was precipitated into 50mL of methanol, filtered, and purified using Soxhlet extraction with acetone, ethyl acetate, and hexanes. The resulting product was collected using chloroform, and filtered through a silica gel plug. GPC was used to confirm the formation of polymer (Figure 4).

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